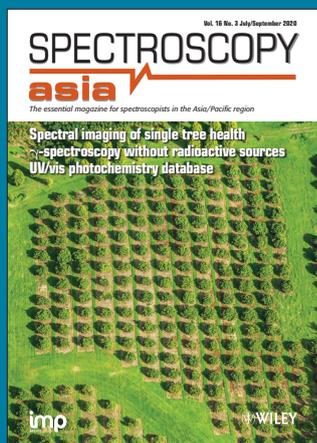


SPECTROSCOPY

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Spectral imaging of single tree health
 γ -spectroscopy without radioactive sources
UV/vis photochemistry database



Combining UAVs and satellites for imaging macadamia trees allows the identification of the health of individual trees. See the News article on page 4.

Publisher

Ian Michael
(ian@impublishations.com)

Advertising Sales UK and Ireland

Ian Michael
Spectroscopy Asia, 6 Charlton Mill,
Charlton, Chichester, West Sussex PO18 0HY,
United Kingdom. Tel: +44-1243-811334,
Fax: +44-1243-811711,
E-mail: ian@impublishations.com

Americas

Joe Tomaszewski
John Wiley & Sons Inc.
Tel: +1-908-514-0776
E: jtomaszewski@wiley.com

Europe and the Rest of World

Vanessa Winde
Wiley-VCH Verlag GmbH & Co. KGaA,
Boschstraße 12, 69469 Weinheim, Germany
Tel: +49 6201 606 721
E-mail: vanessa.winde@wiley.com

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2 SPECTROSCOPYASIA

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CONTENTS

3 Editorial

4 News

8 ^{138}La as a useful isotope for gamma spectroscopy without radioactive sources

Marco Bortoluzzi and Valentina Ferraro

12 Letter to the Editor: Importance of citing full details of spectral library and search program

O. David Sparkman

14 The UV/Vis⁺ photochemistry database

Andreas Noelle and Gerd. K. Hartmann

17 Tony Davies Column: When to automate spectroscopic data processing

Gary Sharman, Marcel G. Simons and Antony N. Davies

20 Sampling Column: Chemical analysis of contaminated soil for sound environmental site assessment. Part 1: the critical role of proper sampling

Jean-Sébastien Dubé and François Duhaime

25 New Products

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In our first article, Marco Bortoluzzi and Valentina Ferraro tell us about " ^{138}La as a useful isotope for gamma spectroscopy without radioactive sources". It is difficult to provide practical experience with gamma spectroscopy in undergraduate laboratories, and the authors have been investigating alternative sources, and the ^{138}La isotope is a suitable candidate. As well as some background on gamma spectroscopy and radiochemistry, Marco and Valentina also provide some sample exercises that could be used for undergraduate practicals.

Our second contribution is from David Sparkman, who will be well known to all readers in the mass spectrometry field. David is concerned about the "Importance of citing full details of spectral library and search program" in papers. As he points out, "even when the same mass spectrum is searched against two different versions of the NIST/EPA/NIH EI Mass Spectral Library using the same search program, two different compounds can be found as the first Hit". There are many possible reasons for this, but the version of the spectral library used and the particular search program used make a difference, and should be included in all references.

Finally, Andreas Noelle and Gerd Hartmann describe *The UV/Vis+ Photochemistry Database*. This collection of photochemical

data and information was started in 1999 and is now an online database updated weekly.

Gary Sharman, Marcel Simons and Tony Davies have a clear idea "When to Automate Spectroscopic Data Processing". I am sure everyone realises that automation is not a panacea, but it can improve the accuracy of manual tasks as well as freeing up our time for more challenging tasks. The authors explore some particular examples they have come across and lessons learned from them.

In Kim Esbensen's Sampling Column, Jean-Sébastien Dubé and François Duhaime start a two-part series on "Chemical analysis of contaminated soil for sound environmental site assessment" with Part 1 on the critical role of proper sampling. Proper sampling of particulate matter for instrumental analysis is a common task, and is crucial for representative measurements. Unfortunately, it is often performed with a disregard for the Theory of Sampling, and so fails.

La Michael

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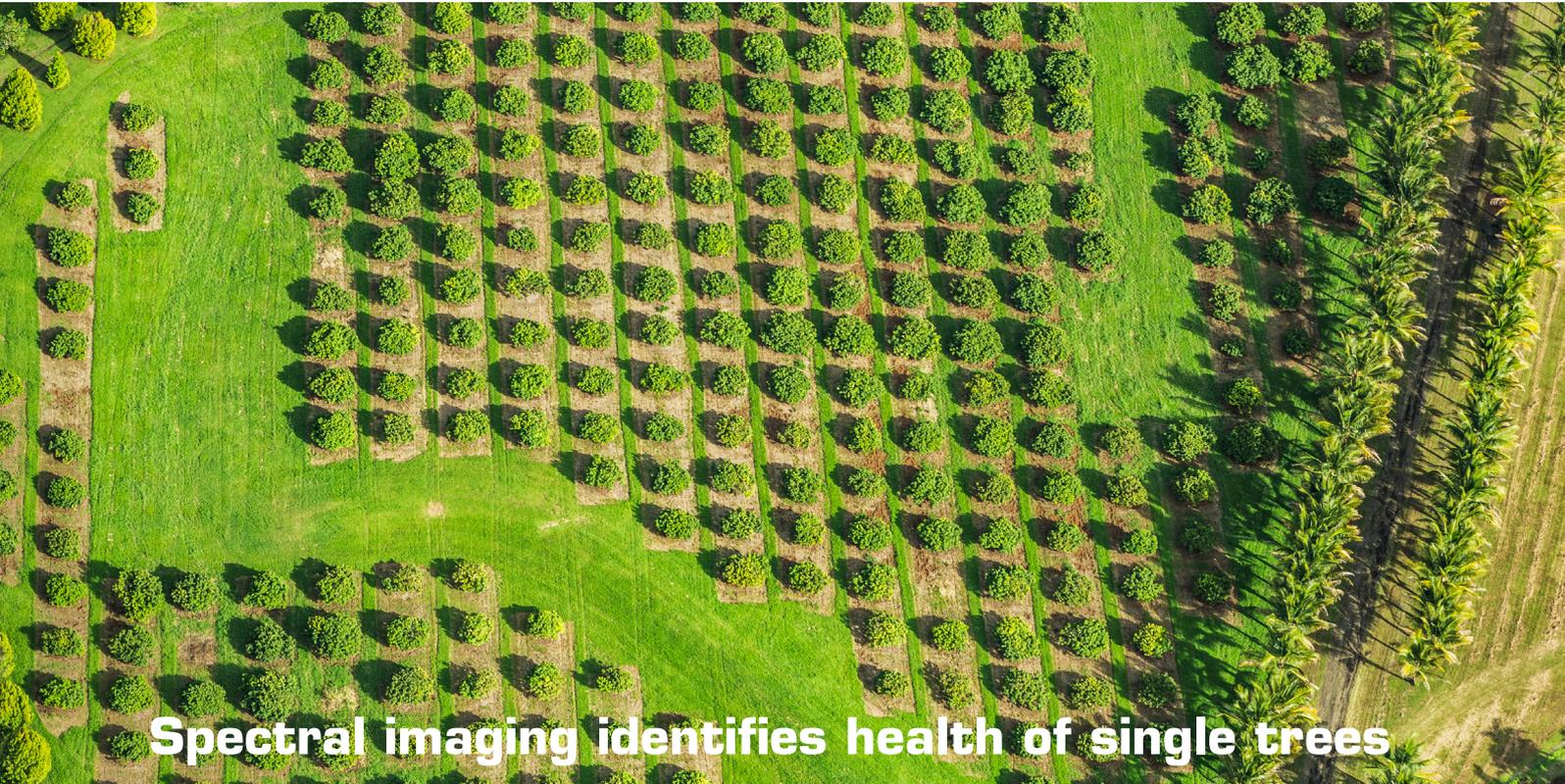
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Spectral imaging identifies health of single trees

Researchers Kasper Johansen and Matthew McCabe at KAUST's Water Desalination and Reuse Center, with co-workers in Australia, have demonstrated the potential of using combined data from satellite and unmanned aerial vehicle (UAV) flights to accurately map the condition of macadamia trees in Queensland. Macadamia nuts are an important export for Australia, but the trees take 15 years to mature and provide their maximum yield, so farmers must identify early any trees that are suffering. "Currently, macadamia farmers rely on manual visual assessment of each tree and its irrigation system, which is time-consuming and often inconsistent", says Johansen, "whereas UAV and satellite remote sensing could evaluate thousands at a time."

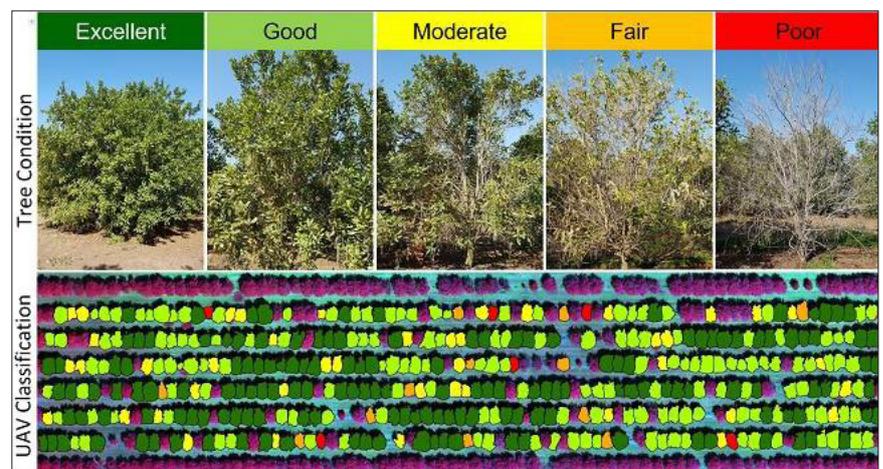
The team studied three plantations containing trees of various ages and varieties. The health of each tree was assessed by an experienced agronomist using a five-point scale from excellent to poor condition. The researchers flew a UAV over the sites to record spectral images in green, red and near infrared, and they acquired data across

several more spectral bands from the Worldview-3 earth observation satellite. Using training data from a few hundred trees, the team developed models relating the spectral data to the ground measurements. The models were then able to correctly classify over 98% of the other trees.

Interestingly, although the detailed spectra from Worldview-3 provided the

most accurate models of tree health, the pixel size of 1.2-m was too coarse to identify individual tree crowns, which could only be done with the high-resolution UAV data. This highlights the benefits of a combined UAV-satellite approach.

Their work was published in *ISPRS Journal of Photogrammetry and Remote Sensing* (doi.org/d45j).



By combining data from UAV and satellite surveys, Johansen and co-workers were able to classify the health of individual trees on a five-point scale across large areas of macadamia plantations. Farmers can then use a map, like the one shown, to find and treat trees at risk. ©2020 Kasper Johansen

Airborne water leak detection using spectral imaging

Almost half of countries' drinking water may be lost before it reaches the tap. A large share of the losses happens in large diameter mains crossing rural areas, where companies have trouble monitoring them due to traditional field surveys being costly and time consuming. European researchers have developed a surveillance service using planes (to survey wide areas) and drones (for sites that are difficult to access) equipped with multispectral and infrared cameras. To analyse the data, they used the "Triangle method", which combines surface temperature measurements and a vegetation index. This is based on the fact that leaks lead to lower surface temperatures, which can be detected by a thermal infrared camera. However, the thermal response of vegetated soils is different from bare ones, making it diffi-

cult to obtain an unequivocal answer in terms of moisture content and potential water loss. The researchers, therefore, added a parameter measuring the vegetation cover fraction, which is inferred by hyperspectral cameras, to get a temperature-dependent humidity scale which varies according to the vegetation. The system has been developed under the EU [WADI project](#).

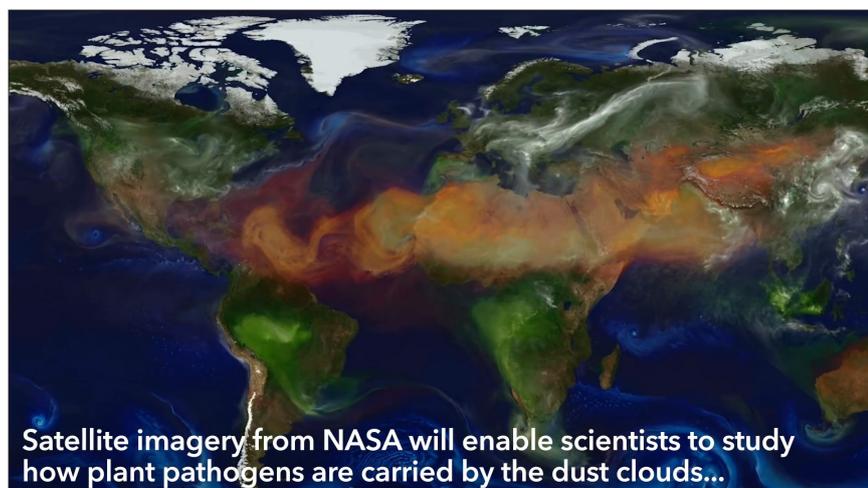
Compared to competing technologies, the WADI system's can monitor complex networks and long pipes (50–90 km h⁻¹ depending on the use of drones or planes) and, as it's airborne, can reach inaccessible or secluded locations over all kinds of terrain. Moreover, the cost of conventional ground detection techniques ranges from 1000 to 5000 euro per km, while the airborne technology ranges from 50 to 200 euro per km.

Imaging spectroscopy to track plant pathogens through the atmosphere

The multidisciplinary team of scientists has been selected for a \$750,000 NASA grant to combine their expertise in remote sensing, climate and earth system computer modelling, plant pathology and genomics to study the effects of soilborne plant pathogens which can travel in dust clouds from Africa to the Western Hemisphere. They will also use Earth system modelling to

predict how regions will change over time and how that may influence plant disease dispersal with dust.

If the origins and landing spots of specific pathogens can be better predicted, farmers can be advised on how to avoid practices that would increase its spread, such as those that kick up dust from farm fields, and



Satellite imagery from NASA will enable scientists to study how plant pathogens are carried by the dust clouds...

NASA remote sensing satellites will help Cornell University faculty members Katie Gold, assistant professor of plant pathology, and Natalie Mahowald, professor of Earth and atmospheric sciences, study the effects of soil-borne plant pathogens which can travel in dust clouds from Africa to the Western Hemisphere. Credit: John Munson/Cornell University

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perhaps grow less susceptible crops where such dust falls.

"We lose anywhere from 15% to 30% of the global harvest to plant diseases annually; here in 2020, people still die because they don't have access to food, because of losses due to plant disease", said principal investigator Katie Gold, assistant professor of plant pathology. "Remote sensing can do a lot help mitigate the impacts of plant disease on the global food supply."

"It's just a fascinating combination of cross-disciplinary work that's going to allow us to address things that no one has been able to address before", said co-investigator Natalie Mahowald, professor of Earth and atmospheric sciences and an expert in atmospheric modelling.

NASA's Release of Research Opportunities in Space and Earth Science Interdisciplinary Science grant is for three years, which will allow the team

to lay the foundation for a global surveillance system to assess risk and track and potentially prevent the global spread of plant diseases.

Other co-investigators include Ryan Pavlick, an imaging spectroscopy technologist at NASA's Jet Propulsion Lab, and Sharifa Crandall, assistant professor of soilborne disease dynamics and management at Pennsylvania State University.

LC-MS analysis of municipal wastewater as a predictor for population socioeconomics

Analytical techniques have been used for many years to monitor chemicals in sewage, for instance tracking cocaine use through its metabolites. Now, an extensive analytical study has been coordinated with the 2016 Australian Census. In a paper published in *Environmental Science & Technology Letters* ([doi.org/d5s8](https://doi.org/10.1039/C9EM00158A)), Dr Saer Samanipour of the Van 't Hoff Institute for Molecular Sciences (HIMS) in Amsterdam reported on the use of liquid chromatography tandem mass spectrometry for analysis of municipal wastewater as a predictor for population socioeconomics.

The study was carried out jointly with colleagues at the Queensland Alliance for Environmental Health Sciences of the University of Queensland, Australia. By coinciding the sampling phase of the

study with the 2016 Australian Census, the researchers were able to correlate the socioeconomic characteristics of Australian communities (following from the census) with sewage composition (following from chemical analysis).

The researchers collected samples from more than 100 sewage-treatment plants and analysed these for the occurrence of "marker" chemicals such as nicotine, caffeine, amphetamine and many more. In total, they looked for 40 chemicals that revealed smoking habits, dietary characteristics and the use of drugs, antidepressants and antipsychotics.

The extensive chemical analysis of all samples, combined with advanced data analysis, led to the conclusion that the chemical fingerprint of sewage is a quite

accurate predictor of the demographic make-up of the community connected to the sewage plant. The researchers developed a model based on their results and tested this with data from nine sewage plants not included in the initial analysis. For the communities around these plants, they were able to estimate key data on education, occupation, income, social life, housing and more within a 25% error margin. They were able to make quite specific predictions ranging from the number of people that had finished secondary school to the number of single parents and car owners.

The researchers conclude that wastewater analysis can be a valuable technique for assessing population socioeconomics, complementary to the vastly more expensive and logistically challenging method of a census.

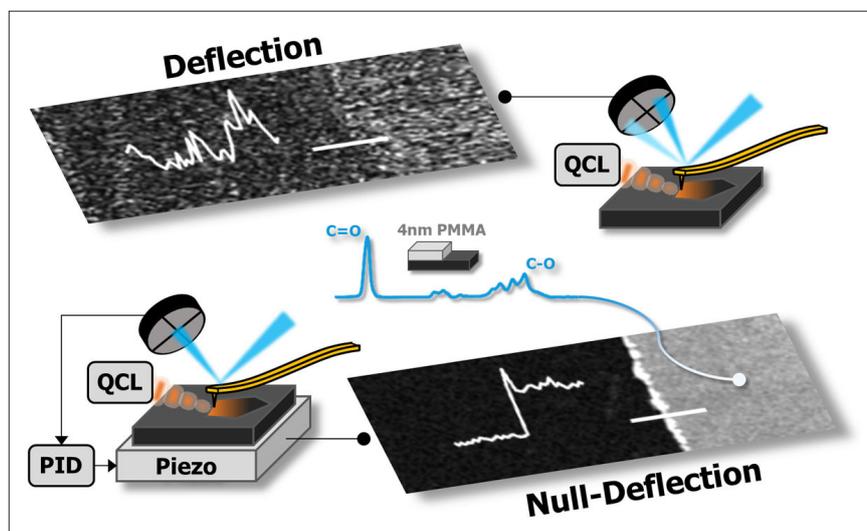


Image illustrating the previous deflection AFM-IR detection compared to the new null-deflection approach.

Improved AFM-IR method

Researchers at the Beckman Institute for Advanced Science and Technology have developed a new method to improve the detection ability of nanoscale infrared chemical imaging using atomic force microscopy. These improvements were developed in the lab of Rohit Bhargava and will reduce the noise that is associated with the microscope, increasing the precision and range of samples that can be studied. The study was published in *Nature Communications* ([doi.org/d5v8](https://doi.org/10.1038/s41467-020-1858-8)).

Atomic force microscopy is used to scan the surfaces of materials to generate an image of their height, but the technique cannot easily identify the molecular composition. Researchers

have previously developed a combination of AFM and infrared spectroscopy called AFM-IR. The AFM-IR microscope uses a cantilever to measure subtle movements of the sample introduced by shining an IR laser. The absorption of light by the sample causes it to expand and deflect the cantilever, generating an IR signal.

"Although the technique is widely used, there is a limit to its performance", said Bhargava. "The problem is that there were unknown sources of noise that limited the quality of the data."

Catherine Murphy, the head of the Department of Chemistry and the Larry Faulkner Endowed Chair in Chemistry, said this new technique developed by the Bhargava lab is exciting. "Our group is interested in using this technique immediately to learn about protein deformation on complex surfaces", Murphy said.

The researchers created a theoretical model to understand how the instrument works and, therefore, identify the sources of noise. Additionally, they developed a new way to detect the IR signal with improved precision.

"The cantilever deflection is susceptible to noise which becomes worse as the deflection increases," said Seth Kenkel, a graduate student in the Chemical Imaging and Structures Laboratory, which is led by Bhargava. "Instead of detecting cantilever deflection, we used a piezo component as a stage to maintain zero deflection. By applying a voltage to the piezo material, we can maintain small deflection with low noise while recording the same chemical information which is now encoded in the piezo voltage."

Instead of moving the cantilever, the researchers use the movement of the piezo crystal to record the IR signal. "This

is the first time anyone has controlled a piezo actuator to detect the signal. Other researchers work around challenges such as noise by using more complex detection systems that don't address the underlying problems associated with AFM-IR", Kenkel said.

"People have only been able to use this technique to measure samples that have a strong signal because of the noise problem", Bhargava said. "With the improved sensitivity, we can image a much smaller volume of samples, like cell membranes."

In addition to measuring more diverse samples, the researchers also hope to use this technique to measure smaller sample volumes. "We could use this technique to look at complex mixtures that are present in small volumes, like a single lipid bilayer", Bhargava said.

IR nanospectroscopy in 3D

Researchers from the Nanooptics Group at CIC nanoGUNE (San Sebastian, Spain) have shown that nanoscale infrared imaging, which is currently used as a surface-sensitive technique, can be employed for chemical nanoidentification of materials that are located up to 100 nm below the surface. The results further show that the infrared signatures of thin surface layers differ from those of sub-surface layers of the same material, which can be exploited to distinguish the two cases. The findings, published in *Nature Communications* (doi.org/d4vb), push the technique one important step further to quantitative chemometrics at the nanoscale in three dimensions.

Optical spectroscopy with infrared light, such as Fourier transform infrared (FT-IR) spectroscopy, allows for chemical identification of organic and inorganic materials. The smallest objects which can be distinguished with conventional FT-IR microscopes have sizes on the micrometre-scale. In nano-FT-IR (which is based on near-field optical microscopy), IR light is scattered at a sharp metallised tip of a scanning-probe microscope. The tip is scanned across the surface of a sample of interest and the spectra of scattered light are recorded using FT detection

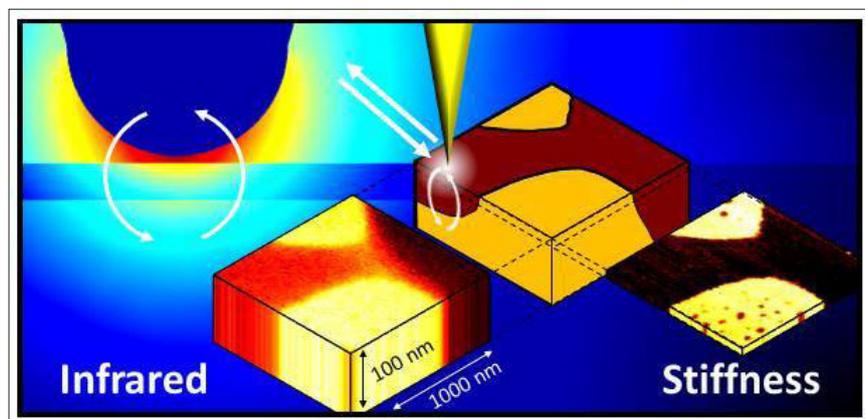


Illustration of sub-surface infrared nanoimaging. Copyright: CIC nanoGUNE

principles. Recording of the tip-scattered light yields the sample's IR spectral properties and thus the chemical composition of an area located directly below the tip apex. Because the tip is scanned across the sample surface, nano-FT-IR is typically considered to be a surface-characterisation technique.

Importantly though, the IR light that is nano-focussed by the tip does not only probe a nanometric area below the tip, but in fact probes a nanometric volume below the tip. Now the researchers at CIC nanoGUNE showed that spectral

signatures of materials located below the sample surface can be detected and chemically identified up to a depth of 100 nm. Furthermore, the researchers showed that nano-FT-IR signals from thin surface layers differ from that of sub-surface layers of the same material, which can be exploited for determination of the materials distribution within the sample. Remarkably, surface layers and sub-surface layers can be distinguished directly from experimental data without involving time-consuming modelling.

^{138}La as a useful isotope for gamma spectroscopy without radioactive sources

Marco Bortoluzzi* and Valentina Ferraro

Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre (VE), Italy

Contacts

markos@unive.it (ID 0000-0002-4259-1027)

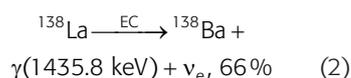
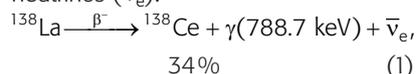
valentina.ferraro@unive.it (ID 0000-0003-2694-2955)

Introduction

Radioactivity is inescapably present in everyday life.¹ Radiochemistry is a topic of significant interest, strongly connected with energy production, medicine and environmental protection. Experiences concerning gamma spectroscopy in Inorganic and Physical Chemistry undergraduate laboratories are, however, hardly widespread, because of obvious problems related to students' safety and the storage of radioactive sources.² Basic knowledge about radioactive decays is usually offered by General and Inorganic Chemistry courses, but the information is not supported by hands-on learning. Safe laboratory experiments could give insight into several aspects related to radioactivity, such as naturally occurring radioisotopes, decay modes and lifetimes, interactions of radiation with matter and detection techniques. The idea of carrying out undergraduate gamma spectroscopy experiments with elements commonly classified as non-radioactive strongly limits the choice of possible samples. Lanthanum is particularly interesting for such a purpose because of the naturally occurring ^{138}La isotope.

The ^{138}La radioactive isotope constitutes 0.0902% of naturally occurring lanthanum. The half-life ($t_{1/2}$) of this isotope is very long, 1.05×10^{11} years. ^{138}La disintegration is due to two parallel processes. 34% of the isotope undergoes β^- decay, with the conversion of a neutron into a proton, turning into the

stable ^{138}Ce . The process is associated with the emission of a 788.7 keV gamma photon (Equation 1). The remaining 66% of ^{138}La disintegrates by electronic capture (EC), i.e. the conversion of a proton to a neutron by interaction with an electron. The EC process leads to the formation of stable ^{138}Ba with the emission of a 1435.8 keV gamma photon (Equation 2).³ The EC and β^- processes also produce neutrinos (ν_e) and anti-neutrinos ($\bar{\nu}_e$).⁴



The two emissions from ^{138}La are comparable with those of other radioactive isotopes present in the environment. For example, the gamma photon emitted by the EC decay of ^{40}K to ^{40}Ar has 1460.8 keV energy.⁵ ^{137}Cs undergoes β^- decay with formation of the metastable $^{137\text{m}}\text{Ba}$. The subsequent decay to the nuclear ground state releases a 661.7 keV gamma photon.⁶ The gamma photons from ^{138}La have higher energy if compared to those emitted by refined samples of ^{238}U . In this case, the radioactivity is associated with the α decay of the isotope, which leads to the formation of ^{234}Th . The latter transforms by β^- decay in ^{234}Pa and the process is associated with the emission of gamma photons having 63 keV and 92 keV

energy.⁷ To better understand the energy scale, just consider that, according to the relationship $E=mc^2$, the mass of an electron is equal to 511 keV.

Scintillation detectors

Gamma photons emitted by ^{138}La can be detected by an instrument known as a scintillator or scintillation detector. A crystal of suitable material can emit a weak flash consisting of photons in the visible-ultraviolet range if hit by a gamma photon. The number of photons constituting the flash is proportional to the energy of the incident gamma photon. One of the most popular materials for scintillator crystals is thallium-activated sodium iodide, NaI(Tl).⁸

Gamma photons weakly interact with matter. For example, the intensity of a 1000 keV gamma photon beam is halved by a lead shield of 0.87 cm thickness.⁴ At a first approximation, the absorption of gamma radiation by a material decreases with increasing energy. The scintillator crystal must be relatively large to detect high-energy gamma photons such as those from ^{138}La . The efficiency is, however, limited to few percentage points.

A photocathode coupled to the crystal emits electrons when hit by light, proportionally to the number of photons in the flash and, therefore, to the energy of the incident gamma photon. The electrons emitted by the photocathode can be amplified by a photomultiplier

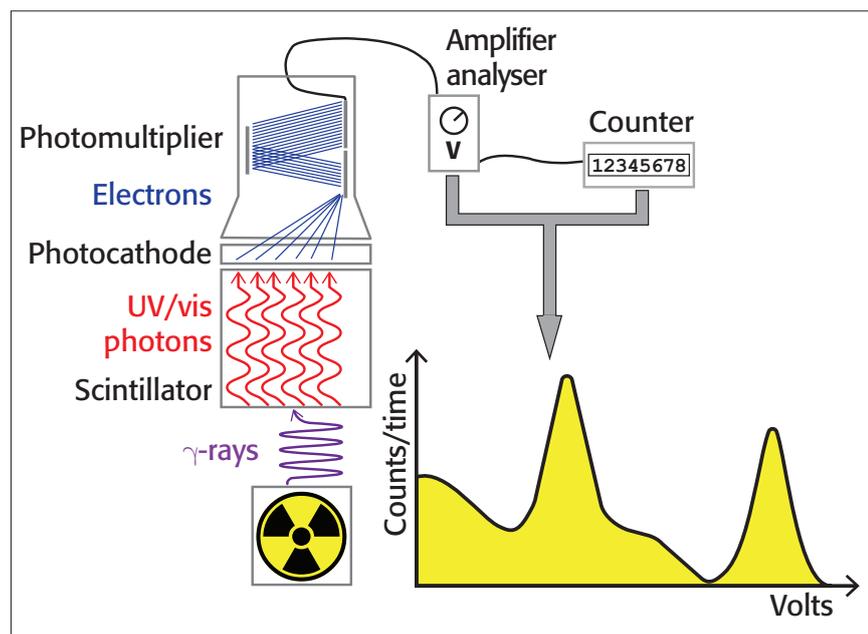


Figure 1. Schematic representation of a scintillation detector.

tube (PMT), thus obtaining a detectable electrical impulse. The amplitude of the impulse, expressed in volts, is linearly proportional to the energy of the gamma photon. The number of electrical impulses in a given time interval can be measured with a counter. With an amplifier/pulse height analyser, it is possible to select the range of pulse amplitudes (in volts) to be counted and build a gamma spectrum with the pulse amplitudes in the abscissa, while the number of counts is reported in the ordinate. The main components of a scintillation detector are depicted in Figure 1.

If the energy of the gamma photons is completely absorbed by the scintillator, the corresponding photopeak is observed in the spectrum. The energy resolution of the photopeak is defined as the ratio between the half-height width and the peak energy. The ratio decreases, i.e. the energy resolution improves, on increasing the photon energy.⁸

The incomplete absorption of energy by the crystal involves the presence in the spectrum of a continuum of signals with energy lower than the photopeak. Gamma photons can impact the electrons of the material by transferring part of their energy, thus obtaining a new photon with lower energy and different direction (Compton scattering).⁴ The

photon generated after the collision can exit the crystal and, in this case, only the energy transferred to the electron will be counted. It can also happen that the gamma photon first hits the material surrounding the source (e.g. a lead shield), transferring part of its energy to it, and the new photon thus generated can interact with the scintil-

lator. The photon energy generated by the Compton scattering, E'_{γ} , depends on the energy of the incident photon E_{γ} and the angle θ between the two photons, as shown in Equation 3. In the equation, m is the mass of the electron and mc^2 is 511 keV. The effects of Compton scattering are depicted in Figure 2.

$$E'_{\gamma} = \frac{E_{\gamma}}{1 + \left(\frac{E_{\gamma}}{mc^2}\right)(1 - \cos\theta)} \quad (3)$$

E'_{γ} coincides to E_{γ} if the angle θ is zero, while the minimum E'_{γ} value is for $\theta = 180^{\circ}$. As a consequence, in the presence of Compton scattering the largest energy transfer to the scintillator occurs when the γ photon hits the scintillator and a γ' photon exits the crystal at 180° with respect to the first one (Compton edge). For example, if E_{γ} is 1435.8 keV, E'_{γ} is 216.9 keV and the energy measured by the detector is 1218.9 keV ($1435.8 - 216.9$ keV). On the other hand, if the γ photon is emitted from the source in the opposite direction with respect to the crystal, the impact with the shielding can produce a photon at 180° with respect to the incident one and the detector could count the 216.9 keV γ' photon.

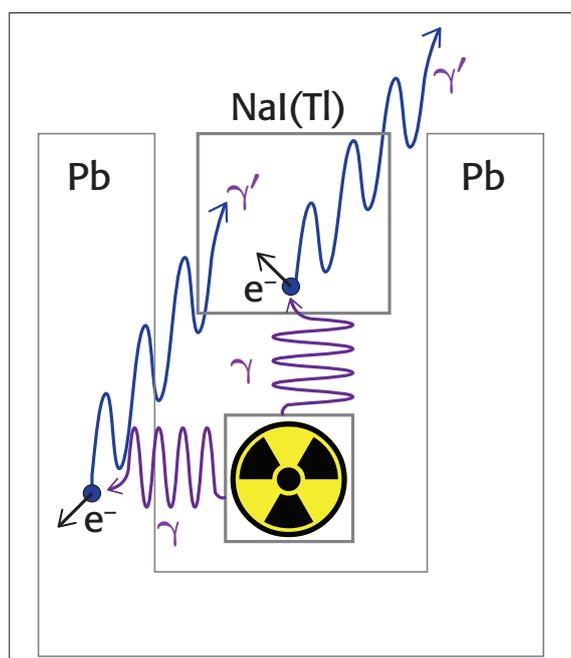


Figure 2. Effects of the Compton scattering on the signals received by the scintillation detector.

Another phenomenon that can lead to the presence in the gamma spectrum of signals at lower energies with respect to the photopeak is pair production, which must be taken into account only for gamma photons having energy greater than 1022 keV.^{4,8} It is worth noting that the mass of an electron (or positron) corresponds to 511 keV. Given the mass–energy equivalence, a gamma photon with energy greater than 1022 keV can interact with matter behaving like an electron–positron pair and a residual amount of energy. For example, a 1435.8 keV gamma photon corresponds to an electron–positron pair plus 413.8 keV. The positron interacts with an electron of the scintillator crystal, leading to annihilation and to the formation of two new γ photons having energies equal to 511 keV, propagating in opposite directions. The electron consumed by annihilation is replaced in the total balance by that deriving from the incident photon, while the residual energy can be absorbed and counted. If the two 511 keV photons are absorbed by the crystal, then all the energy of the incident photon is detected, increasing the intensity of the main photopeak. If one of the two 511 keV photons escapes from the crystal, the detector instead measures an energy equal to $(E_\gamma - 511)$ keV, known as a single escape peak. If both 511 keV photons leave the crystal, the energy detected is $(E_\gamma - 1022)$ keV, corresponding to the double escape peak. The intensities of the single and double escape peaks depend on the size of the crystal used. The process of pair production followed by annihilation can also involve the shielding surrounding the experimental apparatus, and one of the two 511 keV photons can be subsequently counted by the detector (annihilation peak).

Finally, it is worth noting that the electronic structure of the materials undergoes major alterations due to interaction with gamma photons. For example, it is possible to observe peaks in the 75–85 keV range associated with X-rays deriving from transitions in the innermost electronic shell of the lead atoms constituting the shield. Furthermore, if NaI(Tl) is used as a scintillator crystal and the resolution of the spectrum is sufficient,

a second peak having 28 keV less energy may appear close to the main photopeak due to the escape from the crystal of the X-photon associated with an internal electronic transition of iodine.⁹

Lanthanum gamma spectrum

In our experiments, a cylindrical NaI(Tl) crystal with diameter and height of 7.6 cm was used, protected by an aluminium layer, with an integrated photodiode and photomultiplier. The declared efficiency is around 2% for 500 keV photons and drops to about 1.3% for energy values around 2000 keV. The crystal produces approximately 10^4 photons/MeV of absorbed energy (wavelength between 300 nm and 500 nm). The scintillator photomultiplier was connected to a preamplifier (Tennelec TC155A), itself connected to a high-voltage power supply (Ortec 556, set at 670V) and an amplifier/single channel analyser (AMP/SCA, Tennelec TC 246). The amplifier was initially calibrated in order to make the spectrum fall in a suitable potential range. The analyser was finally connected to a counter (Ortec 996).

Gamma emission from 257.9 g of lanthanum oxide (La_2O_3 , CAS number 1312-81-8, purchased from Strem Chemicals) with natural isotopic abundance was investigated. On considering the ^{138}La percentage in nature, the quantity of ^{138}La in the sample is 1.4 mmol, corresponding to 8.6×10^{20} nuclei (N_0). The radioactive decay follows first-order kinetics, so the activity of the sample ($-dN/dt$) is given by Equation 4:

$$-\frac{dN}{dt} = \frac{\ln 2}{t_{1/2}} N_0 \quad (4)$$

The activity of the sample considered here is around 180 Bq (Becquerel, disintegrations/second). Another common measurement unit is the Curie (Ci), corresponding to the number of disintegrations per second of one gram of ^{226}Ra (1 Ci = 3.7×10^{10} Bq). The activity of the La_2O_3 sample is, therefore, around 5×10^{-3} μCi . The sample has very low activity, considering that a radioactive source for didactic purposes is typically around 1 μCi . To detect ^{138}La radioactivity it is, therefore, necessary to shield

the source and the scintillator from the natural radioactivity of the environment. In our experiment the La_2O_3 powder was placed in a polyethylene glass with a diameter of 7.1 cm. The height of the powder was 8.2 cm. The glass was introduced in a lead well with internal diameter of 8.6 cm and depth of 11.3 cm. The thickness of the walls was between 3.8 cm and 5.4 cm. The scintillator crystal was placed over the well and the side wall of the crystal was shielded with 3.1-cm-thick lead. An additional lead screen with thickness around 1.2 cm was placed around the PMT.

The gamma spectrum of La_2O_3 reported in Figure 3 was recorded by varying the centre of the SCA potential window with 0.1V steps. The potential window was set to 0.1V. The counter time was 180 min. Every measurement was carried with and without the sample in order to subtract the background. The error associated with the ordinate values was conservatively estimated by the sum of the square roots of the two counts. The inset of Figure 3 was obtained by reducing the potential steps and window to 0.05V, while the counter time was increased to 420 min.

The gamma spectrum shown in Figure 3 highlights the presence of two main peaks, centred at 8.8V and 4.9V, corresponding to the gamma emissions at 1435.8 keV (EC decay) and 788.7 keV (β^- decay) of ^{138}La . The accuracy of the assignment was verified by replacing the sample with ^{40}K (350.6 g of non-enriched KCl, gamma activity 17×10^{-3} μCi , $E_\gamma = 1460.8$ keV). On the basis of these data it was possible to roughly calibrate the abscissa scale and report it in keV. The energy resolution of the higher energy peak is around 5%, while for the other peak it is 9%. Because of the different sensitivity of the detector on changing the gamma photon energy, the intensities of the two peaks do not respect the relative probabilities of ^{138}La EC and β^- decays. The two peaks are accompanied by the expected Compton scattering. Probably because of the poor activity of the source, no signal related to pair production was detected. The higher energy peak shows a shoulder at lower energy, but the number of points in the

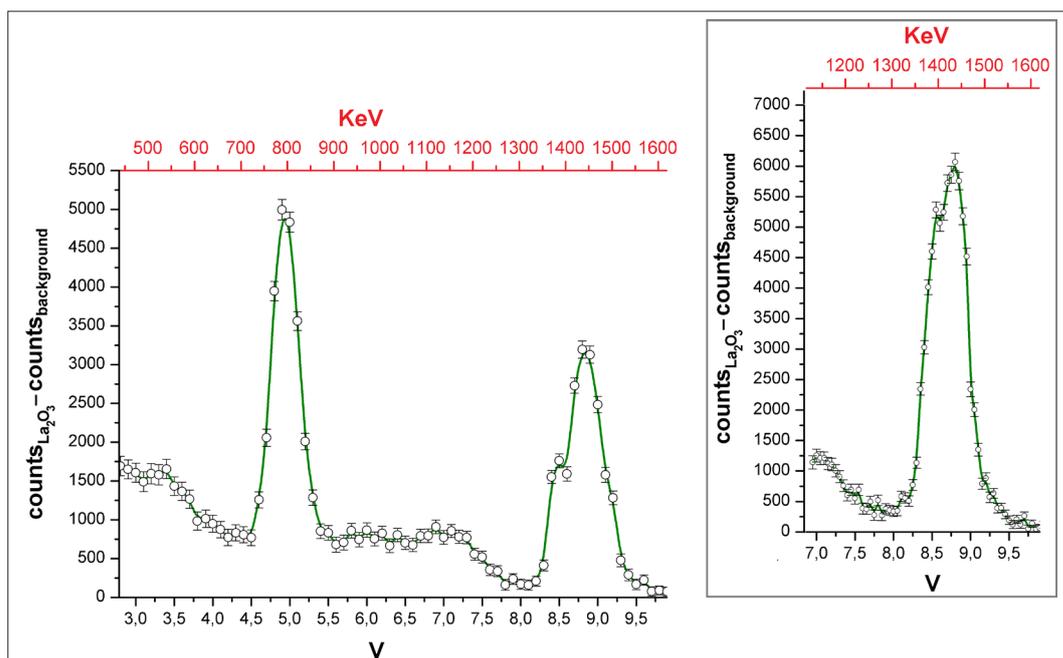


Figure 3. Gamma spectrum of La₂O₃. Inset: portion of the spectrum collected with improved resolution.

spectrum is limited and the points are separated by about 17keV. To verify the existence of the shoulder, that region of the spectrum was collected again with doubled abscissa resolution and longer counting time (see the inset of Figure 3). The shoulder was confirmed, and its energy suggests that it could be related to the escape of an iodine X-photon.

Undergraduate laboratory experiments

The experiment previously described with a SCA analyser requires too much time to be carried out in an undergraduate laboratory. On the basis of the results described, a gamma spectrum with sufficient resolution can, however, be collected overnight using a commercially available multi-channel analyser. If only a SCA is accessible, the gamma activity of the sample in the 450–1600 keV range can be unambiguously distinguished from the background in two hours (one hour measurement for the sample, another one for the background).

Besides La₂O₃, another source that can be safely used by students with the same experimental setup is a potassium salt such as KCl, in order to detect the gamma emission related to ⁴⁰K EC decay. A useful exercise related to ⁴⁰K

is the calculation of the gamma activity of a potassium source (see Exercise 1). KCl can be used by the students for the rough calibration of the amplifier (see Exercise 2).

In all the cases, it is worth noting that there are no safety hazards related to radioactivity, and La₂O₃ and KCl are non-toxic powders.

Exercise 1

Consider a source constituted by m grams of a potassium salt having formula weight W . Search on the web for ⁴⁰K data concerning half-life, natural abundance and relative probability of the EC decay. Use these data and Equation 4 to calculate the gamma activity in Bq and μ Ci.

Exercise 2

The potential range to collect the gamma spectrum is determined by the high-voltage supply of the PMT and the setting of the amplifier. A rule of thumb for most phototubes is that a 10% variation of the high-voltage will change the gain by a factor of two. To calibrate the amplifier use more than 300g of KCl as source and set a counting time around 5 min. Consider a sufficiently large potential window, e.g. 2V. Depending upon the working range of the analyser, set

the centre of the potential window at a suitable value (e.g. 8V if the analyser works in the 0–10V range). Start the first measurement with low voltage supply and good amplification, for example use half of the maximum values for both the settings. Record the counts and repeat the measurement by progressively increasing (about 10% each time) the high-voltage supply. Do not exceed the PMT limit! Counts vs high-voltage supply should show a maximum. Starting from the corresponding high-voltage value, halve the amplification and carry out a new series of measurements, increasing the high-voltage supply by about 2–3% each time. Find the new high-voltage value corresponding to the maximum counts and repeat the procedure until restricted by the PMT and amplifier limits.

Conclusions

Gamma spectroscopy on non-enriched sources is a powerful tool for safely exploring several concepts related to radioactivity, in particular:

- Basic concepts: decay modes, radioisotope half-life, units in radioactivity, activity of a source.

continued on page 13

Letter to the Editor: Importance of citing full details of spectral library and search program

O. David Sparkman

Adjunct Professor of Chemistry and Director of the Pacific Mass Spectrometry Facility, Chemistry Department, University of the Pacific, Stockton, CA, USA. E-mail: osparkma@pacific.edu

A collection of mass spectra of known compounds and the program used to search a spectrum of an unidentified compound are two different entities. The results obtained depend on both. Two different compounds can be found as the first Hit when a search of the same spectrum is performed using the NIST Mass Spectral (MS) Search Program (National Institute of Standards and Technology, Gaithersburg, MD, USA) to search the NIST/EPA/NIH EI Mass Spectral Library (NIST 20) or the *Wiley Registry of Mass Spectral Data*, 12th Edn (John Wiley & Sons, Hoboken, NJ, USA). Two different compounds can be found as the first Hit when the NIST/EPA/NIH EI Mass Spectral Library (NIST 20) is searched using the NIST MS Search Program v.2.4 or the Probability Based Matching (PBM) search program, which is a part of the Agilent Technologies (Santa Clara, CA, USA) ChemStation Data Analysis program. Even when the same mass spectrum is searched against two different versions of the NIST/EPA/NIH EI Mass Spectral Library (NIST 14 and NIST 20) using the same search program (NIST 20's MS Search v.2.4) two different compounds can be found as the first Hit.

There is not one root cause for these differences. In the example of a difference between the search of the NIST 14 and NIST 20 EI libraries using the same search program, it can be as simple as the addition of the spectrum of the

unidentified compound to the library between editions. Spectra for approximately ~60K new compounds were added between these two releases. Or, the different first Hits could be due to complex search algorithm differences in the case of the NIST MS Search program vs the PBM search of ChemStation.

The point is that it is not only necessary to be specific about the publisher of the library but also the edition of the mass spectral library as well as the search program used. Because of my involvement with NIST, I have subscribed to two search strings in Google Scholar Alerts since 5 October 2014 ([NIST Mass Spectral Database] and [nist "mass [spectral | spectra | spectrum]"]). During this period, I have received list of citations for both of these strings every two to five days. Each list contains 5–20 citations to articles that make mention of one of the two NIST Mass Spectral Libraries (NIST/EPA/NIH Library of EI Spectra or the NIST Tandem Library of Production Mass Spectra). Many of these citations also reference the *Wiley Registry* and sometimes other smaller libraries like the flavor and fragrance EI library of Robert P. Adams (Diablo Analytical, Antioch, CA, USA), the Maurer/Pfleger/Weber *Mass Spectral Library of Drugs/Poisons/Pesticides/Pollutants and Their Metabolites*, 2011 Edn (John Wiley & Sons), the Designer Drugs 2020 EI mass spectral library by Peter Rösner (John Wiley & Sons), *SWGDRUG Mass Spectral*

Library etc., to mention just some of the many small mass spectral libraries.

Too often citations to the search of a mass spectral library are simply. "The identity of unknowns was confirmed using the NIST library." Unfortunately, not more than 20% of the articles cite the version (edition) of the mass spectral library, and nearly every article is missing any mention of the program used to search the library. When someone purchases an instrument, they will purchase it with a mass spectral library. Today, this is truer of gas chromatography/mass spectrometry (GC/MS) instruments than tandem mass spectrometers used with liquid chromatography, but with the introduction of the NIST Tandem Library and the fact that ThermoFisher is providing a copy of that Library with every tandem instrument that they sell, this will change.

It is also unfortunate that people are publishing an article in 2020 in which the NIST EI library released in 1998 is being used.

As these instrument age, the researchers using them, especially those that are not mass spectrometrists, don't realise that easily and inexpensive upgradable tools, like libraries of mass spectra and search programs that can greatly expand their existing instrument's usefulness, are available.

The main reason journal article authors need to include not only the name and edition of the mass spectral library

used to confirm or identify unidentified compounds but also which programs were used to search these libraries, so their reader can evaluate the validity of the results.

It is not enough to say, "The identity of the components was confirmed by searching their mass spectra, separately, against the NIST and Wiley libraries". That sentence should read, "The identity of the components was confirmed by searching their mass spectra, separately against the NIST 17 and Wiley 8 libraries using the internal library search algorithm for the Shimadzu GC/MS Solutions V.4.5 software". (The Shimadzu GC/MS Solutions software, like that of most other GC/MS Data Systems, allows only one mass spectral library at a time to be searched.) PerkinElmer, Waters, Agilent's ChemStation (GC/MS and LC/MS) and Agilent's MassHunter (Qual and Quan), Sciex, Bruker and others all have their completely separate proprietary library search routines even through many provide the NIST MS Search Program and libraries in the MS Search format as well as their proprietary format. These proprietary programs and formats can change with changing version of their instrument's software that they accompany; this is why the version number of the data analysis software should be a part of the citation. With the availability of both the NIST MS Search and other third-

party search programs as well as the software's priority search, it is absolutely mandatory that the search software be specified.

It should be remembered that the NIST MS Search Program has both an Identity Search (to be used when it is suspected that a spectrum of the unidentified compound is in the libraries being searched) and a Similarity Search (to be used when it is suspected that there is no spectrum of the unidentified compound in the searched libraries). In the NIST MS Search Program (v.2.4), accompanying NIST 20, there are four different Identity Searches (EI Normal, EI Quick, MS/MS and In-Source HiRes) and five different types of Similarity Searches (EI Hybrid, EI Simple, EI Neutral Loss, MS/MS in EI and MS/MS Hybrid, for use with product-ion mass spectra from atmospheric pressure ionisation produced precursor-ions). Therefore, it is best that not only the version being used is stated but, also, which algorithm is being used when reporting the use of the NIST MS Search Program. Another unique feature of the NIST MS Search, unlike the search routines provided as part of most data analyses' software routines, is that up to 127 different libraries can be searched, simultaneously. Hits are listed according to quality, not according to search order.

The following are examples of proper citations to use when working with one

of the two NIST Mass Spectral Libraries and the NIST MS Search Program.

Search of an electron ionisation spectrum

Identification of an unidentified compound's mass spectrum was accomplished using the NIST Mass Spectral Search Program's, v.2.4, EI Normal Identity Search of the NIST 20 NIST/EPA/NIH EI Mass Spectral Library (mainlib and/or replib) and [name(s) of any other library(ies) searched]. If any Search Constraints were used, these should also be listed; especially if the Retention Index Database was used.

Search of a product-ion mass spectrum

Search of the NIST 20 Tandem Library (hr_msms_nist, lr_msms_nist, apci_msms_nist or (biopep_msms_nist) and [name(s) of any other product-ion mass spectral library(ies) searched] was done using the NIST MS Search Program's (v.2.4) MS/MS Hybrid Similarity Search. If any Search Constraints were used, these should also be listed.

Again, it can't be over emphasised that the library publisher, library edition and software used should be cited in detail.

This Letter to the Editor is being submitted to multiple journals in order to obtain as much coverage as possible on this topic.

continued from page 11

■ Advanced concepts: gamma photons, interaction with matter, Compton scattering.

The measurements suggested here give insight into questions related to natural radioactivity in the environment. The instrumental equipment offers the possibility to work with PMTs, amplifiers and analysers that may also be encountered during other undergraduate laboratory experiments, such as those related to luminescence measurements.

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The UV/Vis⁺ photochemistry database

Andreas Noelle* and Gerd. K. Hartmann

science-softCon, Auf der Burg 4, 63477 Maintal, Germany. E-mail: andreas.noelle@science-softcon.de

The *science-softCon UV/Vis⁺ Photochemistry Database* (www.photochemistry.org) is a large and comprehensive collection of extended ultraviolet, vacuum ultraviolet, ultraviolet, visible and near infrared spectral data and other photochemical information assembled from published peer-reviewed papers. The database contains photochemical data including absorption, fluorescence, photoelectron, and circular and linear dichroism spectra, as well as quantum yields and photolysis-related data that are critically needed in many scientific disciplines. This article gives an outline regarding the structure and content of the *science-softCon UV/Vis⁺ Photochemistry Database*. The accurate and reliable molecular level information provided in this database are fundamental in nature and help in proceeding further to understand photon-, electron- and ion-induced chemistry of molecules of interest, not only in spectroscopy, astrochemistry, astrophysics, Earth and planetary sciences, environmental chemistry, plasma physics, combustion chemistry, but also in applied fields such as analytical chemistry, medical diagnostics, pharmaceutical sciences, biochemistry, agriculture and catalysis.

Introduction

Photochemical data and information such as absorption spectra, fluorescence spectra, photoelectron spectra, circular and linear dichroism spectra, quantum yields etc. are important parameters needed in many scientific disciplines. Back in 1999, there was deemed to be a need for publicly accessible on-line databases containing such data and information in digital format (machine-readable). A first *UV/Vis Spectra of Atmospheric Constituents* CD-ROM¹ was published which contained, at that time, the largest collection of ultraviolet/visible (UV/vis) spectral data available free-of-charge. Based on this CD and the motivation to provide spectral data and information in digital format to the scientific community via the World Wide Web, the *UV/Vis Spectra Database* went on-line in August 2000 as a non-profit project.

In the beginning, the on-line database contained about 1200 spectra/datasheets for 120 substances and the compiled data extended beyond atmospheric research to allow for interdisciplinary application. To enable platform independent usability, both the spectral data as well as the datasheets (metadata such as publication, authors, source, wavelength range, temperature, pres-

sure, phase etc.) are available as plain ASCII text. To guarantee the high quality of the fast growing *UV/Vis⁺ Spectra Database*, an international "Scientific Advisory Group" (SAG) was established in 2004, and the database was operated in accordance with the "open access" definitions and regulations of the CSPR Assessment Panel on Scientific Data and Information (International Council for Science, 2004, ICSU Report of the Committee on Scientific Planning and Review Assessment Panel on Data and Information).²

Since 2004, in addition to publishing the on-line database, every two years a mirror of the on-line database has been published on CD-ROM. The latest edition in the *science-softCon UV/Vis⁺ Spectra Database* series was published in 2019.³ The on-line database currently (as of July 2020) contains about 14,200 spectra/datasheets as well as 5300 graphical representations for about 3000 substances, and is sub-divided into 28 substance groups (e.g. hydrocarbons, pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons etc.). The database is updated weekly. In addition to the inclusion of new data, a main focus of the database is the preservation of data from older publications.

A more detailed description of the database and its applications has been published recently.⁴

As mentioned by the CSPR Assessment Panel on Scientific Data and Information, database maintenance and management are costly.² Collection of data, preparation of metadata and provision of professional data management expertise and institutional support for data dissemination and permanent archiving will add to the overall expense of specific research projects and maintaining the larger research infrastructure.

"Full and open access" to data implies equitable, non-discriminatory access to all data that are of value for science. It does not necessarily equate to "free of cost" at the point of delivery. There are several economic models for providing scientists with access to data for research and education.² The *UV/Vis⁺ Photochemistry Database* allows free and open access to all metadata, and cost-recovery pricing for data (or data licenses) in order to support the full data infrastructure. A choice of charged subscriptions giving full access to the data are available: for example an annual campus-wide licence provides full access to all data and information for less than USD 1 per day (for universities, govern-

mental organisations, non-profit organisations) and a "One-Time Registration" licence allows perpetual access to all data and information. Both licenses include a copy of the 12th edition of the *UV/Vis+ Spectra Database* CD-ROM.³ In addition, those colleagues who support us in maintaining the database through the provision of new or missing data and information can get personal free-of-charge access to all data and information. More information is available at www.photochemistry.org.

Database structure and content

The database contains spectral information (gas, liquid and solid phase) from the extreme ultraviolet to the near infrared spectral regions (EUV-VUV-UV-Vis-NIR) and related data (e.g. information concerning publications on quantum yield studies or photolysis studies) from published peer-reviewed papers. Besides absorption spectra, which comprise most of the available data, fluorescence spectra, photoelectron spectra, circular and linear dichroism spectra, quantum yields etc. are available. The database is structured into 28 categories, which just provide a rough classification.

The datasheets provide metadata (substance name, formula and CAS number, data source, full reference, including title, authors, journal and DOI when available, spectral range and resolution, temperature, pressure, phase etc.), as well as data in various forms obtained and presented in the literature. This includes, for example, absorption data measured over a specific wavelength/energy range in tabulated form. In many applications (e.g. quantum yield studies or photolysis studies), the absorption cross-section (σ) or the molar extinction coefficient (ϵ) at a specific wavelength (λ) are determined, and these single wavelength data are also included in the database. For many substances temperature dependent data are available.

Most of the available data are from published peer-reviewed papers (>99%), data presented at scientific meetings and conferences are also available (<0.5%), as well as data from PhD

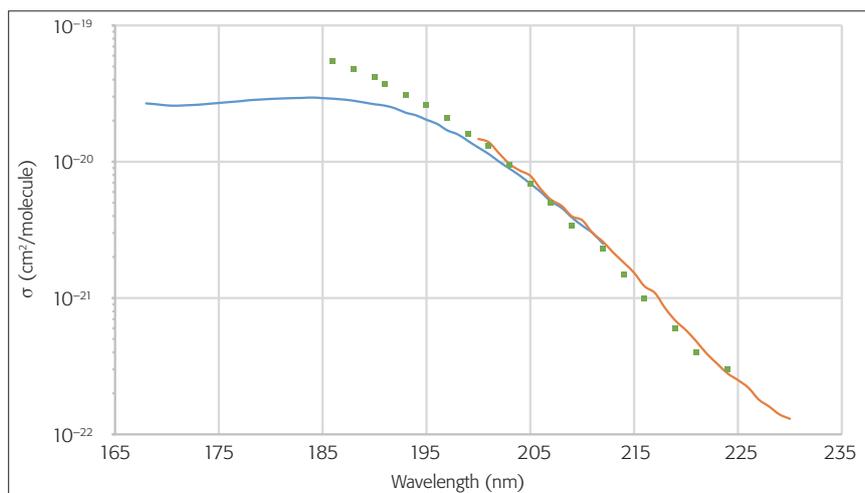


Figure 1. UV absorption spectrum of COF_2 obtained by Noelle⁵ (blue curve), Noelle *et al.*⁶ (red curve) and Molina and Molina⁷ (green squares).

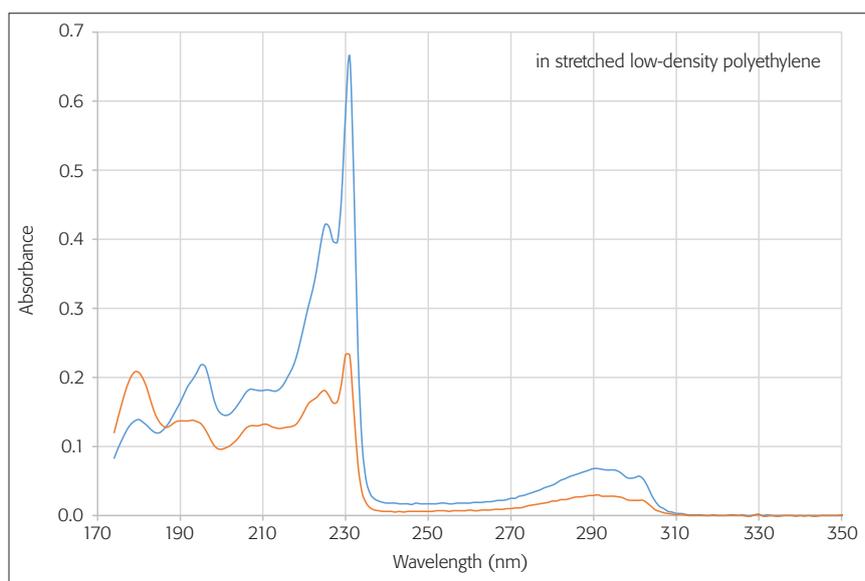


Figure 2. Linear dichroism absorbance spectrum of dibenzo-*p*-dioxin.⁸ The absorbance curves were recorded with the electric vector of the sample beam parallel (blue line) and perpendicular (orange) to the stretching direction of the polyethylene polymer.

theses, reports and unpublished material (<0.5%). As an example of the database structure and contents, absorption data of carbonyl fluoride (COF_2) from three different sources are presented in Figure 1. The data sets are as provided by the authors or listed in the relevant publications. To enable platform independent usability, all data are provided as plain ASCII text.

More recently, almost 3000 graphical representations, mostly from older

publications have been digitised and added to the database. In addition, we have converted more than 100 datasets from "floppy discs" and hence prevented these data from being lost as technology has evolved.

Since 2019 the database has been extended to include circular and linear dichroism spectral data (Figure 2). The absorbance curves were recorded with the electric vector of the sample beam parallel and perpendicular to the stretch-

ing direction of the polyethylene polymer.

Outlook

The *science-softCon UV/Vis+ Photochemistry Database* is continually evolving and growing. As of July 2020, it contains about 14,200 spectra/datasheets as well as 5300 graphical representations for about 3000 substances and is sub-divided into 28 substance groups (e.g. hydrocarbons, pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons etc.) This is a tremendous effort and requires a lot of manpower, not to mention technical infrastructure. We hope that the database proves useful to the scientific community and will facilitate their day-to-day work.

Since the support by the scientific community is crucial for such a photochemistry database, we would like to encourage all colleagues to assist us in maintaining the database and join our initiative "Photochemical Data and Information Sharing Platform—Share Photochemical Data & Information, Find Answers".

This initiative should develop the photochemical database towards a photochemical data sharing platform. The advantage of such a photochemical data sharing platform is that the more scientists provide their data for inclusion in the database, the better is the chance for all users to find specific photochemical data within the database. In addition, the platform becomes increasingly

beneficial for use across multiple disciplines.

Database examples (datasheet, data, graph) are available at www.photochemistry.org.

Since the "UV/Vis+ Photochemistry Database" is operated as a non-profit "open access" database, any support from both sides, academic and commercial, would be highly appreciated.

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When to automate spectroscopic data processing

Gary Sharman,^a Marcel G. Simons^b and Antony N. Davies^c

^aMestrelab Research S.L, Feliciano Barrera, 9B-Bajo 15706, Santiago de Compostela, Spain

^bExpert Capability Group - Measurement and Analytical Science (ECG-MAS), Nouryon, Zutphenseweg 10, 7418 AJ Deventer, Netherlands

^cSERC, Sustainable Environment Research Centre, Faculty of Computing, Engineering and Science, University of South Wales, UK

I read with interest a recent article in *Chemical Science* originating out of Jonathan Goodman's group at the University of Cambridge. Jonathan is another long-standing IUPAC campaigner for scientific data standardisation and his group has been working on an improved solution to tricky nuclear magnetic resonance (NMR) spectra interpretation.¹ Their approach exploits modern higher processing speeds to enhance their fully automatic molecular structure elucidation software. Their DP4-AI uses the quantum chemical Gauge-Independent Atomic Orbital Density Functional Theory (GIAO-DFT) method calculations starting from chemical structures with undefined stereochemistry. ¹H and ¹³C-NMR peak picking algorithms handle noisy spectra to predict relative stereochemistry. A statistical value is generated for the likelihood that each of the candidate molecules is correct based on the analysed spectra with almost no need for human intervention. This makes it an ideal tool to rapidly solve difficult problems like natural product library validation.

Clearly, there is still strong demand for improved NMR data interpretation and prediction software. I wondered how much such systems were being used on a day-to-day basis in industry, so talked to Gary Sharman, who has enjoyed a 20-year career in analytical science in the pharmaceutical industry and Marcel Simons, a very experienced NMR expert and one of my old colleagues at AkzoNobel/Nouryon.

Why do automation?

Many years ago, I heard a comment that has stuck in my mind and still raises a smile when I have occasion to remember it. One of the pharmaceutical industry customers of Creon-LabControl AG were testing an innovative combined ultraviolet/visible (UV/vis) and mass spectrometry (MS) automated approach for natural product library screening against "known chemistry" to select extracts for further work. After testing for a while, the customer explained to the software developers the reason behind his excitement. Completely ignoring the technological advances and clever programming that had gone into the system being tested, the customer simply pointed out that the automated spectroscopic data processing system effectively eliminated the boring repetitive work. Extracts that were of no interest (known chemistries) were automatically removed allowing him and his team to very rapidly focus on the extracts of interest that were potential new active molecules. "I can finally spend most of my time doing the expert job my company is actually paying me for".

So much for the thoughts that people increasing automation might be responsible for taking jobs away from spectroscopists! Gary Sharman highlighted three areas that can be seen as major drivers for better automation:

- Lost opportunities: problems that we would not even dare to start without automation.
- Free up time for more interesting work. We all became spectroscopists

for the tricky, interesting problems, not to churn a handle on routine analysis and be bookkeepers. Let automation take care of the drudgery so you can focus on the fun problems. (Like the UV/vis-MS example above.)

- Less silly mistakes/book-keeping errors. We all like to think we are accurate and precise, but the fact is humans make lots of silly mistakes, particularly in collating data. Computers do not make these kinds of mistakes.

Have realistic expectations

The danger of having so much automation at our fingertips is that we might be setting ourselves up for some spectacular falls when the automation encounters problems it simply cannot master. You often see this in much simpler systems such as gas chromatography (GC)/MS database search results of electron ionisation spectra. We have discussed many innovative solutions in this column in the past, but time and again I see reports where the first database hit is cited as being the compound identified—even if the chemistry of the proposed molecule can have nothing to do with what is actually being worked on. If the scientist/student had taken the time to look further down the hit list they would have found a substance that made much more sense in terms of the experiments being undertaken.

So, as Gary put it... If you want perfectly assigned NMR spectra every time—give up now! A much better aim is

TONY DAVIES COLUMN

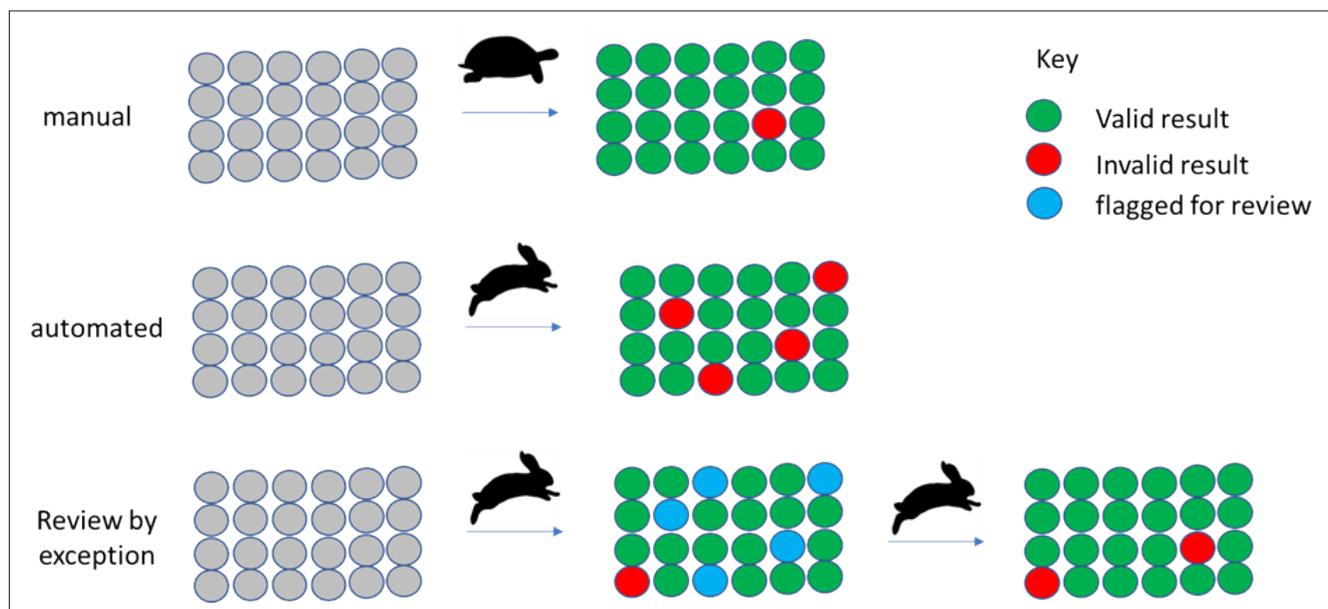


Figure 2. Automation supporting and reducing manual data analysis by focussing on the suspect results.

to really ask yourself what level of errors you are prepared to tolerate, and how that trades off against effort. For example, consider the quality control of a large library; without automation you may conclude it cannot be done. With automation perhaps we have 5% false positives. It is not perfect, but surely better than having no data on purity.

So, ask yourself what level of errors you are willing to accept. Be realistic. Everyone says “I want 100% accuracy”, but not even an experienced spectroscopist can achieve that. You might make a trivial error like mixing up two samples or simply working on complex chemistries which you are unfamiliar with.

The automation process

Gary described the process in a similar way to Jonathan Goodman’s group and this actually applies for different types of spectroscopy (Figure 1).

Although this might be seen as a rather simple schema, it is good to see how automation will benefit us at the various steps in the process.

- Data preparation and metadata extraction. Not to be overlooked—this may be one of the quick wins. For example, automatically finding and opening connected bits of data, looking up a structure and loading

it, saving results—all parts that take time and are tedious bookkeeping, but every process needs them.

- Data processing such as peak picking and categorisation. This can be a very crucial part of the process. Many automated structure validation “mistakes” that are just down to poor peak picking of the data.
- Prediction—unless we are looking up a known thing in a database, we typically must predict the expected result to allow comparison. This could be

Compound	m/m%	mol%	A/C
A	76.2	61.3	3.92
B	19.4	35.2	
C	4.4	3.4	

Compound	m/m%	mol%	A/C
A	66.0	49.1	2.38
B	27.7	46.4	
C	6.3	4.5	

Figure 4. At the end of a complex automated NMR data processing method, the customers question may boil down to “is the ratio of the concentration of two compounds within specific target boundaries to the quality criteria”. In this figure, the results show a pass and the lower a fail.

quite simple (what is the expected ion for MS) or complex (a prediction of NMR by *ab initio* methods).

- Matching predicted to experimental. For some applications, this may be trivial: is the biggest peak in the mass spectrum the same as the m/z I expect. For proton NMR, with the complexities of coupling, overlap and higher order effects, it is exceedingly difficult.
- Scoring and output—we need to return a useful value that can be used to set actions. We might also want to return “quality factors” that indicate if the result is to be believed or if manual review is a good idea: these two things may well be orthogonal. A fail in the test may not mean the data needs review, and a pass may not mean it is a valid result.

Review by exception strategy

Although you may regard this as an oversimplification, manual analysis is “slow and accurate”. Automation is often seen as “fast but error prone”. By flagging samples for review where there is a reason to believe the automated result may be suspect, we can get the best of both worlds (Figure 2).

TONY DAVIES COLUMN

We do not work alone!

One of the critical questions which we are always asking is exactly how does some new wonder-software fit into our daily working practices and processes?

- The automation steps are only half the problem—how are you going to link your process to other processes in your organisation? This can make or break the automation. Workflow tools like the Swiss KNIME, the Konstanz Information Miner (a free and open-source data analytics, reporting, and integration platform)² or Biovia's Pipeline Pilot³ can be valuable here. Also, having information exposed through APIs or web services makes integration easier.
- Constraints. You may have to work with legacy systems, other software with particular requirements or unhelpful interfaces to other data. This can be a major part of the problem that impacts design and implementation.
- The soft part—no one likes to be told by a computer they made a mistake. To get acceptance for a system, it may need thought about how people are informed of failures. For example, an e-mail saying you did something wrong with your boss copied in is probably a bad move. Flagging an error to an expert who reviews it and has a quiet word might be more accepted.
- New problems. Real world data is not perfect. Low signal-to-noise, poorly prepared samples and other components like residual solvents may lead to failures that a person would deal with as part of accepted normal practice.
- Edge cases. Software is built and validated on limited sets of test data. You can guarantee that over time edge cases will be detected that it does not handle well. Hopefully over time, more and more edge cases are dealt with and they become less and less frequent.

So, sticking with the world's COVID-19 theme, an Automated Structural Verification (ASV) software package like Mestrelab's "Verify" module can do an excellent job of assigning a molecule, such as a pharmaceutical active ingredient in a clean sample. Expecting a perfect assignment every time may be setting our sights too high. Imperfections do not stop a system being useful.

Enabling non-spectroscopist colleagues

Marcel Simons and colleagues have been working hard to help support colleagues from other disciplines in a speciality chemicals research and manufacturing area in a way that embodies many of the advantages listed above, but in a quite different environment. Their challenges are far more to do with quantitative analysis by NMR rather than purely structure elucidation. The Expert Capability Group's open shop NMR has to cope with a very high workload of business- and time-critical samples—often being generated out of normal laboratory hours. They started configuring automated spectroscopic data analysis back in 2006. With instrument vendor support, they have developed and deployed over 30 automated methods that do tasks such as data processing for manufacturing plant support. These methods go well beyond the out-of-the box tools, and are designed to work using simple sampling strategies on all liquid samples with usable signals even without the use of deuterated solvents.

The automation results are basically processed spectra and a dedicated Excel file with the desired integrals and calculated molar ratios and/or calculated and normalised weight percentages. Depending on the targeted recipient of the automated processing and the demands of the specific business customers, conditional formatting is applied highlighting the results in green if the processing has delivered

the expected result and red if the data is not what was expected and additional actions are potentially required (Figure 4).

Conclusions

So, it looks like there is a good clear case for continuing to develop faster and less error prone automated spectroscopic data processing. Jonathan's group have made their new software available under the Open Source MIT license, so if you feel like trying it out while you sit at home worrying about a second COVID-19 wave it can be downloaded from GitHub.⁴

Gary was one of the authors on a recent paper that pulled together many of the topics discussed here.⁵ The paper discusses an automated system to verify new compound registrations. At its core was Mestrelab's Verify engine which automatically verified registered structures against their NMR and liquid chromatography-MS data. This was wrapped in a web service to make access by external processes simple. Bookkeeping tasks, scheduling and interfaces to other systems were taken care of by a KNIME server, and a streamlined review process was put in place to ensure there was a human face put on dealing with any problem samples.

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Chemical analysis of contaminated soil for sound environmental site assessment. Part 1: the critical role of proper sampling

Jean-Sébastien Dubé, ing. PhD and François Duhaime, ing. PhD

Laboratoire de géotechnique et génie géo-environnemental, Département de génie de la construction, École de technologie supérieure, 1100 Notre-Dame ouest, Montréal (QC), Canada H3C 1K3

Proper sampling of particulate matter for instrumental analysis is a common task in many applied scientific, technology and engineering fields. It is a crucial task for ensuring that measurements made on a given set of samples are representative estimate of the parameters of interest in the original sampling target. Unfortunately, sampling particulate matter is in many fields performed without a scientific basis, mostly because its critical role is ignored, or at best, misunderstood, and because of an unawareness of, sometimes a disregard for, the Theory of Sampling. This two-part column illustrates this important point using experience in the field of geo-environmental engineering.

Environmental site assessment guidelines require representative sampling, but do not define how: a recipe for decision-making disaster

A noteworthy example of how sampling is performed without a proper scientific basis is the sampling involved in environmental site assessment of *contaminated soil*. In this context, soil samples are analysed for their content of contaminants (chemical, physical). For chemical contaminants, analytical protocols generally require a few grams of soil for analysis only, and specify that this small quantity **must** be representative of the field parcel from which it is derived. This implies that a few grams of soil **must** represent a volume up to several hundred cubic metres of particulate matter in the field. This implies a mass reduction of nothing less than six to nine orders of magnitude, while ensuring that at each stage of the mass reduction process the resulting sub-sampled quantity of matter still

represents the entire original soil parcel. With the current state-of-affairs in this field (guidelines, standards, tradition, ignorance) this is a well-nigh impossible task. We find it incumbent upon us to sound a serious alarm within the field of geo-environmental engineering—but the examples and lessons described below have a much wider impact in many applications fields with *similar* heterogeneity issues.

The representativeness of an analytical measurement, i.e. the degree to which it represents the real contaminant content in the soil, compositionally as well as spatially, is directly related to the representativeness of the *sampling process*. This means the degree to which the proportion of each type of constitutive element of the soil, particles and contaminant(s) is preserved during the “from-field-to-analysis” sampling/sub-sampling process.

However, in the vast majority of current cases, the degree of repre-

sentativeness is not assessed, far less even mentioned. In most guidelines for sampling of contaminated soils, representativeness is a vague concept, mostly owing to some form of wishful thinking. Without a formal **definition** of representativeness and guidelines on **how to obtain** a desired degree of sampling representativeness (called “fit-for-purpose representativity”), sampling is performed more or less intuitively, haphazardly or based on subjective judgement. This approach is called grab sampling in the Theory of Sampling (TOS). It most commonly involves taking the desired mass of soil (“not-too-much”) from some accessible part of the soil in *one increment*. In today’s practice in the field, this would result in a grab sample of a few hundred grams which is sent to the laboratory, where a grab sub-sample of a few grams is then taken for analysis.

Below are two realistic, real-world examples of how this approach to

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sampling can produce extremely poor results.^a

Assessment of zinc contamination

The first example is typical of a common situation in the practice of environmental assessment. A field sample from a site contaminated with zinc (Zn) was sent to an analytical laboratory by a geo-environmental consultant charged with the environmental assessment study. Field and laboratory sampling were performed by grab sampling. As per common practice, the laboratory was charged with providing a single analytical result from the material in the container delivered. This measurement resulted in a Zn concentration of 1900 mg kg^{-1} , thus indicating a contamination well above the regulation threshold for the current usage of the site (see further below). This result would lead to the demand that the soil from the parcel must be removed.

However, several *in situ* semi-quantitative measurements were also made by the consultant on the soil parcel with the use of a portable X-ray fluorescence spectrometer, and these had indicated a possibly smaller concentration.

Therefore, the consultant asked the laboratory for “a second measurement” based on the same sample container. This time the results came in at 79 mg kg^{-1} . Such a major discrepancy “naturally” prompted a third measurement, which, however, failed to detect any Zn in the soil! At the end of a very confusing day, a total of seven individual measurements were made based on the same 300 g soil sample as shown in Table 1.

Que faire?

As a way of trying to shift the burden of explaining these wildly varying results to the consultant, the laboratory concluded that the sample received was not homogeneous. Although this conclusion is correct, such a conclusion is profoundly



Typical test pits in geo-environmental engineering site soil characterisation. One attribute rules the day: “significant heterogeneity”. It is obvious that any single field sample (a grab sample in the TOS parlance) will not be able to represent the entire site. For this job, diligent compliance with the TOS’ principle of *composite sampling* is necessary (see part 2).

naïve as **all** soils are heterogeneous, it is only a matter of to which degree (TOS).

This self-evident truth was exacerbated in the present case by severely “incorrect” sub-sampling in the laboratory (grab sampling from the *same* field sample container). So, whatever heterogeneity was revealed only pertained to the scale of the volume of the field container. Whether this is the same

heterogeneity characterising the significantly larger site volume under investigation is still a completely open question: how well does the field container represent the entire site?

The applicable regulatory thresholds were 140 mg kg^{-1} (I), 500 mg kg^{-1} (II) and 1500 mg kg^{-1} (III), each value representing the maximum allowed Zn concentration in soil for specific

Table 1. “Autopsy” of a single 300 g field soil sample, and the resulting soil remediation status (categorisation).

Measurement	Concentration (mg kg^{-1})	Categorisation based on measurement
1	1900	>III
2	79	<I
3	<4	<I
4	<4	<I
5	<4	<I
6	700	II–III
7	25	<I

I, II and III represent regulatory thresholds of 140, 500 and 1500 mg kg^{-1} , respectively.

^aFor the record: the examples and procedures discussed here pertain to significantly heterogeneous materials that **cannot** be subject to mixing before sampling. If a significantly heterogeneous lot to be sampled *happens* to be so small that it is economically feasible to mix it thoroughly in its entirety, the rules of the game have been altered because mixing leads to a significantly reduced distributional heterogeneity. However, the resultant lot is still compositionally heterogeneous and still needs to be treated as such. Such cases are exceedingly rare, and consequently of overwhelmingly little interest within geo-environmental engineering.

SAMPLING COLUMN

usages of the site, or specific means of disposal of the excavated soil. Table 1 also shows the categorisation of the soil with respect to these thresholds based on each of the seven “replicated” measurements.

It comes as no surprise that the consultant was now confronted with the confounding problem of correctly *categorising* the soil parcel represented by one field sample, but seven analytical results. If the categorisation decision had been made based on a single measurement, as is the usual practice, a highly significant error would have been introduced. This would have transferred unwarranted significant uncertainty to the site remediation process. The key issue is, of course, that under “normal practices” this would not even have been known to any of the stakeholders involved.

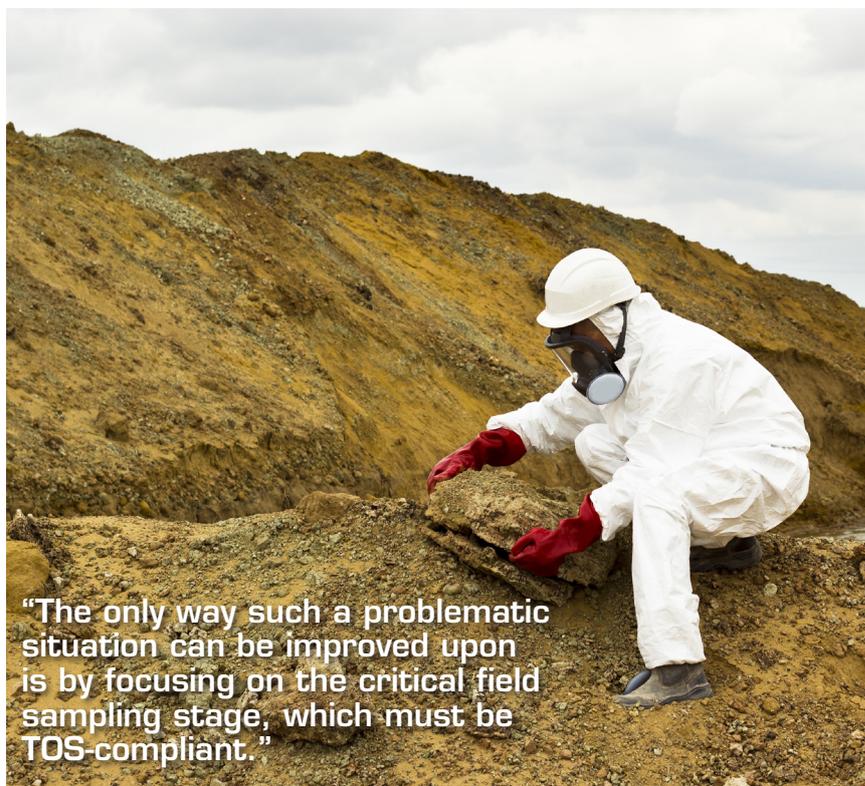
It would be hazardous to fit a statistical distribution to such a small dataset in which 43% of the data are left censored. However, it is possible to roughly *estimate* the categorisation probabilities based on proportions as shown in Table 2.

If the consultant had used the first measurement, as in current practice, he would have categorised the soil as larger than criterion III and, therefore, in need of disposal off site (A). But the probability that this decision would have been correct is only 14.3% (Table 2).

The consultant was, therefore, well advised to ask the laboratory for supple-

Table 2. Estimates of categorisation probabilities (categories A, B, C are identical to categories I, II, III in Table 1).

Category	Probability
$x < A$	0.714
$A < x < B$	0
$B < x < C$	0.143
$x > C$	0.143



“The only way such a problematic situation can be improved upon is by focusing on the critical field sampling stage, which must be TOS-compliant.”

mental measurements. While these vary widely, a Kaplan–Meier (KM) estimate of the mean Zn concentration, 388 mg kg^{-1} ,^b indicates that the soil could be categorised as being lower than criterion III, and thus kept on the site. This decision would have had an 85.7% probability of being correct. The problem of categorising the soil becomes more acute when the soil must be excavated and disposed of off site, since the disposal cost is related to the contamination level category. In the present case, based on the singular initial measurement, the soil would have been categorised as larger than criterion III, and disposed of at a larger cost, most probably incurring unnecessary expenditures from the site owner. However, based on the KM mean of 388 mg kg^{-1} , the soil would have been

categorised as between criteria I and II, and thus disposed of at a much smaller cost or even reused as fill material in some jurisdictions. This example illustrates well how much uncertainty can be introduced in the decision-making process if based on a single 300 g field soil sample.

It can come as no surprise then that the documented uncertainty points to the highly likely situation that the target lot from which this single field sample originated must be significantly heterogeneous itself. The key issue is: is the single field sample representative of this target lot? To answer that, attention must be directed elsewhere: **how** was the primary sample (the field container) sampled in the field? Were the principles and rules in the TOS complied with, or not?

^bNote that calculating the mean Zn concentration by arbitrarily substituting the censored concentration measurements, i.e. $< 4 \text{ mg kg}^{-1}$, by 0 or 4, we obtain a mean Zn concentration ranging from 383 mg kg^{-1} to 388 mg kg^{-1} . While these estimates of the mean are close to the KM estimate in this case, arbitrary substitution in environmental datasets can lead to unreliable and biased estimates of descriptive parameters). Dennis Helsel (doi.org/fdmnj8) comments on arbitrary substitution: “There is an incredibly strong pull for doing something simple and cheap”. This statement can just as aptly also be applied to grab sampling at all stages from field to aliquot.

Introduction to the Theory and Practice of Sampling

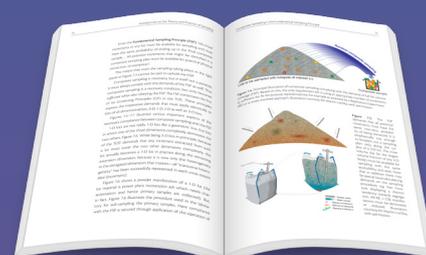
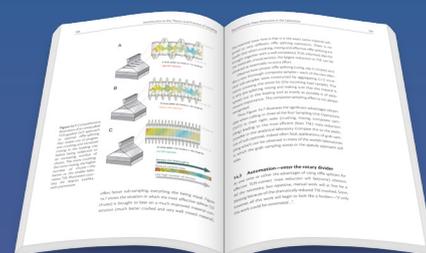
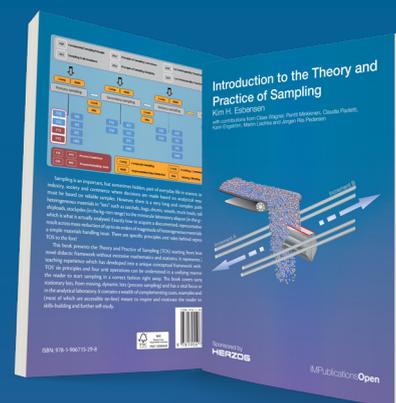
Kim H. Esbensen

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

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

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

NEW
BOOK



“I recommend this book to all newcomers to TOS”

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

“One of the book’s major advantages is the lavish use of carefully designed didactic diagrams”

impopen.com/sampling

IMPublicationsOpen

SAMPLING COLUMN

Testimony

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

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

Dr Melissa C. Gouws, InnoVenton Analytical, Port Elizabeth, South Africa

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The situation depicted is common and typical, but it is not acceptable. The only way such a problematic situation can be improved upon is by invoking a stronger focus on the characteristics of the full sampling process, notably the primary field sampling stage.

This case is also “representative” of the ill-informed practice of pouring more money into the analysis stage, i.e. making a larger number of measurements from each primary sample. Instead, more care should be taken in reducing variability at the primary

sampling stage. It should not be difficult to understand that the debilitating heterogeneity revealed in Table 1 is only a reflection of the state-of-affairs in the singular field sample upon arrival at the analytical laboratory. No manner of repeated analysis based on this sample alone, can produce any information as to the real-world heterogeneity of the **entire** soil parcel, which **must** be larger but to an unknowable degree. The obvious solution is an appropriate deployment of *composite sampling* covering the entire 3-D parcel site.

Preliminary conclusion, Part 1

The first part of the *full* sampling-and-analysis process occur in the field and is often performed by the consultant’s field technician. This gap in the “chain of custody” of the sampling process between the consultant and the laboratory is particularly problematic, especially as much as the current incorrect sampling practices are left without a clear responsibility. No one takes full responsibility for the representativeness of the complete sampling process in such circumstances.

Fix your sampling, not your results

In part 2 we will further illustrate how measurement variability can be controlled at the sampling stage with a second real-world example from a recent study conducted at École de technologie supérieure, Montréal, in partnership with the same consultant involved in the first example presented here. In this second study, we compare the uncertainty derived from grab sampling to that derived from a TOS-compliant composite sampling process.

References

A complete list of References will be included in part 2.

NEW PRODUCTS

INFRARED

FT-IR spectrometer-based milk analyser

PerkinElmer has launched the LactoScope™ FT-B instrument, an FT-IR spectrometer for testing and adulterant screening for liquid dairy products such as whey, raw and skim milk, shelf stable milk and cream with under 40% fat content. It has a smaller footprint than PerkinElmer's Lactoscope™ FT-A system, which analyses milk, yogurt, ice cream, concentrates and creams with up to 55% fat. The FT-B produces results in <45s with a typical accuracy level of under 1% CV (relative standard deviation). For large processors, the instrument can serve as a second instrument in milk intake areas to help ease liquid sample throughputs in addition to the Lactoscope™ FT-A system. For small- to mid-sized dairies and milk intake points with high volumes, the LactoScope™ FT-B instrument also provides low cost of ownership.

The LactoScope™ FT-B is integrated with the easy-to-use Results Plus software and provides rapid implementation with minimal training, as well as analysis and reporting that are compatible with the Lactoscope FT-A solution, PerkinElmer's DA 7250™ NIR Analyser and LIMS systems. This makes it easy to



move between different platforms and instruments across liquid and solid dairy testing. Further, the Lactoscope FT-B instrument ties into the PerkinElmer Net Plus™ cloud solution to enable remote configuration, monitoring, calibration and team collaboration.

PerkinElmer

► <http://link.spectroscopyasia.com/32-066>

Handheld FT-IR and SERS analyser measures low concentrations of illegal substances

The Thermo Scientific Gemini analyser now comes with LowDoseID, specifically to address the rising trend of low concentrations of illicit substances. The Gemini combines Fourier transform infrared (FT-IR) and surface enhanced raman scattering (SERS) into one device to facilitate comprehensive and confirmatory chemical identification for substances with a concentration between 1% and 10%. The ability to detect small amounts of substances enhances accuracy and efficiency for first responders, particularly when identifying the presence of Fentanyl, heroin and cocaine.

In addition to new functionality through the introduction of LowDoseID, the Gemini has also undergone a software update. The version 1.8 software enhances ease of use with on-screen colour-coded alerts based on analysis results and an expanded factory chemical library, as well as smoother operation.

Thermo Fisher Scientific

► <http://link.spectroscopyasia.com/32-082>



MASS SPEC

SCIEX OS software

SCIEX has introduced SCIEX OS Software, initially available on the Echo® MS System and the SCIEX Triple Quad™ 7500 LC-MS/MS System. Key features include: Auto-detection of sample failures results in auto-corrective action; Review by exception flags mean less manual checking of results; Results are optimised with powerful integration algorithms; Peak modelling improves peak finding and integration, requiring less user input and there-

fore reduces time for data review; Automated result checking and outlier removal minimises the time it takes to establish an approved calibration range; Intuitive audit trails ensure full traceability and accountability to achieve data precision, completeness and consistency.

SCIEX

► <http://link.spectroscopyasia.com/32-079>

NEW PRODUCTS

SCIEX Triple Quad 7500 LC-MS/MS system

SCIEX has launched the next generation of its flagship nominal mass spectrometer, the SCIEX Triple Quad™ 7500 LC-MS/MS System – QTRAP® Ready, which has the highest level of sensitivity in the SCIEX portfolio. Workflows can be simplified due to a linear dynamic range of up to six orders of magnitude. The new D Jet™ Ion Guide allows users to characterise analytes that were previously undetectable, and the design also captures more ions from the spray plume. The new OptiFlow® Pro Ion Source reduces the need for extensive sample preparation, allowing users to quantify more trace analytes at lower levels, and integrated E Lens™ Technology increases ion sampling. The OptiFlow® Pro Source's modular capability enables interchange between high flow and low flow, and between ESI and APCI, without manual adjustments.

A simple upgrade path enables additional QTRAP functionality scan types to improve confidence. MRM3 workflows can push quantification levels through matrix interferences.

SCIEX

► <http://link.spectroscopyasia.com/32-078>



Waters' MassLynx software now interfaces with Skyline software

For customers with Xevo TQ-S micro and Xevo TQ-XS mass spectrometers running on MassLynx™ Software version 4.2, Waters is introducing a new interface to Skyline software, the freely available, open source software for targeted proteomics. The interface will enable scientists to develop optimised LC-MS/MS multiple reaction monitoring (MRM) methods for the quantification of peptides or protein digests by the surrogate peptide approach. The MassLynx/Skyline interface is an easy-to-use tool

for auto-optimising and fine-tuning high-sensitivity MRM assays on tandem quadrupole mass spectrometers for bioanalytical or targeted proteomics experiments that are part of drug discovery research. The MassLynx/Skyline interface can be downloaded for free from the Waters Marketplace (see link below).

Waters

► <http://link.spectroscopyasia.com/32-073>

DESI XS imaging for Waters high-resolution mass spectrometers

The new desorption electrospray ionisation (DESI) XS source is now available on the Waters SELECT SERIES Cyclic IMS, SYNAPT™ XS and Xevo™ G2-XS QToF mass spectrometers. Waters acquired the rights to DESI™ from ProSolia and the Purdue Research Foundation in 2018. When coupled to a mass spectrometer, DESI XS produces a visual map of the spatial distribution of small molecule drugs, metabolites and lipids within a variety of sample and surface types. With DESI XS, scientists can image tissue samples, screen metabolites in bacterial colonies, identify individuals from fingerprints taken directly from various surfaces and examine cross-sections of natural products like roots and tubers. As a direct ionisation source, DESI XS eliminates the need for sample preparation and chromatography prior to the introduction of the sample into the mass spectrometer.

Waters

► <http://link.spectroscopyasia.com/32-072>



New fragmentation option for Waters Cyclic IMS system

Waters has introduced the electron capture dissociation (ECD) fragmentation technique for its SELECT SERIES™ Cyclic™ IMS system, through a partnership with e-MSion, Inc. ECD is an electron-based fragmentation technology that, combined with ion mobility mass spectrometry and collision induced dissociation (CID) available with the Cyclic IMS System, gives scientists improved sequence coverage for native proteins and surrogate peptides and additional structural information about larger proteins that might not have been possible before. The Waters™ Cyclic IMS System can perform scalable ion mobility separations and is also capable of IMSⁿ experiments (e.g. selecting an ion by IMS, fragmenting the ion, selecting a particular fragment by

tion (CID) available with the Cyclic IMS System, gives scientists improved sequence coverage for native proteins and surrogate peptides and additional structural information about larger proteins that might not have been possible before. The Waters™ Cyclic IMS System can perform scalable ion mobility separations and is also capable of IMSⁿ experiments (e.g. selecting an ion by IMS, fragmenting the ion, selecting a particular fragment by

NEW PRODUCTS

IMS and repeating the process) which derives detailed structural information about a single analyte.

Waters

► <http://link.spectroscopyasia.com/32-071>

Pfeiffer Vacuum introduces new gas analysers

Pfeiffer Vacuum has introduced the OmniStar and ThermoStar GSD 350 compact, portable benchtop gas analysers for use at atmospheric pressure. The gas inlet is fitted with a heated capillary for use at up to 350°C. This prevents vapours from condensing during process gas analysis. Thanks to the two-stage inlet system, an almost segregation-free gas supply is possible. The ThermoStar solution was specially developed for coupling with thermo balances. The inlet system with a quartz capillary and a platinum orifice ensures that even the smallest concentrations can be analysed. The OmniStar was developed for a wide range of applications and uses a stainless steel capillary as well as a valve which can interrupt the sample gas stream. Unlike other analytical methods, the two new devices allow simultaneous detection of all gases within the mass range.

The new PV MassSpec software enables qualitative and quantitative analyses. This software offers a clear and user-friendly platform for recording and displaying measurement data and parameter settings, and complete measuring procedures can be programmed and automated. With a range of instruments available, the mass ranges of 1–100 u, 1–200 u and 1–300 u are covered.



The new instruments have low detection limits (depending on the mass range) of up to <math><100\text{ ppb}</math>, gas consumption of 1–2 sccm and fast measuring time (up to

Pfeiffer Vacuum

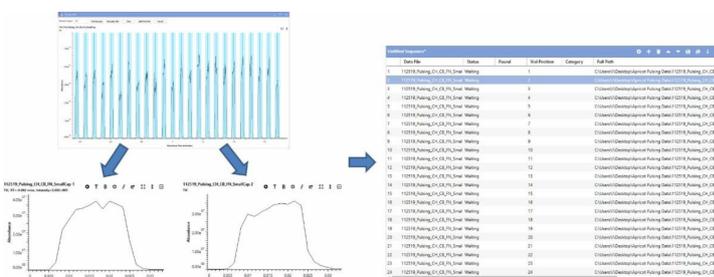
► <http://link.spectroscopyasia.com/32-075>

New software for DART-MS

In collaboration with SpectralWorks, IonSense have added features to their AnalyzerPro XD software to permit parsing of samples within a single data file to individual data files for each sample. After parsing, each of the individual parsed data files can be exported to CSV files with the mass spectrum masses and intensities. You can also search each parsed data file against any NIST MS database or your own database. Target compounds can be mapped and wells containing your targets can be identified with the visual heat map. Also, the amount in each well can be determined and quantified. Classification with PCA or the use of other statistical analysis techniques can be performed to further analyse your data.

IonSense

► <http://link.spectroscopyasia.com/32-081>



NMR

2D-barcode NMR tube scanner

The Express Scanner from Ziath ensures the traceability of samples in 2D-barcode nuclear magnetic resonance (NMR) tubes. It can decode a full rack of 2D-barcode NMR sample tubes in under 3s. Traditionally 2D-barcode NMR tubes are difficult to read with a conventional scanner, as the caps are on the top of the tubes and most scanners are designed to read from underneath. The Express scanner is designed to operate on top



NEW PRODUCTS

of the sample tubes without applying any weight which could damage them. In addition, for Bruker NMR spectrometer users, Ziath provides a dedicated slide for their tube carriers which can only be inserted in one orientation: thereby conserving the origin position (the "A1" position) each time.

The Express Scanner is supplied with a controller which regulates scanning and data processing using Ziath industry-standard

Datapaq software (version 3.17) or new DP5 web-enabled software, which enable exporting of tube barcodes in tables, as text, JPEG, XML, XLS files and in JSON formats. The Express Scanner controller can be separated and positioned under your lab bench.

Ziath

► <http://link.spectroscopyasia.com/32-080>

RAMAN

High-sensitivity NIR Raman spectrometer

Teledyne Princeton Instruments has introduced the TPIR-785 Raman spectrometer, an ultra-high-sensitivity spectrometer for NIR Raman spectroscopic application areas such as biology, medical research and life science where NIR excitation lasers (785 nm and 830 nm) are preferred. It uses an f/2 spectrograph with custom-designed lens optics to provide high light throughput and imaging quality in the NIR spectral range. The TPIR-785 also allows users to tailor the instrument's performance for optimal spectral resolution (up to 5 cm^{-1}) or optimal spectral range (up to $80\text{--}3650\text{ cm}^{-1}$). The system includes a 785 nm Raman probe, a universal fibre adaptor, a manual adjustable slit, and a high-power and temperature-stabilised 785 nm laser.

The TPIR-785 Raman system uses a proprietary CCD that has NIR quantum efficiency $>70\%$ at 1000 nm. This "super-deep-depletion" sensor has a 1340×400 array composed of $20\text{ }\mu\text{m}$ square pixels and can be thermoelectrically cooled to -90°C for ultra-low dark current, allowing integration times from $10\text{ }\mu\text{s}$ to hours. The detector has spectral rates higher than 1 kHz, readout speeds up to 16 MHz and employs two readout ports. A new NIR optimised eXcelon™ process eliminates etaloning fringes and improves quantum efficiency. The high imaging quality spectro-



graph paired with large format detector allows the use of large fibre bundles for improved collection efficiency or Raman imaging measurement.

Teledyne Princeton Instruments

► <http://link.spectroscopyasia.com/32-069>

Enhanced nanoparticle analysis

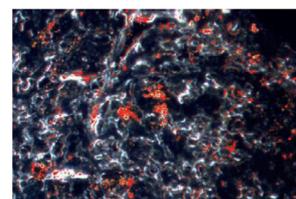
HORIBA Scientific has announced products using technology from CytoViva, Inc. that combine HORIBA's Raman microscopes with CytoViva's hyperspectral imaging (HSI) microscopy module and enhanced darkfield (EDF) illumination. This integration is of interest for applications related to nanomaterials research, drug delivery, nanotoxicology studies and SERS nanoparticles characterisation. HSI microscopy allows rapid imaging across the sample with high sensitivity. Coloured images generated from the spectra guide the user to easily locate nanoparticles and features of interest. CytoViva's patented EDF illumination improves the signal-to-noise ratio up to ten times over standard darkfield microscopes. The detection limit in size improves sufficiently to allow visualising nanoparticles as small as 10 nm when isolated. Integrating Raman with HSI and EDF allows users rapidly to visualise the sample and target regions of interest. They can then perform Raman measurements from the identical field of view to provide and confirm the chemical identify of nanoparticles or other sample elements.

In the figure, gold nanoparticles are imaged in tissue (top), with the corresponding optical (bottom left) and Raman (bottom right) spectra showing clear differences between the nanoparti-

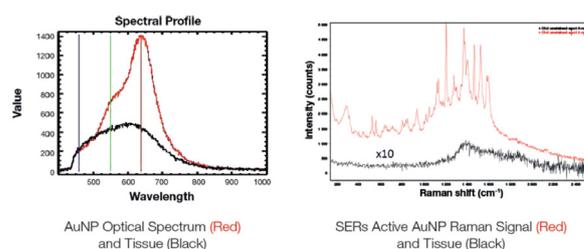
cles and tissue. Visualisation of the nanoparticles is simple with the HSI, while Raman provides a detailed chemical fingerprint.

HORIBA Scientific

► <http://link.spectroscopyasia.com/32-070>



Hyperspectral Mapping (Red) of Image Pixels



AuNP Optical Spectrum (Red) and Tissue (Black)

SERS Active AuNP Raman Signal (Red) and Tissue (Black)

NEW PRODUCTS

New handled Raman spectrometer

B&W Tek have introduced a new version of their TacticID[®]-1064 1064nm handheld Raman analyser that can analyse substances

through opaque barriers. The TacticID[®]-1064 ST uses their patented STRaman[®] technology.

B&W Tek

► <http://link.spectroscopyasia.com/32-074>

SOFTWARE

KnowItAll 2020 upgrade

A new version, KnowItAll 2020, has been released. There is a simplified interface to streamline workflow for spectral search. It also integrates spectral mixture analysis and spectral deformation capabilities directly into the interface. Spectral processing and IR and Raman functional group analyses have been streamlined. A new layout combines previously separate applications for each technique into a smart application that can recognise file type. IR Spectra Classification for Designer Drugs allows researchers to submit an unknown spectrum for quick classification using Wiley's new IR Designer Drug Models. Compound classes include: amphetamines, anabolic steroids, barbiturates, benzodiazepines, cannabinoids, cathinones, cocaine-type substances, opioids, phencyclidine-type substances, phenethylamines, piperazines, steroids, tryptamines.

Enhanced Simultaneous Multi-Technique Search has improved ability to search unknown spectra from disparate multiple tech-

nique spectra simultaneously and visualise the results on a scatter plot. Increased Chemical Intelligence with The new Related Compounds View provides increased insight into analyses by exploring a fuller view of compounds related to scientific results. This view interconnects all available reference data by structure, name, synonym and CAS registry number to add a high level of chemical intelligence to the entire platform.

DEA Controlled Substance Prediction enables users to match a structure with Drug Enforcement Agency 21 CFR Regulations on controlled substances. New tools in the enhanced structure drawing make it easier to move, highlight and select objects. There is also a more comprehensive set of pre-defined substituent fragments and expanded "fuzzy" structure representation features.

John Wiley & Sons

► <http://link.spectroscopyasia.com/32-083>

Software to combine EM spectroscopy and AFM data

Oxford Instruments and Digital Surf have announced the release of Relate software for users of Oxford Instrument's tools for materials characterisation. Relate software provides correlation of spectrometry (EDS and EBSD) data with AFM data and microscopy images with easy-to-use tools for rapid manual and semi-automated correlation of multiple images. 3D and 2D visualisation of composite data sets show EDS, EBSD and EM image layers combined with topography and material properties as measured by AFM, helping to reveal the micro- and nano-characteristics

of a sample. Correlated quantitative data can be analysed by extracting underlying data values in addition to qualitative images (e.g. x-ray counts for each element). Data and images can be organised and reports published in popular formats (PDF, Word etc.). The interactive workflow is documented allowing traceability during the image analysis process.

Oxford Instruments NanoAnalysis

► <http://link.spectroscopyasia.com/32-067>

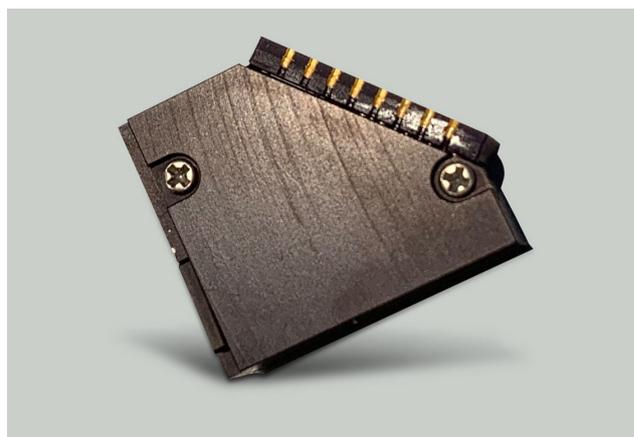
UV/VIS

Improved version of the PEBBLE VIS ultra-compact spectrometer

Ibsen Photonics has released an improved version of its ultra-compact PEBBLE VIS OEM spectrometer. The new PEBBLE VIS combines an ultra-compact form factor of only 20×15×8mm with high resolution and sensitivity as well as environmental ruggedness. The wavelength range has been shifted towards the UV to cover 360–830nm, and the resolution is still 6nm. The pure transmission-based optics inside PEBBLE provide high sensitivity, low stray light and thermal stability. The detector is a CMOS array with 256 pixels, and the electronics interface is a tiny flex-connector that fits on the new miniature DISB-105 read-out electronics.

Ibsen Photonics

► <http://link.spectroscopyasia.com/32-076>



NEW PRODUCTS

X-RAY

New tube-below WDXRF spectrometer from Rigaku

Rigaku Corporation has introduced the Rigaku ZSX Primus IVi tube-below sequential wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The new spectrometer has a tube-below configuration optimised for the measurement of a variety of sample types including liquids, alloys and plated metals. The efficiency of the new drive sequence decreases time between multiple high-speed precision measurements. The redesigned control systems optimise a series of movement sequences, also resulting in shortened measurement times. A patented vacuum partition system is used for analysing liquids. Because the spectroscopic chamber is separated from the sample chamber when changing helium gas, the conversion from vacuum atmosphere to helium atmosphere can be completed in under two minutes. Helium consumption is further reduced compared to models where the spectroscopic chamber must also be fully purged.

The Rigaku optical system is resistant to impact by sample surface height, and enables suppression of X-ray intensity changes caused by variation in distance from the tube. Accuracy of analysis is enhanced by minimising the effects from differences in fusion moulds used in glass bead formulation and the impact of uneven sample surfaces. The enhanced ZSX Guidance software, that comes with the spectrometer, guides the user through automated optimised analysis settings. The software includes a quantitative application auto-configuration features that automatically sets measurement conditions and various corrections based on the user's own standards. An error



prevention function, which can set an access level for each operator, was also added for worry-free operation. The software is programmable for routine, everyday analysis using removable sample trays. Sample ID settings for each tray facilitates easy copy-and-paste for efficient measurements. Improved accuracy of liquid sample analysis is achieved by enabling the correction of geometry effect caused by the geometry of liquid sample cups.

Rigaku

▶ <http://link.spectroscopyasia.com/32-077>

Handheld XRF analyser with light element detection

The new Vanta Element-S handheld X-ray fluorescence (XRF) analyser provides fast light element detection at an affordable price, adding to the family of entry-level Vanta Element XRF instruments. The S model is equipped with a silicon drift detector (SDD) to analyse light elements such as magnesium (Mg), aluminium (Al), silicon (Si), sulfur (S) and phosphorus (P) in alloys. It is suitable for scrap recycling, basic PMI, metal manufacturing and precious metals, measuring ferrous metals, aluminium, copper, stainless steel, nickel and gold karats. The analyser offers on-screen grade ID and comparison for the light elements Mg, Al and Si in seconds. Its SDD detector can distinguish similar alloy grades such as 303 stainless steel from 304, and aluminium 6061 or 6063 from 1100.

The Vanta Element-S weighs 1.32kg and is IP54-rated to resist dust and moisture and built to pass a 1.2m drop test (MIL-STD-810G) to help protect from the occasional drop or jostle. Other protective features include a stainless-steel faceplate and a Prolene® window with Kapton® mesh support that easily sticks on and peels off for tool-less window changes in the field. Optional wireless connectivity is available, and users can connect to the Olympus Scientific Cloud™ for wireless data sharing and access to convenient fleet management tools, as well as

the Olympus mobile app or the company network. The analyser also has a 1-GB microSD™ card to store results and two USB ports to export data.

Olympus IMS

▶ <http://link.spectroscopyasia.com/32-056>



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