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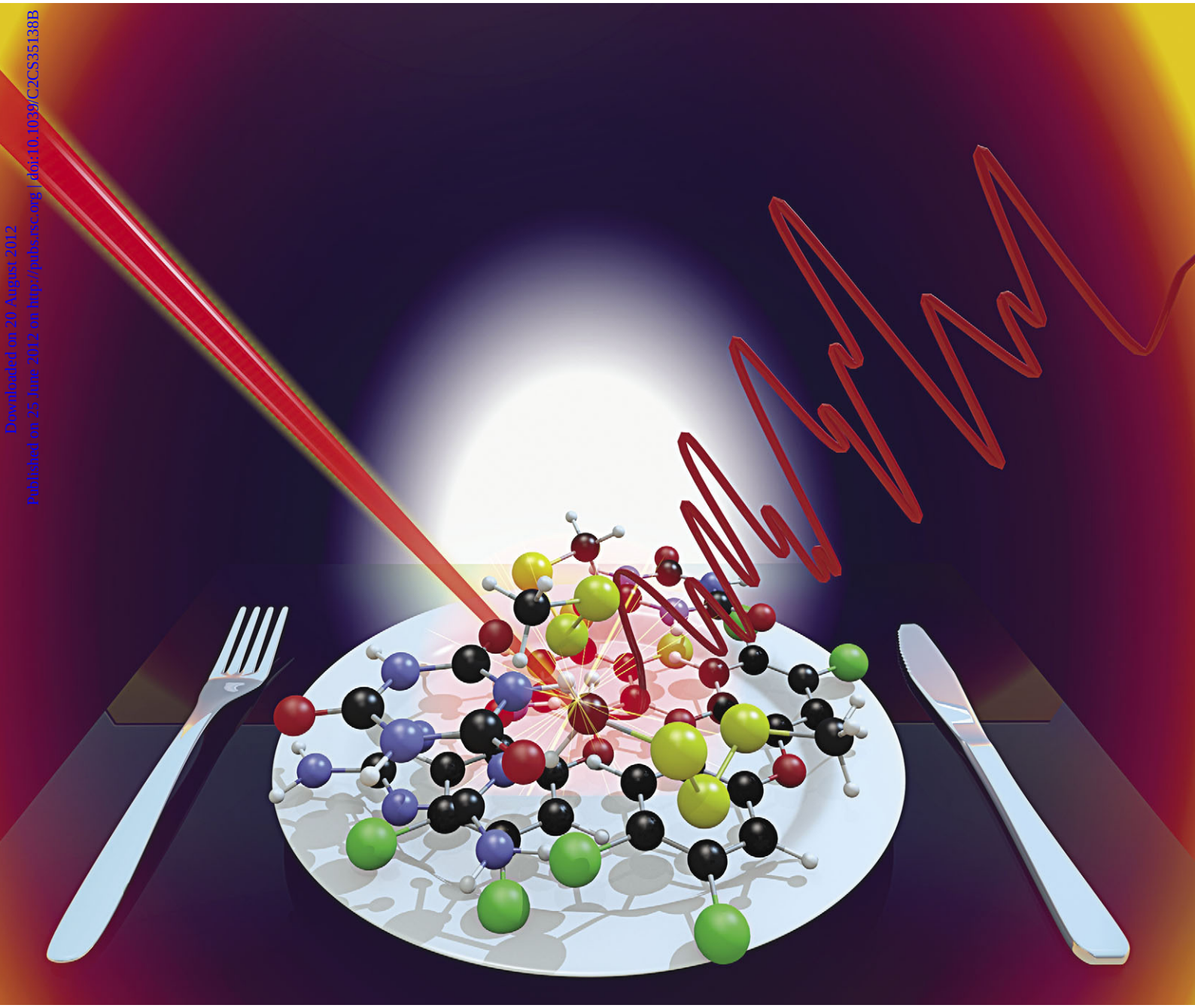

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CRITICAL REVIEW

Fingerprinting food: current technologies for the detection of food adulteration and contamination

David I. Ellis,*[a] Victoria L. Brewster,[a] Warwick B. Dunn,[ab] J. William Allwood,[a] Alexander P. Golovanov[c] and Royston Goodacre[ab]

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Major food adulteration and contamination events seem to occur with some regularity, such as the widely publicised adulteration of milk products with melamine and the recent microbial contamination of vegetables across Europe for example. With globalisation and rapid distribution systems, these can have international impacts with far-reaching and sometimes lethal consequences. These events, though potentially global in the modern era, are in fact far from contemporary, and deliberate adulteration of food products is probably as old as the food processing and production systems themselves. This review first introduces some background into these practices, both historically and contemporary, before introducing a range of the technologies currently available for the detection of food adulteration and contamination. These methods include the vibrational spectroscopies: near-infrared, mid-infrared, Raman; NMR spectroscopy, as well as a range of mass spectrometry (MS) techniques, amongst others. This subject area is particularly relevant at this time, as it not only concerns the continuous engagement with food adulterers, but also more recent issues such as food security, bioterrorism and climate change. It is hoped that this introductory overview acts as a springboard for researchers in science, technology, engineering, and industry, in this era of systems-level thinking and interdisciplinary approaches to new and contemporary problems.

Introduction

Major food adulteration/contamination events with international impacts and consequences, such as the milk scandal in China and the Irish pork crisis (both in 2008) and the resultant media attention, throw into sharp focus the requirement for continued vigilance, research and development of rapid analytical and detection techniques for food, feedstuffs,[1] and food-related products[2–4] and systems.[5] The problem of food adulteration is by no means a contemporary phenomenon and is likely to be as old as the food processing and production systems themselves.[6] In the 'modern' scientific era, the first to address this issue was the German analytical chemist Frederick Accum who completed a treatise on adulteration of food and culinary poisons published in 1820.[7] This was the first serious attempt to expose both the extent and dangers of food adulteration.[8] Table 1 lists some of the adulterants identified by Accum and Hassall at this time, and some of these 'additives' are seriously toxic to humans, one of the more worrying ones was the practice of using red lead (Pb_3O_4) to give a vibrant colour to cayenne pepper.

This seminal work was followed three decades later by further in-depth analyses of food adulterants in thousands of food and drink samples, initiated by the then editor of *The Lancet*, Thomas Wakley, undertaken by the physician Arthur Hill Hassall and published in *The Lancet* in the 1850s.[8,9] This was subsequently followed by food regulation becoming part of UK law, such as the Adulteration Act of 1860 and the Sale of Food and Drugs Act 1875 (the basis for many modern food regulation Laws globally). By the end of that century however, it was still apparent that the practice of adulteration was rife and knew no international boundaries. In an article from the New York Times in 1900, the then Consul General to France, James T. Dubois, reported to the US State Department that: "in spite of the activity of the authorities in endeavouring to suppress the debasement of the food supply; the adulterators continue to grow even bolder, and extend their depredations with discouraging rapidity and success".[10] The report went on to describe the adulteration of a wide range of products, such as chocolate, wine, butter, tea, cheese, coffee, and milk; whereby milk was diluted and then 'certain kinds of soap' used to restore its colour.

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The World Health Organisation (WHO) called China's international milk crisis: "one of the largest food safety events the UN health agency has had to deal with in recent years". This involved melamine (Fig. 1), a nitrogen-rich organic base normally used in plastic manufacture, which was added to food products, including milk, to raise nitrogen-based tests spuriously for protein content.[11] The sequence of events started in May 2007 when a number of cats and dogs died in the USA after ingesting melamine-contaminated pet food imported from China,[12] followed in December of the same year by the first reports in China of sick babies with discoloured urine (who had ingested deliberately adulterated milk), with the first child fatality occurring on 1 May 2008. It was reported that by the end of the year there were an estimated 300 000 victims in China, including six child fatalities due to kidney damage, with a further 860 infants hospitalised.[13,14]

The contamination widened and spread to several other countries, where a number of food products tested positive for melamine. These included egg powder in Japan and South Korea, batches of eggs in Hong Kong, biscuits in Switzerland, confectionary in New Zealand, baking powder in Malaysia, and many countries around the world recalled a range of potentially contaminated products.[15] In addition to melamine adulteration of milk powder within China, animal feedstuffs and other products had also regularly been adulterated for short-term economic gain, with a blatant disregard for the potential health consequences[16] and resultant impacts on international trade. During and following the scandal, much research effort has been focussed on the detection of melamine in a wide range of products using a wide variety of analytical techniques. These include: in milk and milk products by chromatography[17] and low temperature plasma probe and MS;[18] in animal feed by chromatography and tandem MS;[19] in cereal flours by HPLC;[20] in muscle tissue by LC–MS;[21] in pet food by ELISA[22] and UPLC and tandem MS;[23] in gluten, chicken feed, cakes and noodles by surface enhanced Raman

David I. Ellis

David Ellis was educated on the Welsh coast at the University of Wales, Aberystwyth obtaining a BSc in Environmental Science and a PhD in Analytical Biotechnology/Microbiology. His research involving the rapid and quantitative detection of foodborne bacteria using FT–IR and machine learning has been widely publicised, featuring on BBC TV and radio, at the National Science Museum in London, as well as in the national and international press. He is now Senior Experimental Officer/Laboratory Manager for Roy Goodacre (biospec.net) and Douglas Kell's labs (dbkgroup.org) in the School of Chemistry, Manchester Institute of Biotechnology (MIB), The University of Manchester, UK.

Victoria L. Brewster

Victoria Brewster studied for her BSc in Chemical and Forensic sciences at The University of Bradford, and went on to obtain her MPhil in the application of Raman spectroscopic methods to forensic analysis. Currently, Victoria is developing spectroscopic methods for the characterisation of proteins at the Manchester Institute of Biotechnology, School of Chemistry, University of Manchester, UK, through a BBSRC CASE PhD studentship in collaboration with Avacta Plc.

Warwick B. Dunn

Warwick Dunn obtained degrees in Analytical Chemistry at The University of Hull and moved to The University of Manchester in 2003 to develop and apply bioanalytical tools in systems biology research. He is employed at The School of Biomedicine as Lecturer in Applied Metabolomics and as the Metabolomics Lead in The Centre for Advanced Discovery and Experimental Therapeutics. Warwick has the research objectives to investigate molecular processes related to mammalian diseases and in discovery and development of therapeutics. Warwick is an International Board member of the Metabolomics Society and is a member of the editorial board of the journal Metabolomics.

J. William Allwood

After having been schooled and worked in the picturesque South Shropshire countryside for 20 years, Will Allwood moved to Aberystwyth (Ceredigion) where he studied for a BSc in Microbiology and completed a PhD in the areas of metabolic profiling and molecular plant pathology. Will has since worked as a postdoctoral research associate for the Wheat Pathogenesis team at Rothamsted Research and for the last five years within the School of Chemistry at The University of Manchester, firstly on an EU funded project, META–PHOR Metabolomics for Plants, Health and Outreach, and secondly performing clinical metabolic profiling applications with Cancer Research UK.

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Table 1 Some food adulterants identified by Accum and Hassall in the 1820s and 1850s

	Adulterant	
Food product	For bulking/weight	For appearance/taste/aroma
Cayenne pepper	Bulked with ground rice, mustard seed husks, sawdust, salt	Coloured with red lead, vermilion, venetian red (derived from nearly pure ferric oxide, Fe_2O_3), turmeric
Cocoa and chocolate	Arrowroot (*Maranta arundinacea*), wheat, maize, sago, potato, tapioca flour, chicory	Venetian red, red ochre (hydrated iron(III) oxide), other iron compounds
Coffee	Chicory, roasted wheat, rye flour, potato flour, roasted beans, acorns	Burnt sugar (known as black jack) as a darkener
Confectionery		White comfits coloured with Cornish clay (kaolinite, $Al_2Si_2O_5(OH)_4$), red sweets coloured with red lead and vermilion, green sweets were often found coloured with copper salts (*i.e.* copper acetate, $Cu(CH_3COO)_2$) and Scheele's green (copper arsenite, $CuHAsO_3$)
Custard powders	Wheat, potato flour, rice flour	Lead chromate ($PbCrO_4$), and turmeric to enhance the yellow colour
Gin	Water	Cayenne, cassia (*Cinnamomum aromaticum*), cinnamon, sugar, alum (hydrated potassium aluminium sulfate, $KAl(SO_4)_2{\cdot}12H_2O$), salt of tartar (potassium carbonate, K_2CO_3)
Olive oil		Often contained lead from olive presses
Pickles		Coloured green with copper (Cu^{2+}) salts
Porter and stout	Water	Brown sugar, *Cocculus indicus* (commonly known as fishberry or Levant nut and a primary source of picrotoxin, a poisonous crystalline alkaloid, $C_{30}H_{34}O_{13}$), copperas (Iron(II) sulfate, $FeSO_4$), salt, capsicum, ginger, wormwood (*Artemisia absinthium*), coriander and caraway seeds, liquorice, honey, *Nux vomica* seeds, also known as poison nut, from the strychnine tree (a major source of the highly poisonous alkaloids strychnine ($C_{21}H_{22}N_2O_2$) and brucine ($C_{23}H_{26}N_2O_4$), cream of tartar (Potassium bitartrate, ($KC_4H_5O_6$), hartshorn shavings (horns of the male Red Deer, *Cervus elaphus*), treacle
Red cheese		Coloured with red lead (lead tetroxide, Pb_3O_4), and vermilion (mercury sulfide, HgS)
Tea	Previously used tea leaves, dried leaves from various plants other than tea, starch, sand, china clay	Plumbago, gum, indigofera, Prussian blue ($Fe_7(CN)_{18}{\cdot}14H_2O$) for black tea, turmeric, orpiment (arsenic sulfide, As_2S_3), copper salts for green tea
Vinegar		So-called 'sharpened' with sulfuric acid (H_2SO_4), and containing dissolved tin and lead when boiled in pewter vessels

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scattering (SERS) and HPLC;[24] in rice concentrates by LC;[25] in meat and pet food using LC–MS;[26] and finally by ultrasound assisted HPLC in pet food[27] as well as ultrasound assisted electrospray ionization MS in untreated milk and wheat gluten.[28]

The so-called 'Irish pork crisis' became public in December 2008, when it was revealed that animal feed contaminated with industrial oil had been provided to over 50 beef and pork farms and one dairy farm across the Republic of Ireland and Northern Ireland. During routine monitoring of Irish pork at this time, elevated levels of polychlorinated biphenyls (PCBs) were found in pork and further investigation revealed the presence of dioxins and dioxin-like PCBs up to 200 pg WHO-TEQ/g fat,[29] 200 times the recommended amount in meat, which is 1–3 ng WHO-TEQ/kg fat (a WHO-TEQ is the World Health Organisation's definition of a toxic equivalency

Alexander P. Golovanov

Alexander Golovanov was born in Russia, where he graduated from the Moscow Institute of Physics and Technology in 1988. He obtained his PhD in Chemistry in 1994 studying the structure of cobra neurotoxin using NMR spectroscopy. In 1998 he moved to the UK, and from 2001 was appointed Senior Experimental Officer and NMR Manager at The University of Manchester. In 2006 he joined the academic staff in the Faculty of Life Sciences, The University of Manchester, where he leads a research group and continues to work in the area of NMR applications to Structural Biology.

Royston Goodacre

Roy Goodacre is Professor of Biological Chemistry at the School of Chemistry, The University of Manchester, UK. His group's main areas of research (http://www.biospec.net/) are broadly within analytical biotechnology, metabolomics and systems biology. His expertise involves mass spectrometry, FT–IR and Raman spectroscopy, as well as advanced chemometrics and machine learning. He is Editor-in-Chief of the journal Metabolomics, a founding director of the Metabolomics Society and a director of the Metabolic Profiling Forum.

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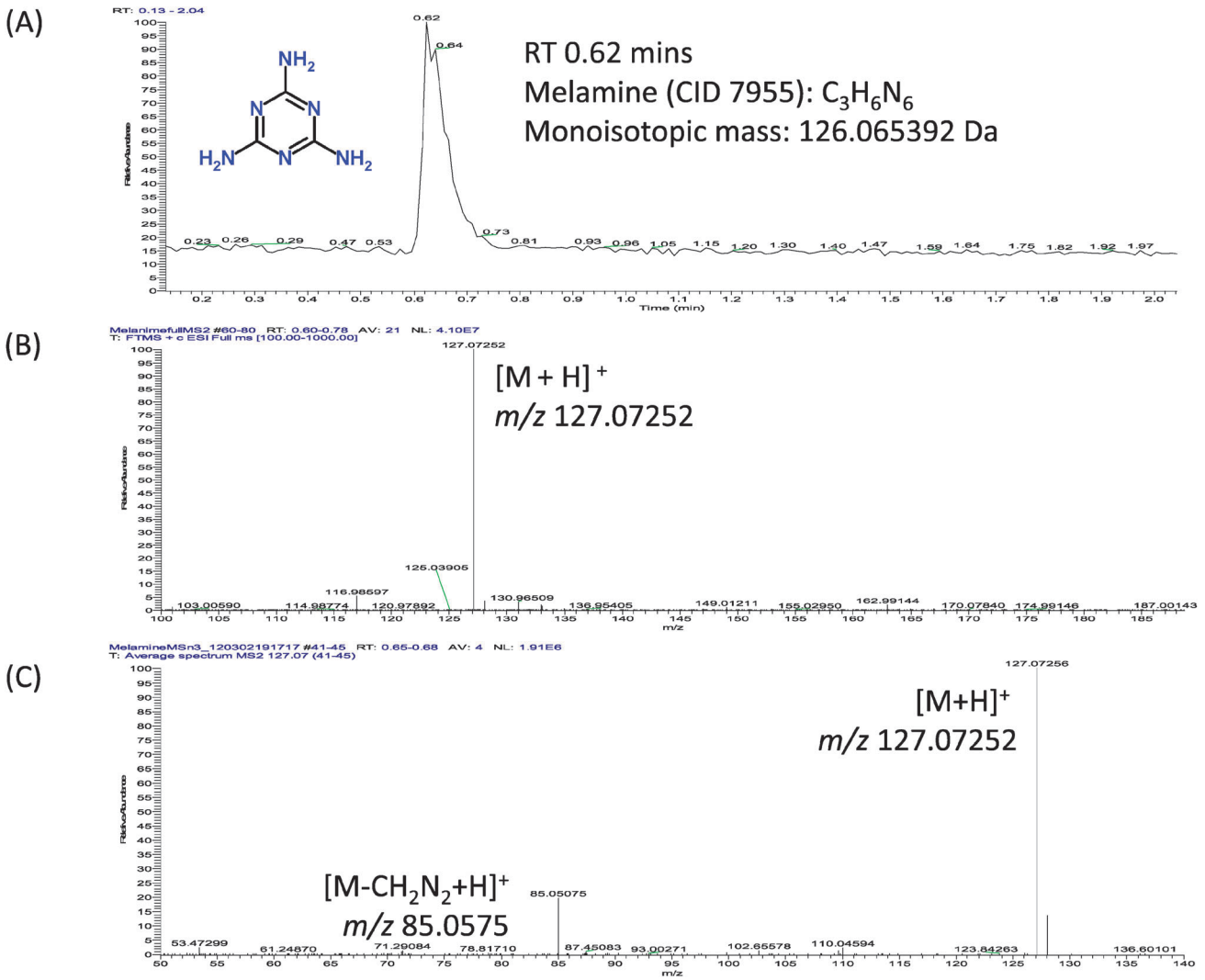

Fig. 1 Reverse phase C18 ultra high performance liquid chromatography (UHPLC) mass spectrometry system analysis of melamine: (A) UHPLC chromatogram showing melamine eluting at 0.62 min; (B) ESI + /LTQ-Orbitrap XL MS full scan mass spectra of melamine in positive ion mode; (C) ESI + /LTQ-Orbitrap XL MS collision induced dissociation (CID) fragmentation mass spectra.

factor to the most toxic dioxin; http://www.foodstandards.gov.uk/multimedia/faq/dioxins_qanda/). This led to a mass recall of pork products, and within several days thousands in the industry had lost their jobs and in excess of 20 countries had banned the import of Irish pork. Later reports confirmed that dioxins were also detected in beef, then milk, from two dairy farms in Northern Ireland, reported to be the result of dioxin residues in the fat of animals which had previously eaten contaminated feed.[30] This was reminiscent of an earlier incident in Belgium in January 1999, when feed contaminated by transformer oil was distributed to farms in Belgium and to a lesser extent the Netherlands, France and Germany. As a consequence of the Belgian incident alone, it has been stated that between 10–15 kg of PCBs and 200–300 mg of dioxins were ingested by 10 million Belgians and that neurotoxic and behavioural effects in neonates were expected but could not be quantified.[31–33]

Unfortunately, events with international impacts such as these are not unique or infrequent. With electronic mass media these are rapidly published throughout the global community, with the subsequent knock on effects and product recalls being equally swift. Some of the more prominent of those publicised in recent history (apart from those already mentioned) include: carcinogenic red dye Sudan-1 found in some chilli powder and tomato based products;[34,35] BSE in the late 1980s and early 1990s (a result of scrapie infected meat and bone meal (MBM) being fed to 'ordinarily' herbivorous cows);[36,37] Spanish Toxic Oil Syndrome in 1981 from the consumption of denatured rapeseed oil intended for industrial use;[38–40] and polyethylene glycol (anti-freeze) and raw methanol adulteration of wines.[41,42] In addition to these cases, where food adulteration was a means for fraudulent economic gain (or attempts at cost savings in terms of using cheaper ingredients), during the last decade this area has become open to a perhaps more sinister and destructive potential, that of deliberate adulteration/contamination of the food supply as an act of bioterrorism.[43–45]

It is apparent that the subject of detection science in foods, is by its very nature huge in scope and that all of the detection methods cannot be covered with any depth in a single review of this size;[46] indeed, they would very easily fill several volumes.

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Therefore, the authors wish to give a 'flavour' of some of the methods used by discussing a selection of the rapid detection technologies currently available, and a number of their applications to a variety of food and feedstuff authentication/adulteration problems. These include vibrational spectroscopies (such as infrared and Raman techniques), notable for both their rapidity and portability, nuclear magnetic resonance (NMR) spectroscopy, again notable for its rapidity (and, like vibrational techniques, having the potential for high-throughput analyses) and finally, a range of MS-based, chromatographic and other technologies. It is hoped that this will encourage the general reader to explore this area in greater depth, as well as raising awareness of the range of possibilities available in this exciting and rapidly developing era of interdisciplinary detection science.

Fourier transform infrared (FT–IR) spectroscopy

FT–IR spectroscopy allows for the extremely rapid, high-throughput and non-destructive analysis of a wide range of sample types in both research and industrial environments. This technique is based on the principle that when a sample is interrogated with an infrared beam (usually in the mid-infrared from 4000–400 cm^{-1} or near-infrared 14 000–4000 cm^{-1}), functional groups within the sample will absorb this radiation and vibrate in one of a number of recognized ways (such as stretching or bending vibrations)[47] and these vibrations/absorptions can then be correlated directly with (bio)chemical species. The resultant infrared absorbance spectrum can therefore be described as a chemical 'fingerprint', as it is characteristic of the particular sample under analysis and hence, every chemical or biochemical substance will have its own unique infrared profile.[48,49]

A significant proportion of the work undertaken in recent years has concentrated on the mid-IR part of the electromagnetic (EM) spectrum, as this part of the spectrum is where the fundamental vibration is seen (as opposed to overtones or harmonics in near-IR) and is particularly information rich. With relevance to biological applications the mid-IR can be further broken down into specific regions, or windows, of biological interest such as: C–H_x stretching vibrations from fatty acids (3050–2800 cm^{-1}); C=O, N–H and C–N from proteins and peptides (1750–1500 cm^{-1}); C–O and C–O–C from polysaccharides (1200–900 cm^{-1}); and P–O vibrations from nucleic acids (1245–1220 and 1090–1085 cm^{-1}).

The rapidity and reproducibility of FT–IR spectroscopy is demonstrable through the large body of research published using this technology, and indeed, its rapidity cannot be overstressed as 1000s of spectra can be collected within a 24 h period.[48] Moreover, due to its holistic nature, FT–IR has been recognized as a valuable tool for metabolic fingerprinting,[49–51] as it is able to analyse carbohydrates, amino acids, fatty acids, lipids, proteins, nucleic acids and polysaccharides rapidly and simultaneously with a minimum amount of sample preparation or background training. Whilst one of the potential limitations of FT–IR spectroscopy is that the absorption of water is very intense in the mid-IR, this problem can be overcome either by dehydration of samples, reconstituting in D_2O, subtraction of the water signal, reduction in path length, or through the use of attenuated total reflectance (ATR) as a sampling method.[52–55] Alternatively, one may use the related vibrational technique, Raman spectroscopy (*vide infra*). A further perceived disadvantage is that as a holistic measurement is made containing biochemical information from across the whole of the IR (or Raman) spectrum, validated and robust chemometrics must be used in order to translate data into information;[49,50,56,57] the various approaches for chemometrics will be detailed below. Typical FT–IR and Raman spectra from milk can be seen in Fig. 2.

Applications of FT–IR spectroscopy have been broad in scope, and within the biosciences this was assisted in the 1990s by the technique being demonstrated to be particularly useful for the discrimination of axenically cultured bacteria,[58–61] and

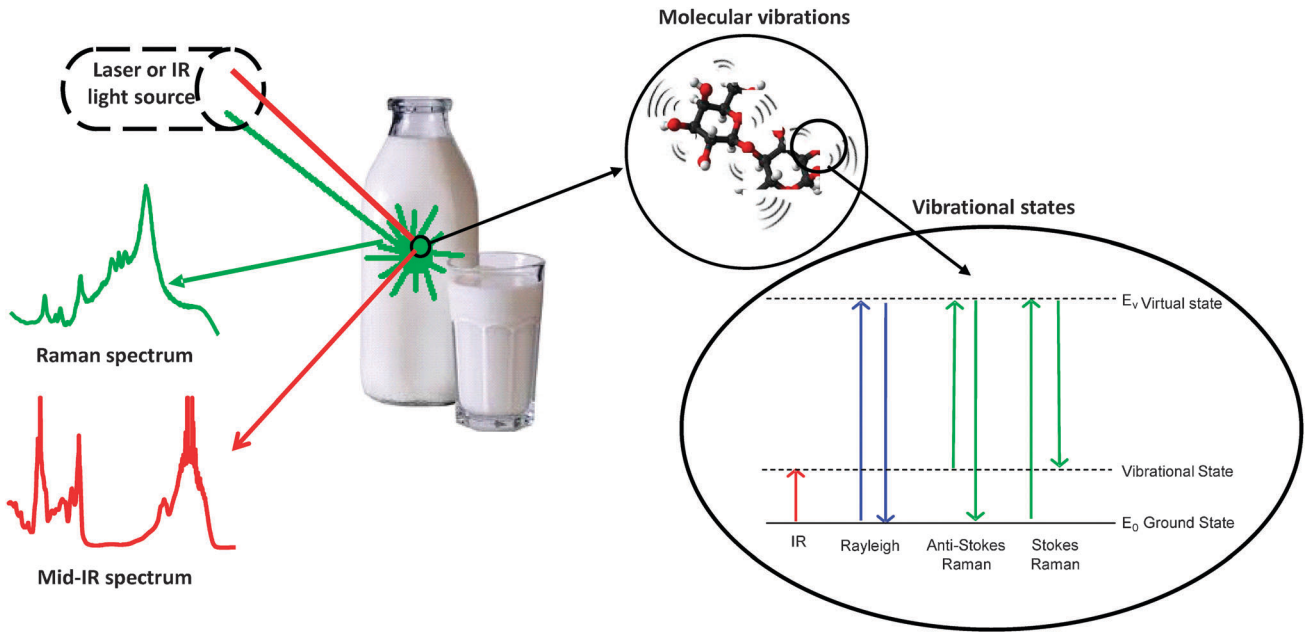

Fig. 2 Schematic showing collection of typical Raman and FT–IR spectra collected from whole milk. The molecular vibrational states along with a simplified Jablonski diagram are also shown.

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work on food-related bacteria continues.[62] The work undertaken during the 90s spawned a considerable amount of interest which has led to other areas of research, such as disease diagnostics[50] and metabolomics;[48,63] more specifically referred to as metabolic fingerprinting.[49,51,64] Concomitant with these multidisciplinary applications, FT–IR and particularly near-infrared (NIR) spectroscopy have also been viewed as exceptionally useful spectroscopic tools for the analysis of foodstuffs.

During the last decade it has become increasingly evident that mid-infrared (MIR) spectroscopy has considerable potential for industrial applications in the food, feed, and related industries. This includes those sectors involved in the production, processing, packaging[65,66] and retail industries, in addition to the regulatory bodies responsible for monitoring the food chain from farm to fork.[67–70] Such applications have included those involved with product authenticity and adulteration (Fig. 3 illustrates this with respect to fruit juice adulteration), studies into the characterization and determination of adulteration of edible oils for example,[71–73] and rapid determination of total *trans* fat content in foods.[74] Whilst *trans* fatty acids are known to be present in low levels in various foodstuffs, like dairy[75] and meat produce[76] for example, the major source for concern in terms of human health are the commercially hydrogenated *trans* fats found in some food products.[74] It is consumption of a diet high in these artificial fats which can elevate levels of serum low-density lipoprotein (LDL)-cholesterol and lower levels of high-density lipoprotein (HDL)-cholesterol,[74] leading to increased risk of coronary artery disease.[77,78] Thus the detection of this modification is important.

Studies by Mossoba[74,79,80] and others have clearly demonstrated the efficacy of ATR as a rapid and accurate sampling method for *trans* fat analysis in foods. Many of these have utilised what they termed the *trans* absorption band at 966 cm^{-1}. Previously, this had a limit of detection of 5% *trans* fat, although this limitation has been overcome with a more recent methodology which uses the height of the negative second derivative of the 966 cm^{-1} band. This newer methodology has been shown to determine *trans* fat levels in unknown samples as low as approximately 1% of total fat.[81] One recent study used partial least squares regression (PLSR) to build a calibration model using the height of the second derivative at 966 cm^{-1} and applied a handheld diamond ATR spectrometer for the measurement of *trans* fats in several edible oils, including peanut, safflower, corn and coconut oils.[82] Other applications have included the direct measurement of *trans* fats in French fries acquired from

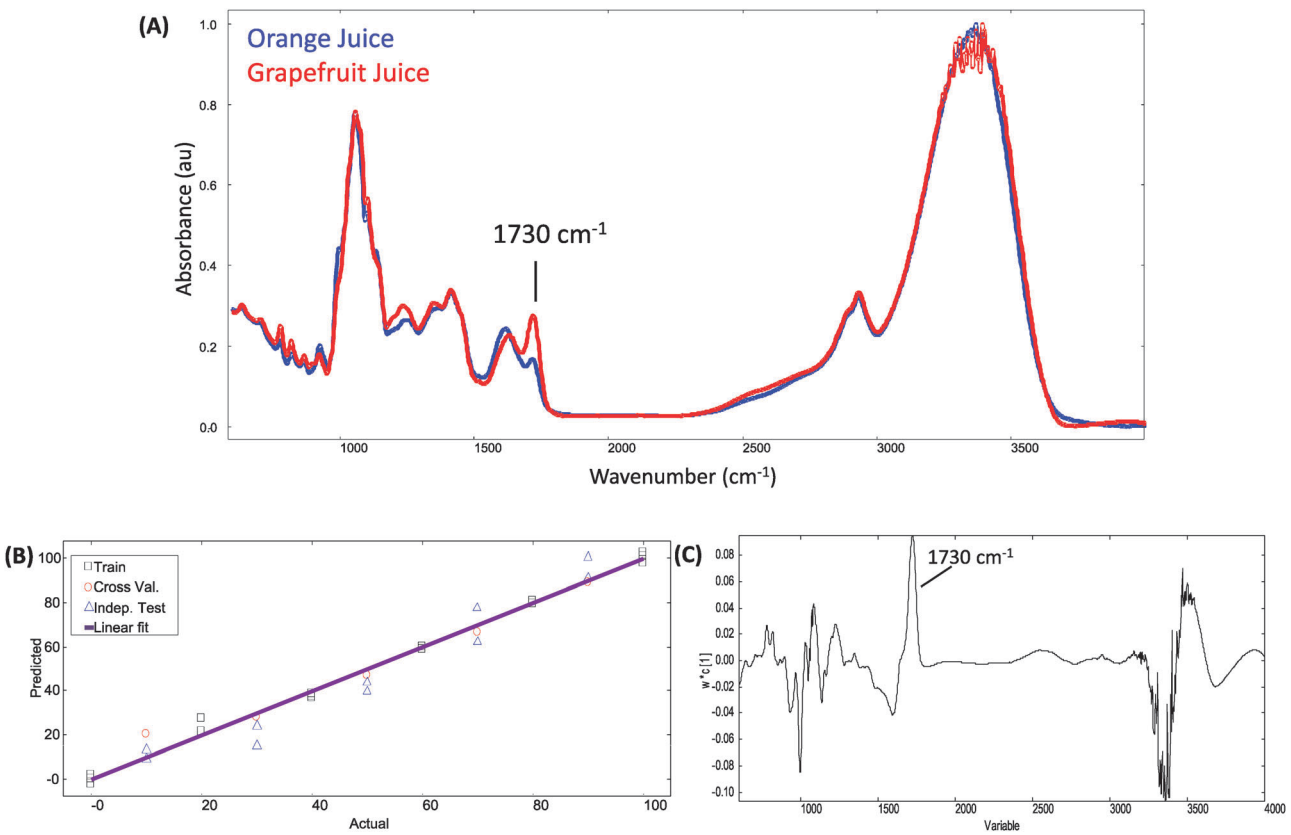

Fig. 3 (A) FT–IR spectra of pure orange juice (red) and pure grapefruit juice (blue). This demonstrates that the two juices can be discriminated between based on spectral features, the most prominent of which is the highlighted band at 1730 cm^{-1}, which can be assigned to the C=O stretching in the flavonoid component of the grapefruit juice. (B) PLS predictions from FT–IR data of orange juice adulterated with grapefruit juice (0–100% in 10% steps). Each point represents one spectrum (data were pre-processed using extended multiplicative scatter correction (EMSC)[344] (polynomial order 7) and column mean centred). (C) PLS loadings from the 1st latent variable (w*c[1]), highlighting the vibrational modes on which the PLSR model was based. These bands correlate well with those highlighted in (A). Spectra were collected on a Bruker Equinox 55 infrared spectrometer, employing a motorised HTS module. Samples were spotted onto a 96 well silicon plate. Spectra were acquired over 4000–600 wavenumbers, 64 scans were co-added and averaged.

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local food outlets with no sample preparation and pressed directly against a ZnSe ATR crystal,[83] determination of *trans* fats from cereal-based South Asian foods[84] and a wide variety of cereal-based snack products[85] as well as deep fat frying oils.[86]

Other applications of FT–IR have included determination of the quality, structural characteristics and identity of dairy products,[87,88] bacterial spoilage of milk[53] and bacterial growth interactions in milk leading to dominating metabolic effects,[89] identification of modified starches[90] and rapid identification of foodborne fungi have also been undertaken,[91,92] amongst others.[93]

A number of studies have also been undertaken on meat and meat products, with many focussing on adulteration and authenticity issues, and several more concerned with bacterial spoilage/contamination and food poisoning. These have included studies discriminating meat at the species level,[94,95] and at the intra-species level,[96] as a first step in product authentication, as well as attempts to detect beef adulterated with offal.[97] Rapid detection of microbial spoilage[51,98] has been undertaken on both poultry and beef using FT–IR[52,99–101] and the first publication of a food metabolomics study was undertaken using FT–IR spectroscopy.[52] These studies focussed on acquiring a biochemical fingerprint of metabolites formed as a result of the growth and enzymatic activity of bacteria *in situ* on the meat surface. Rather than having first to separate physically the microorganisms from the substrate (which is generally the case) and undertaking the time-consuming analysis and enumeration of the bacteria themselves. This has enhanced and accelerated the detection of microbial spoilage from hours to seconds and could theoretically be used to detect other forms of contaminating substances or bacteria.[102,103] The recurring theme in these studies is the need to replace traditional methods which can take days to obtain results on the level of bacterial spoilage. These retrospective measurements are not useful as the food has usually left the retailer and entered the food chain and may cause illness. Therefore rapid detection and quantification within minutes is highly desirable in order to allow adequate control within HACCP (hazard analysis critical control point) regulated systems.

Near infrared (NIR) spectroscopy

For many decades much of the food-related infrared research was almost exclusively reserved to NIR spectroscopy, perhaps due to the robustness and simplicity of instrumentation, its highly precise and efficient nature and its portability. Though in terms of portability, more recently handheld portable FT–IR[82] and Raman[104–107] instruments are also becoming more widely available (see both the FT–IR and Raman sections), though these are not yet as mature as NIR. Indeed, in regards to the maturity of this technique, it has been stated that on/in-line NIR instrumentation has a proven record of 40 years[108] in the food processing industry, particularly with respect to continuous monitoring and control of process and product quality.[109–111] The rapidity of this method also allows for frequent measurements at all stages, from production and collection of raw ingredients, through process monitoring to quality control of finished products.[109] These instruments usually have a very high signal-to-noise ratio[112] and, like MIR, can measure multiple components in a food sample simultaneously, in addition to having remote sampling capability allowing for the collection of real-time information in a process stream.[113]

For food and feedstuff analyses this method clearly has many advantages similar to those of MIR (both being infrared methods), though two main advantages that near-IR has over mid-IR analysis is that: (1) *near*-infrared light penetrates much deeper into an intact food sample (>10 mm), as well as through various packaging materials that are transparent to NIR light;[114] (2) the water absorbance in the near-IR is not as strong as in the mid-IR so analyses are more routine and no additional accessories are needed (*e.g.*, ATR). In terms of limitations, one of the main perceived disadvantages has been stated to be the low sensitivity to some minor constituents,[112] though this can also depend on the chemical species being detected and the complexity of the food matrix under analysis (*vide infra*). Food science-related NIR embodies a large and vibrant research community and, as already mentioned, a long history of applications in industry and both its inclusion here and its continuing contribution to food science are not to be underestimated.[115,116]

It is perhaps not surprising that many of the research applications of NIR to food and feedstuff analysis cover similar areas to FT–IR in the MIR, such as *trans* fat analysis[117,118] and food spoilage for example.[119] Indeed, one very recent study used both NIR and MIR in an attempt to extend current knowledge of the ability of both these methods for the rapid detection of microbial spoilage in poultry.[120] For this study the authors utilised outer-product analysis (OPA),[121] a method said to enable the emphasis of co-evolutions in spectral regions from data acquired from two different domains (heterospectral), or from a single domain (homospectral) following spectral perturbation.[120,122] This particular study by Alexandrakis and co-workers involved the collection of NIR and MIR spectra from 65 poultry samples over 14 days at 4 °C. Multiplicative scatter correction-transformed NIR spectra and standard normal variate-transformed MIR spectra were first analysed using PCA and partial least squares-discriminant analysis (PLS-DA) prior to OPA. Results from OPA were reported from the wavenumber ranges 1550 nm–1996 nm (NIR) and 1000 cm^{-1}–1188 cm^{-1} (FT–IR), as they were said to contain information highlighted in OPA revealing a relationship from both methods.

The authors found that the most significant process detected by both infrared spectroscopies and highlighted by the OPA approach was proteolysis. Further, they stated that this was not due to the decrease in protein content of the muscle food *per se* but rather as a function of an increase in absorption in both NIR and MIR wavelengths corresponding to free amides and amines. These correlations validate the results and conclusions made by two earlier MIR studies and mentioned above,[52,101] and by a very similar study using short-wavelength NIR detection of the microbial spoilage of chicken.[123] This latest study by Alexandrakis and co-workers further demonstrates the potential of infrared spectroscopy for the rapid non-destructive detection of microbial spoilage in foods. One other study using this approach and the same platforms employed OPA of NIR–MIR data for the authentication of the protected designation of origin (PDO) of Spanish cheese.[124]

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A significant number of studies have been undertaken with NIR for the authentication of a wide variety of food products. These include meat and poultry,[125,126] detection and identification of transgenic corn,[127] provenance and classification of edible oils and fats with a high degree of accuracy[72,128] and a recent study estimating the concentrations of polyunsaturated fatty acids and their biohydrogenation products in the subcutaneous fat of cattle beef cows, to identify whether they had been fed flaxseed.[129]

In regards to detection of deliberate adulteration or accidental contamination, other recent studies have also utilised both MIR and NIR in combination with statistical methods to develop rapid and sensitive detection methods for melamine in complex dairy matrices.[130,131] These were shown to be truly rapid methods, and especially so in the case of NIR. The study by Mauer and co-workers for example was able to differentiate unadulterated infant formula powder from samples containing 1 ppm melamine with an assay time of 1–2 min to detection, with FT–IR requiring up to 5 min. The more recent study by Balabin and co-workers used a variety of non-linear regression methods for pre-processing and spectral analysis of NIR and MIR data to detect triazine derivative products in liquid milk, infant formula and milk powder just below 1 ppm (0.76 ± 0.11 ppm).[130] Other NIR studies include deliberate adulteration followed by spectral analysis of meat and poultry (beef, lamb, pork and chicken),[125] as well as the assessment of meat adulteration with processed animal proteins (PAPs).[132] In addition to studies concerning milk adulteration with less expensive components such as water or whey,[133] faecal contamination of fruit,[134] mycotoxin infected[135] or adulterated forage/feed products[136] and spirulina powder.[137] As well as NIR investigation of the levels of specific chemical species in foods and beverages such as the typical complications regarding the NIR measurement of water[112] for example, or detection of phenols in wines.[138,139] For those interested in NIR analysis, many reviews and several books have been published on this key tool in food science and the reader is directed to more recent reviews by Cozzolino,[108] Cen and He,[140] Woodcock *et al.*[113] and Huang *et al.*[109] amongst others.

Raman spectroscopy

Raman spectroscopy is a versatile, non-destructive analytical technique which, like IR spectroscopies, provides a unique spectral fingerprint of many analytes. The technique is seemingly ideally suited to the analysis of foodstuffs, largely due to the diversity of analytes which can be probed; ranging from macro-food components, such as lipids, proteins[141] and carbohydrates, to the minor components such as dyes, pigments and flavourings.[142] Also of interest are the microorganisms which play a role in food spoilage.[143] The utility of Raman spectroscopic instrumentation is greatly increased by the ability to couple it to microscopes resulting in 1 μm resolution which is ideal for single microbe identification or trace analyses and when interfaced with fibre optic probes for *in situ* or online analysis.[106,144–146] Like infrared spectroscopy, minimal or no sample preparation is required. However, Raman spectroscopy offers a distinct advantage over FT–IR spectroscopy in that the confocal nature of the technique allows samples to be profiled through a variety of transparent materials, allowing analysis of food products through plastic or glass packaging (as does NIR, already mentioned above). Moreover, Raman spectroscopy is able to detect analytes in solutions with minimal interference from water. The combination of the above properties with the possibility of portable instrumentation makes Raman spectroscopy a promising technique for food science.[147]

Whilst Raman and infrared are both vibrational spectroscopies, infrared measures the *absorption* of energy, whereas Raman spectroscopy measures the *exchange* of energy with EM radiation (Fig. 2). This radiation is at a specific wavelength, usually provided by a monochromatic light source in the visible to near-IR part of the EM spectrum. In Raman spectroscopy a sample is illuminated with light from a laser and the interaction of photons from this EM radiation with molecules in the sample induces a series of molecular vibrations. The collected scattered photons will be either Rayleigh (elastically) scattered or Raman (in-elastically) scattered. The Raman spectrum obtained is a measure of how much energy a photon has lost (Stokes Raman scattering) or gained (anti-Stokes Raman scattering) which is expressed as a wavenumber shift. Stokes Raman scattering is most commonly measured as this is of higher intensity than anti-Stokes scattering, due to the low probability of the molecule being in a excited vibrational state (*viz.* $v = 1$, $v = 2$) (See Table 2 for a summary of different types of Raman scattering and Fig. 2 for the different vibrational energy levels). Unfortunately the Raman effect is typically very weak as only 1 in every 10^6–10^8 photons are in-elastically scattered. However, there are a number of ways to enhance the Raman effect; these include resonance Raman (RR) spectroscopy, surface enhanced Raman scattering (SERS) and tip enhanced Raman scattering (TERS). In RR spectroscopy the sample is excited with a frequency of light which is within the

Table 2 Summary of different types of Raman scattering

Raman scattering	Properties	Scattering probabilities
Conventional	Sample is excited by a monochromatic light source and inelastic light scattering occurs. Two types of light produced: Stokes (energy loss) and anti-Stokes (energy gain) scattering. Can be plagued by fluorescence.	1 in 10^{6-8} photons
Resonance Raman (RR)	Sample is excited with a frequency of light that is within the molecular absorption bands of the sample. Excitation of this type is in resonance with the electronic transition.	Typically 10^4 enhancement
UV resonance Raman (UVRR)	Used to excite specific chromophores such as nucleic acids and aromatic amino acids. Deep UVRR measurements below 260 nm are not plagued by fluorescence interference.	Typically 10^4 enhancement
Surface enhanced Raman scattering (SERS)	Requires close proximity adsorption onto a roughened metal surface, a colloidal solution or roughened electrode (usually Ag or Au). The enhancement explained by two processes; an *electromagnetic enhancement* effect (thought to dominate), and a charge transfer mechanism, known as *chemical enhancement*. Has a fluorescence quenching effect. Can be coupled with RR to 'tune' for a specific chromophore for additional resonance.	10^3–10^{14} enhancement Single molecule detection possible

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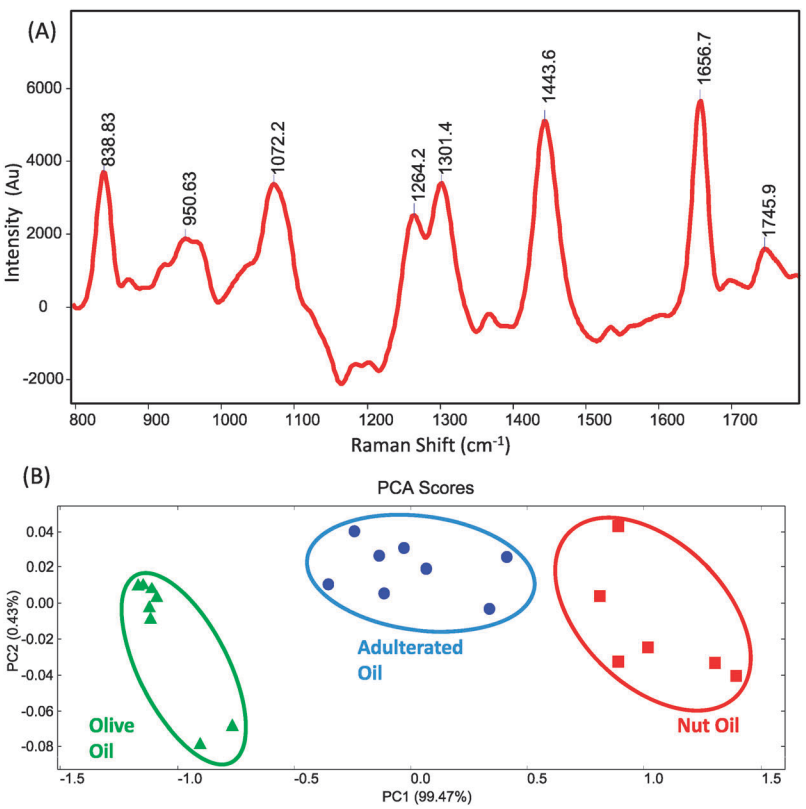
molecular absorption bands of the sample. This excitation is in resonance with the electronic transitions, allowing the Raman scattering to be enhanced by a factor of 10^4 over conventional Raman scattering.[148,149] Deep UV resonance Raman (UVRR) spectroscopy is ideally suited to the study of biological materials, as the chromophores that are measured are the aromatic amino acids and the nucleic acids.[148] By contrast, SERS involves the analyte being in close proximity to a roughened metal surface or a colloidal solution, usually silver or gold.[150–153] This gives an enhancement of the Raman signal typically $10^{3–6}$ over conventional Raman, with claims of 10^{14} reported for specific analytes[154,155] thereby allowing single molecule detection. Whilst the closely related TERS combines atomic force microscopy (AFM) and Raman spectroscopy together.[156]

As already noted above, adulteration is a major concern for both the food industry and consumers for many reasons,[96] is far from contemporary and yet it is often still difficult to detect, due of course to the fact that the adulterant components are usually very similar to the authentic product, and very often purposefully so. Once a specific test has been designed to identify an adulterant, potential fraudsters can become aware of this and then add or remove that component from the adulterated foodstuff. An example of this is naringin, a major flavonoid glycoside found naturally in grapefruit (metabolized to the flavonone naringenin in humans, whose pattern was developed as a rapid method for the detection of orange juice adulteration with grapefruit juice[157–159]). Aside from being blatantly dishonest, this form of adulteration can also have serious health implications resulting from pharmacological interactions, such as the clinical modulation of drug transport, altering their bioavailability and hence effectiveness with potentially serious consequences.[160–162]

One notable food adulteration example is the production of high-value edible oil, in particular extra-virgin olive oil, whereby cheaper oil of a similar chemical makeup is often added in order to mimic the more refined and expensive oil, thereby reducing manufacturing costs, and fraudulently increasing profits (Fig. 4). This can be particularly problematic for example when nut oils (such as unrefined hazelnut oil) are used, as consumers may be hypersensitive to this adulterant. Chromatographic methods of edible oil authentication have proved unable to detect adulterations at low concentrations (5–20%) as the major chemical compositions are very similar.[163] Other methods, such as electrospray and pyrolysis MS[72,164,165] and NMR spectroscopy,[166] have been employed with some success, but none have the simplicity and rapidity of Raman spectroscopy which has proved exceptionally useful in this area.

Work by Baeten and co-workers[167] has shown that FT-Raman and FT–IR spectroscopy used in conjunction with stepwise linear discriminant analysis (SLDA) can distinguish between olive oil and hazelnut oil. This discrimination was mainly based on a shift



(C)

Raman Shift (Cm^{-1})	Functional Group	Vibrational Mode
838	$-(CH_2)_n-$	C-C stretching
950	RHC=CHR	C=C bending
1072	$HC-CH_3$	CH_3 bend
1264	RHC=CHR	=C-H Scissoring
1301	$-CH_2$	CH Scissoring
1443	$-CH_2$	CH Twisting
1656	RHC=CHR	C=C stretching
1745	RC=OOR	C=O stretching

Fig. 4 (A) Raman difference spectrum of olive oil subtracted from olive oil adulterated with 10% unrefined hazelnut oil for the region 800–1800 cm^{-1} (obtained at 785 nm). (B) PCA scores plot (PC1 *vs.* PC2) of the Raman spectra from pure olive oil, pure (hazel)nut oil, and olive oil adulterated with 10% nut oil. (C) Band assignments from oils; major bands correlate well with those reported in the literature.[168,170] Raman data were collected using an Ocean Optics portable Raman probe, operating with a 532 nm excitation wavelength. Spectra were collected over 200–2000 wavenumbers with 30 s exposure time.

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in the C=C band from 1670–1660 cm^{-1}. This study also differentiated between extra virgin olive oil and olive oil adulterated with hazelnut oil, with a limit of detection for hazelnut oil in Turkish olive oil of 8% v/v. In earlier studies López-Díez and colleagues[168] also demonstrated that Raman spectroscopy could distinguish between pure olive oil and oil adulterated with hazelnut oil, by employing a 785 nm excitation source and PCA. Multivariate analysis methods, such as PLSR and genetic programming (GP), were used to quantify the amount of hazelnut oil in a variety of olive oils at levels of commercial interest (0–20%) successfully. Olive oils may also be adulterated with sunflower or vegetable oils and their similar triacylglycerol and fatty acid composition has meant that detection by conventional techniques can be problematic. FT-Raman spectroscopy, in conjunction with PLSR, has been used to detect vegetable and sunflower oil adulteration of olive oil at concentrations as low as 1% v/v.[169] In this study PLSR was performed on the full spectrum, as well as investigating various strategies for wavelength selection, such as pair wise minima and maxima selection (PMMA). More recently, El-Abassy and co-workers[170] used Raman spectroscopy with a 514.5 nm laser excitation wavelength. Previously only NIR excitation wavelengths had been used to avoid fluorescence contributions. The authors discovered that signal intensity was increased by use of a higher energy laser and that some components (mainly carotenoids) gave resonant enchancement at this wavelength allowing analysis at lower concentrations. Using this method it was possible to differentiate between 13 different oils using PCA and PLSR was able to quantify the level of adulteration with a detection limit of 0.05%.

In addition to concerns over adulteration, work has also been undertaken on the geographical origin and provenance of oil. Marini and colleagues used artificial neural networks (ANNs) in conjunction with Raman data to identify the geographical origin of European oil samples from a variety of regions[171] and were able to distinguish between binary blends of oils from different cultivars, with a prediction error of 5–7.5%. ANNs are a supervised non-linear multivariate methods consisting of groups of interconnecting artificial nodes, designed to simulate the way brain neurons communicate and have been previously used to detect the adulteration of extra virgin olive oils.[172,173] More recently Korifi and co-workers combined confocal Raman spectroscopy with PLS and PLS-DA to authenticate the PDO labels of six French virgin olive oils. In this study the authors focussed on determining the fatty acid and triacylglycerol compositions of oils in order to achieve a prediction accuracy of 92.3%.[174] Similar approaches have previously been used to confirm botanical and geographical origins of European honey.[175]

Another problem area for product authentication is fruit juices and whilst there are many examples of this using FT–IR and NIR spectroscopy, applications of Raman spectroscopy in this area are limited and this is due to the fluorescent nature of the pigments in the juice, although this can be overcome using SERS as this is fluorescence quenching whilst also enhancing the Raman cross section; an example of such an approach is for the analysis of Sudan I in chilli powder.[176] Key examples include the detection of yeast in apple juices,[177] monitoring the production of clarified apple and apricot juices[178] and the use of SERS to evaluate the quality of tomato juice.[179] In addition, SERS has been used for the analysis of pesticides present not only in the juice but also on the surface of the fruit.[180]

Raman spectroscopy has a rich history as a tool for studying protein conformation both in solution and in solid state. Many such studies take advantage of the sensitivity of the Amide I band (1650–1680 cm^{-1}) and Amide III band (1200–1300 cm^{-1}) to conformational changes in proteins. This approach has been applied in many cases to the study of food proteins and perhaps most notably in changes which occur in muscle foods during preservation treatments, such as changes in myofibrillar and connective tissue proteins in that occur during freezing and after frozen storage.[181] UVRR spectroscopy has been used to monitor the conversion of oxy-myoglobin to deoxy-myoglobin during the pressure treatment of meat products[182] and the decrease in α-helix and increase in β-sheet content in electron beam irradiated fish products.[183] Raman spectroscopy has also successfully been combined with PCA and PLSR in this area to monitor tertiary changes occurring in protein isolates from kidney beans[184] and soya products.[185]

In comparison to FT–IR and NIR spectroscopies, there is little literature on the use of Raman spectroscopy to monitor food spoilage directly. The relatively recent *in situ* investigation of meat quality through packaging using a portable, hand-held Raman probe[186] is among these few. That being said, the detection of food spoilage bacteria by Raman spectroscopy has been reported by many groups[62,187] and as chemometric and spectroscopic techniques have become more sophisticated both single cell analysis and strain level identification has been possible.[188] Finally, SERS has been used to identify *Salmonella* spp., *Escherichia coli* and many other foodborne pathogens with unambiguous results, and portable SERS systems are beginning to be developed for the express purpose of on-line bacterial identification in food products.[189–193]

Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a fingerprinting technique which takes advantage of the magnetic properties of certain nuclei.[194] As with the vibrational approaches already mentioned above, it can be used to identify functional groups and provides valuable structural information and determines the physical and chemical properties of atoms within a molecule. NMR spectroscopy can be used across a wide range of sample types, including solids and solutions, as well as complex mixtures[195] (Fig. 5). The vast majority of elements possess a magnetic spin number greater than zero which is necessary for the NMR effect and common nuclei observed by NMR spectroscopy have a spin quantum number of $\frac{1}{2}$, resulting in two spin states. The transitions between these two spin states are detected when the nucleus is placed in a magnetic field and induced by radiation in the radiofrequency region of the electromagnetic spectrum.[194] The radiation is able to move through a variety of materials with ease with minimal heating effects and is sensitive to different chemical environments. Of course, foods can be readily described as complex systems in terms of both their chemistry (often containing multiple compounds varying in terms of their nature, volume, and abundance), and physically (frequently in multiphase systems).[196,197]

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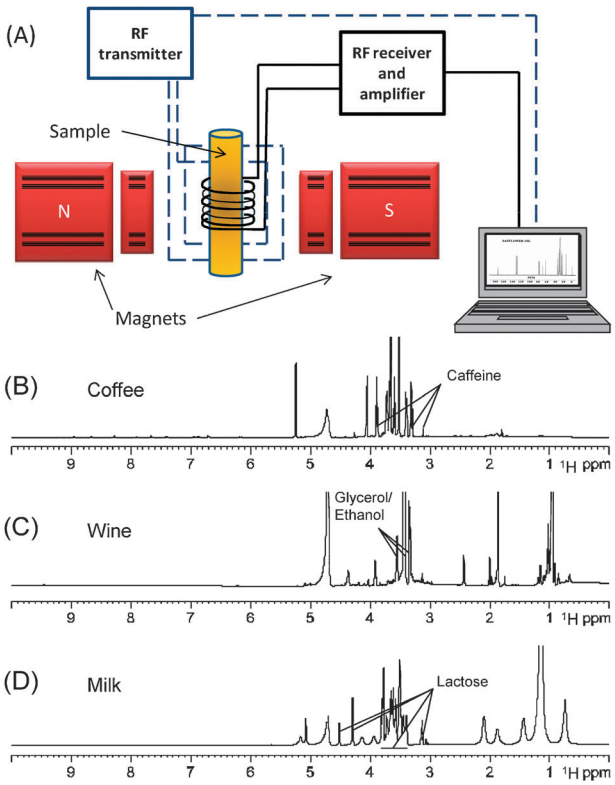

Fig. 5 (A) Generalised schematic of NMR spectroscopy. Typical one-dimensional solution ^{1}H NMR spectra of (B) coffee, (C) wine and (D) milk. Spectra were recorded on a 600 MHz Bruker Avance spectrometer equipped with a Cryoprobe, using 0.5 mL samples. Individual signals in these spectra report the presence of various chemical components (namely, their hydrogen atom environments), and may need to be assigned to allow their identification. Only signals from soluble components are visible in these spectra. The strongest signals shown are clipped. The spectra illustrate the somewhat limited dynamic range available for identification of trace contaminants: very strong signals present in each spectrum may mask weaker signals from minor components, complicating analysis. Minor contaminating species, with concentrations below 50–100 μM, may not be readily identified.

Fortunately, NMR spectroscopy has been said to be exquisitely sensitive to different chemical environments, which allows for distinction of a wide range of chemicals in a mixture, as well as being a quantitative and highly reproducible technique.[198] However, care must be taken to control that environment as pH can affect the robustness of these metabolite fingerprints.[199] Moreover, an NMR spectrum can contain resonances which provide significant quantities of structural information; this further enables the identification of individual constituents through the interpretation of chemical shifts for example.[198] However, as with all the approaches mentioned thus far, NMR does suffer from relatively low sensitivity, especially so if compared directly to mass spectrometry based techniques (*vide infra*).[200,201] Whilst this is the case at the moment, there is momentum within the NMR research community to move towards ever higher magnetic fields in order to improve sensitivity and to explore hyperpolarizability effects.[202] NMR spectroscopy therefore presents itself as another potential tool of choice for the analysis of foods and feedstuffs, and indeed, it has a substantial record of food-based applications over the last three decades.[42,203]

Applications of NMR spectroscopy have included studies based on the adulteration of a wide range of beverages including wines,[204] beer,[205] spirits[206] and fruit juices.[207] A number of these studies have clearly demonstrated that stable isotope ratios are particularly important in authenticity analysis of food and food ingredients,[208] due to the different metabolic pathways used by plants to generate sugars; sugar beet plants fix CO_2 *via* the C_3 pathway, whilst sugar cane uses the C_4 pathway.[209] Indeed, several of these and other studies have employed a technique known as site-specific natural isotope fractionation, or SNIF-NMR.[210,211] This technique determines the relative deuterium and specific deuterium-site locations in a molecule, providing information about a food sample regarding chemical pathway formation for example, and/or its provenance or geographical origin.[212] A considerable body of work has been undertaken using SNIF-NMR related primarily to authenticity of fluidic food samples such as maple syrup and fruit juices amongst many others,[210,211] and indeed, more comprehensive reviews have been composed on this specific area.[46,213]

As with many of the other fingerprinting techniques discussed above, a significant number of studies have used NMR within the framework of systems biology and in the field of metabolomics/metabonomics[214,215] and more appropriate to this article, food metabolomics. These have included combined studies (^{1}H NMR and LC–MS) for the direct analysis of the aromatic composition of some beverages (such as beer, grape juice and wines).[197] Other more recent combined studies (^{1}H NMR and GC–MS) have involved quantifying polar extracts and identifying the major metabolites of interest (*i.e.* sugars, organic acids, and amino acids) in melon fruit. As well as investigating the spatial localization of metabolites within the fruit mesocarp.[200] Additional metabolomic investigations have included global metabolic profiling and characterization of the complex metabolome of aged soy sauce. This is because quantifying the level of microbial or enzyme related metabolites produced during the fermentation and aging process (such as betaine for example), could be used as an assessment of quality[216] (and conversely, as an assessment of fraudulent labelling). For a far more comprehensive overview of food metabolomics studies and in particular those related to NMR (amongst some other techniques), the reader is directed to a review by Wishart.[63]

Finally, other diverse food-based applications of NMR have included several studies of muscle foods, such as the composition and authenticity of meat,[217] its provenance and geographical origin,[218,219] quality,[220] as well as the provenance and classification of fish,[221,222] the quality and identification of dairy products[88,223] and the adulteration of honeys with commercial sugar syrups.[224] NMR has also been applied to the analysis of commercial culinary spices adulterated with Sudan I–IV dyes,[225] the carcinogenic red dye already mentioned above, which has previously been analysed in foods using various mass spectrometry techniques. As with other fingerprinting approaches, a number of studies have again been undertaken with edible oils, such as olive oils[222,226–228] and fish oils;[229,230] these have been concerned with provenance, composition, or

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adulteration and/or authentication of these foodstuffs. One of the most recent of these involved the detection of the adulteration of olive oils with hazelnut oil.[226] Different admixtures of these two oils were analysed by ^{1}H NMR and ^{31}P NMR, fatty acids for example were determined by ^{1}H NMR and ^{31}P NMR being used for the determination of minor compounds including phenolic compounds, diacylglycerols, sterols, and free fatty acids. Classification of the oils based on the fatty acids and the concentration of minor compounds was undertaken using canonical discriminant analysis (CDA) and classification binary trees (CBTs). Whilst both multivariate methods were said to provide good discrimination between the two oils, it was stated that CBT classification was superior, as it combines linear algorithms as principal components and simple non-linear techniques such as ANNs.[226]

Data processing

For targeted analyses of specific adulterants in food there is little need for data processing. For example, if one were interested in detecting grapefruit adulteration in orange juice then naringin can be readily detected and levels easily quantified with high performance liquid chromatography (HPLC). This is because the retention time of naringin under explicit LC separation conditions is known and there is no need for complex data processing, merely the construction of standard curves for absolute quantification. By contrast, spectroscopy is typically performed without recourse to prior chromatographic separation and therefore the spectra are highly complex; this being a result of all chemicals being detected simultaneously. Whilst these 'composite' spectral fingerprints contain relevant information on adulterants in the foodstuff, this information needs to be extracted using chemometric methods. The focus of these chemometric methods is to build a multivariate model which best describes the system under analysis.[231,232]

Due to the large number of variables collected in infrared, Raman and NMR spectroscopic investigations of food adulteration, the aim of combining these high dimensional data with multivariate analysis (MVA) is to simplify the data matrix. This marriage of chemometrics with spectroscopy is the key to the success of fingerprinting methods in the area of food forensics.[233] There are many algorithms within the 'chemometrics zoo' and a recurring theme within spectroscopic analyses is the development of a range of different chemometric approaches for detection and quantification of food adulteration, contamination, or spoilage.

The chemometrics pipeline has several data handling stages:[234,235] (1) The first step is the design of the experiment and this should be as rigorous as possible and aim to capture adequately the domain under analysis; multivariate models cannot extrapolate and so exemplar spectra must be included within reasonable ranges and include many possible outcomes else the model will not generalise. (2) The data are then collected along with any associated metadata (data about the data; such as plant species of fruit juice analysed, level of adulterant, country of origin, harvest time, ripeness, *etc.*) and stored securely if possible within a database. (3) Data can rarely be analysed directly and need some pre-processing and pre-treatment (Table 3); these include for example baseline corrections, binning, normalisation routines and scaling. (4) The data are then ready for analysis by the chosen chemometrics algorithm and include adequate statistical validation (*vide infra*). (5) Following this stage the data are then interpreted and the results collated for dissemination.

The multivariate algorithms used for data analysis fall into three categories; these address particular problems and are used for exploratory analysis, classification or quantification. Within food analysis explanatory data analysis typically uses unsupervised learning and the multivariate algorithms seek to discover natural groupings in the data.[236] The output of these algorithms is an ordination plot or dendrogram and these graphical representations (or projections) of the original data allow the investigator to cluster objects (samples) together on the basis of their perceived closeness in the high dimensional spectral space (Table 4). These methods thus allow one to distinguish objects or populations. A popular algorithm used for such a purpose is PCA and this results in the generation of a scores plot (a scatter plot which summarise variation in samples). Any grouping that arises within the PCA scores could be due to some specific chemical difference between samples. If groups do appear then these can then be interpreted chemically

Table 3 Definition of common chemometric terms

Multivariate data	Spectroscopic data comprising many variables (*e.g.*, absorbances at specific wavenumbers for FT–IR, or ion counts at specific m/z for MS) collected on the samples. Often referred to as the X-data or input data.[327]
Metadata	Data about the data. This information is used in classification or quantification modelling, often referred to as the Y-data or the output data.[327] These are the traits one is interested in; *e.g.*, country or species of origin, level of adulteration, *etc.*
Pre-processing	Methods used to go from raw data to clean data ready for analysis.[235] This may include removing baseline artefacts, peak-picking or alignment.
Pre-treatment	Transforming the pre-processed data to make them suitable for analysis.[235,328] This typically includes normalisation, scaling, transformations and removing any outliers (unusual atypical samples) in the data.
Unsupervised learning	Analysis conducted on only the X-data with the goal to generate clusters from these input data.[235] This process is often referred to as dimensionality reduction or simplification. After clustering ordination (2D or 3D) plots or dendrograms (tree-like diagrams) are used to visualise the clusters.
Supervised learning	Analysis conducted on both the spectroscopic X-data and Y-data. This process uses some mathematical transformation to associate the X-data with the target trait (Y-data). This process is often achieved by reducing the error between the models output prediction and the actual known target trait.[235] It is therefore essential that the Y-data must be unequivocally known during model construction.
Classification modelling	The goal is to classify samples into groups. This may be for different countries of origin. For example, if there are three countries then the Y-data are encoded such that a '1' is placed in the correct country and '0s' elsewhere, so that country A is represented by '100', B by '010' and the third country C as '001'.
Quantitative modelling	The goal here is to quantify the trait of interest. This is usually the level of adulterant/contaminant and the Y-data is simply the level of the trait of interest.

Table 4 Chemometric strategies and methods employed for the analysis of spectroscopic data

Modelling method	Model type	Unsupervised or supervised	Comments	References
Principal components analysis (PCA)	Exploratory	Unsupervised	Very old method used to explore the data to look for any obvious clusters and for the detection of outliers. These are viewed in ordination plots of the PC scores. Relevant chemical information can be extracted from the loadings matrix.	329, 330
Hierarchical cluster analysis (HCA)	Exploratory/ Summative	Unsupervised	Generates a dendrogram which is a tree-like structure where the leaves are the samples and the branches shows their relationships	331, 332
Self-organising (feature) maps (SO(F)M)	Exploratory	Unsupervised	Kohonen neural network based on unsupervised learning. Output nodes cluster similar samples together	333
Partial least squares regression (PLSR)	Quantitative	Supervised	Multivariate linear regression method	334
Discriminant analysis	Classification	Supervised	Series of algorithms that perform classification resulting in scores plots where the goal is to separate clusters according to group classifications. Includes linear discriminant analysis (LDA), discriminant function analysis (DFA), factorial discriminant analysis and the very popular PLS-discriminant analysis (PLS-DA)	332, 335, 336
Artificial neural networks (ANNs)	Quantitative or classification	Supervised	Multilayer perceptrons (MLPs) are powerful approaches that can map non-linear functions from X-data to Y-data.	337, 338
Evolutionary-based analysis	Quantitative or classification	Supervised	Series of algorithms to perform variable selection. Based on Darwinian concepts. Common methods include genetic algorithms (GAs) and genetic programming (GP)	339–341
Classification and regression trees (CART)	Classification	Supervised	Results in a tree where the leaves are categories of samples and the branches are decision boundaries	342
Random forests	Classification	Supervised	An ensemble classification algorithm that uses many CART solutions to allow more robust predictions.	343

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by inspecting the corresponding loadings vectors as these summarise variation in the variables and can highlight which inputs (vibrational frequencies or chemical shifts) are important for such a separation. An additional use for these exploratory multivariate approaches is to identify outliers which are atypical samples and these can arise either from the samples themselves or from analytical artefacts.

The goal of classification is to identify an unknown sample into the correct group. This could for example be with respect to the country or region of origin of a particular foodstuff. These classification algorithms are categorical in nature and are based on supervised learning (Table 4). For supervised learning to be effective primary reference data must be used. This primary reference data refers to the sample origin (region, botanical, production method) and is the desired response (output) that one wants from the algorithm; for example with respect to geographical location of extra virgin olive oil production Tuscany is considered as the most desirable oil as it has perceived higher quality and hence is a more valuable oil. One may therefore wish to discriminate between oils produced in Tuscany from those 'lower grade' oils from other Italian regions. In supervised learning these primary reference metadata (target(s) or output(s)) are paired with the input data (vibrational frequencies or chemical shifts). The goal of supervised learning is to find a model or mapping that will correctly associate the inputs with the targets. There are many different types of supervised algorithms that are used for the analysis of infrared, Raman and NMR data and these have been highlighted in the text above; details of these and their main characteristics are summarised in Table 4.

The third and final category of multivariate analysis is based on quantification. As the name suggests the aim here is for the algorithm to generate predictions on the level of something of interest; this could be the percentage level of adulteration or the bacterial load within, or on, a food for example. These algorithms also involve supervised learning but the primary reference data is the level of the target determinand(s). A particularly popular algorithm used is PLSR which is based on multivariate regression. Similar to PCA this is a projection method, but rather than extracting the maximum variance from the spectra, in PLSR the projection is with respect to the concentration of the target determinand(s). The output from PLSR is a real numerical value (*e.g.*, % adulteration, ng mL^{-1} contaminant) and can be compared with known targets to assess the accuracy of the multivariate model. Finally, the PLSR loadings plot can also be used to extract those features which are related to the determinand being quantified.

Validation is a vital step in any multivariate data analysis and must not be omitted else the results are questionable. This is especially the case for supervised learning algorithms which have no say over the initial data that they are trained with.[56] The golden rule is "garbage in–garbage out".

As detailed above the first stage in supervised learning is model construction. In this calibration phase a training set is employed which contains training pairs of spectroscopic input data (X-data) with known target outputs (Y-data). After which validation of this model occurs. There are different approaches to validation of the multivariate model and all use some resampling of the initial data that are collected during this calibration phase.

Model validation is needed to make sure that conclusions about the model are statistically valid.[56] During supervised learning it is essential to test the validity of the model being constructed. This is achieved by re-sampling the training set either by: (a) separating it into two sets a training set and a monitoring set; or (b) using re-sampling methods so as to select subsets from the training data, while keeping the training pairs together.[237] There are several re-sampling strategies.

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In the simplistic method leave-one-out validation is used where a single training pair is selected, the model is constructed with the remaining samples in the training set, the model is then tested by comparing the predictions of the sample left out with the known real target. This process is repeated until all samples have been left out once. This modelling set allows the meta-parameters (*e.g.*, number of latent variables to use) of the model to be estimated accurately. More complex methods include splitting the data into several slices and one slice is used to monitor the model and the remainder used as the training set. Finally, more comprehensive model validation involves bootstrapping and permutation testing.

In bootstrapping[238,239] samples are selected using a replacement method. One can think of this as having all samples analysed (say $n = 100$) in a bag. A single sample is taken out randomly and its number noted, this sample now forms part of the training data, and the sample is placed back into the bag. This random sample picking process is repeated until all (100) samples are in the training set; this will include the same sample multiple times, and on average 63.2% of all of the samples will have been selected for training. The remainder (36.8%) are used as the monitoring or test data. This bootstrapping process is repeated many times (1000 times is typical) and all accuracy and precision statistics are generated on the distributions from the test data sets only. To supplement this approach permutation testing[240,241] is sometimes used to evaluate whether the specific classification of samples in two designed groups (*e.g.*, country 1 *versus* country 2 of origin) is significantly better than any other random classification in two arbitrary groups.[242] This null distribution is formed by performing many permutation tests (typically 1000 times), using the same spectroscopic data but with the Y-data ('1s' or '0s') randomly assigned (permuted) to different countries of origin. The rationale behind the permutation test is that with the wrong class labels, the newly calculated classification model should not be able to predict the classes very well. Distributions can be generated for model accuracy (or error) and compared with those from bootstrapping (tested with the correct Y-data labels).

After the model is constructed using the approaches above it is tested for generalizability using an independent test set not used in model construction. For the ultimate test this final independent test set should be given to the investigators double-blind encoded so that no one can influence the choice of the best model. The code can subsequently be broken by a third party and used to check the model's performance.[172]

In summary, the chemometrics pipeline has many stages and there are many chemometric approaches that can be used for data analysis. These are chosen depending on the analysis type be it exploratory analysis, classification or quantification. A definition of common chemometric terms can be found in Table 3, and a summary of the main chemometric themes and methods are detailed in Table 4. Further reviews are also available specific to this area of course, and the interested reader is directed to a review of supervised pattern methods in food analysis for example by Berrueta and colleagues.[243]

Mass spectrometry

Another powerful analytical technique is mass spectrometry which operates by the formation of positively or negatively charged analytes (ions) and subsequent measurement and detection of the mass-to-charge (m/z) ratio of these ions.[244] Mass spectrometers operate through sample introduction, ion formation in the ionisation source, ion separation based on their m/z ratio in a mass analyser and finally ion detection. Sample introduction can involve chromatographic or electrophoretic separation of analytes prior to detection (gas chromatography, liquid chromatography, capillary electrophoresis) or direct introduction to the mass spectrometer which includes direct infusion (or injection) mass spectrometry (DIMS),[245] desorption electrospray ionisation (DESI)[246] and matrix assisted laser desorption ionisation (MALDI).[247] The formation of charged analytes in the ionisation source is a necessary requirement as subsequent mass analysis applies electrical and magnetic fields which will only create separation of ions of different m/z ratios if the analytes are charged (either with a positive or negative charge). Ionisation sources include MALDI, DESI, electron impact ionisation (EI) in combination with gas chromatography (GC), as well as atmospheric pressure ionisation (API) sources including electrospray ionisation (ESI) and atmospheric pressure chemical ionisation (APCI), often combined with liquid chromatography (LC). Mass analysers apply electrical or magnetic fields to separate ions of different m/z ratios and include quadrupole, triple-quadrupole, ion trap, time-of-flight (ToF), magnetic sector, Orbitrap and Fourier transform ion cyclotron resonance (FTICR) mass analysers. When combined with chromatographic separation this provides the ability to analyse complex samples containing analytes of similar or identical masses and physicochemical properties with specificity provided by mass and chromatographic separation (Fig. 6).

Mass spectrometers offer a number of advantages and limitations for application in the food industry. Targeted analytical methods of *high specificity* and *sensitivity* are available to quantify analytes of interest accurately. Quantification of analytes is typically applied with liquid chromatography coupled to triple quadrupole mass spectrometers (LC–MS/MS) which provides sufficiently high levels of sensitivity and specificity.[248–250] GC–MS platforms are also applied for analyte quantification.[251,252] The coupling of chromatography and mass spectrometry platforms also enables the detection of analytes in complex samples at sub-μg ml^{-1} or sub-μg g^{-1} concentrations. Indeed, LC–MS/MS platforms are the gold standard for performing quantification in the food industry and many other industries including the pharmaceutical industry for regulatory purposes. However, these methods require extensive sample preparation and therefore time from sampling to acquisition of results. This can be significantly longer (minutes to hours) than for other techniques including FT–IR, NIR, Raman and NMR. Other mass spectrometry methods can be applied with minimal (*e.g.* MALDI) or no (*e.g.* DESI) sample preparation and allow rapid analysis times, though generally with lower sensitivity and specificity compared to the targeted methods for analyte quantification.

Mass spectrometry has been applied in a range of studies in the food industry, though detection of food contamination is by far the most frequent application. Contamination by pathogenic bacteria which cause food poisoning in humans is an important application area with the majority of cases being associated with *Salmonella* contaminated food. In adults, large doses are required

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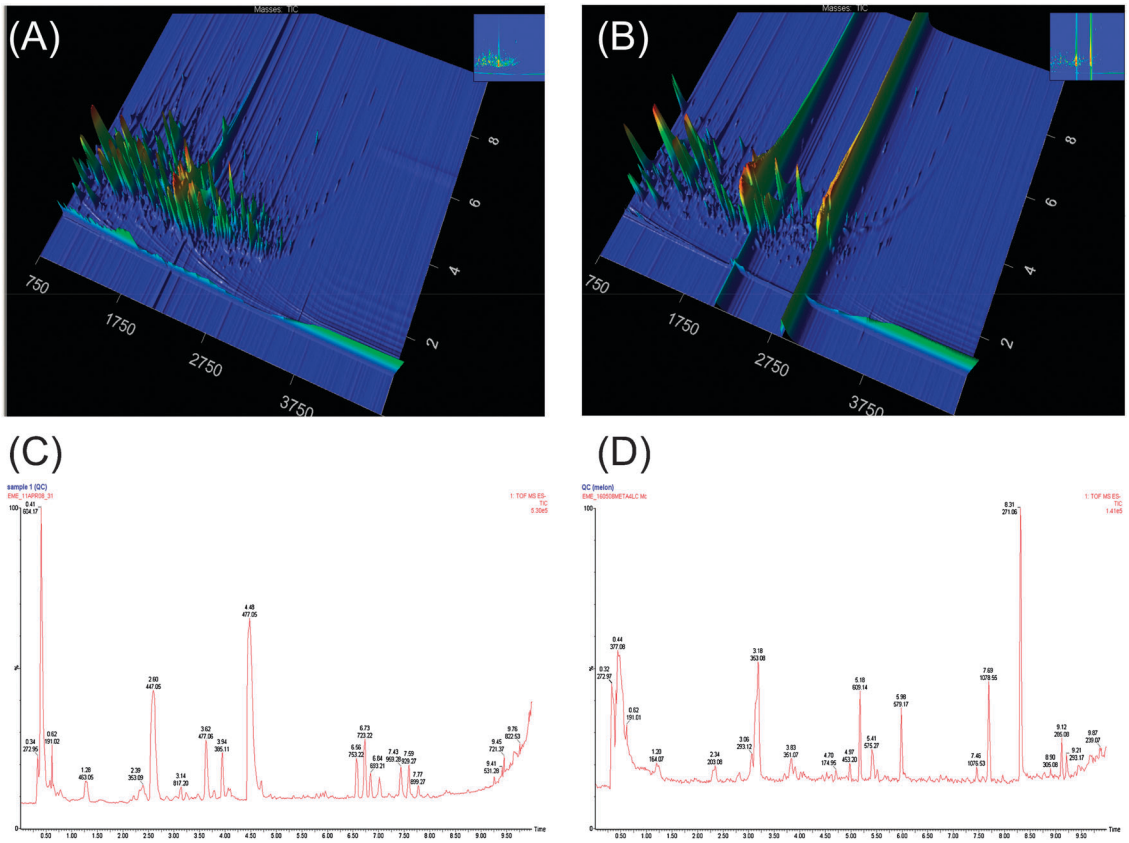

Fig. 6 2-Dimensional gas chromatography – electron impact – time of flight mass spectrometry (GC × GC-EI-ToF/MS) total ion chromatograms for (A) broccoli and (B) melon generated according to the method of ref. 345. Ultra high performance liquid chromatography – electrospray ionisation – time of flight mass spectrometry (UHPLC-ESI-ToF/MS) negative ion mode total ion chromatograms for (C) broccoli and (D) melon generated according to the method of ref. 346.

to cause illness but in children, the elderly, or the immunocompromised, low doses can result in serious illness. Therefore, the detection of bacterial contamination at low levels is essential. Xu and colleagues have developed metabolic profiling methods for the detection of *Salmonella typhimurium* in pork and its discrimination from the natural spoilage microflora. One method developed the extraction of metabolites from meat samples followed by analysis by GC–MS,[102] whilst this was not a particularly rapid method, further research from the same group led to the development of a rapid protocol applying the collection of volatile organic compounds (VOCs) and analysis by thermal desorption into GC–MS.[103] Fig. 7 shows the mass spectrum for dimethlytrisulfide, produced by *S. typhimurium* and this VOC was able to differentiate between natural spoilage and contamination by this pathogen. Although sample collection and preparation is simple, a specific and sensitive analytical platform is needed for robust analysis of the volatilome. Bhattacharjee and co-workers have also applied the analysis of VOCs to detect *S. typhimurium* contamination of fresh and aged beef strip loins[253] and contamination by other natural products which present health risks have also been investigated. The study of pyrrolizidine alkaloids in honey[252] and how these can lead to downstream contamination in the food chain (candy, soft drinks, power bars and cereals, baby food and even jelly babies) have been undertaken,[254] as well as the study and detection of specific mycotoxins.

Mycotoxins are toxic secondary metabolic products synthesised by fungi which colonise food products and can cause health problems ranging from irritation to a weakened immune system to death. Mycotoxins include the aflatoxins, ochratoxin A, B and C and fumonisins, all of which have been studied in dried fruits[255] and chemical structures are shown in Fig. 8 for these three types of mycotoxins. Aflatoxins have been detected in brazil nuts,[250] ochratoxins have been quantified in Belgian beers,[256] as well as barley grains,[257] and their presence in Hong Kong foodstuffs have been surveyed, where it was found that 32% of all samples contained detectable levels, though at concentrations significantly lower than legal limits set in the EU.[258] Fumonsins have been studied in cereal products[248] and dried vine fruit.[259] Other food contaminants investigated include endocrine disrupting chemicals,[260] Sudan I dye,[261] epoxidised soybean oil in baby food,[251] polycyclic aromatic hydrocarbons (PAHs) in milk[262] and drugs including furazolidone residues in pigs.[263] Recently, DESI has been introduced and its potential for the detection of pesticides, natural toxins, veterinary drugs, food additives, adulteration, and packaging migrants contamination in foods have been presented.[246,264] The power of DESI comes from its ability to be coupled with hand-held or on-site mass spectrometers for screening of contamination during sampling before further detailed studies in food analysis laboratories.

Authentication of food products have included the use of isotope ratio mass spectrometry (IRMS). As mentioned previously,

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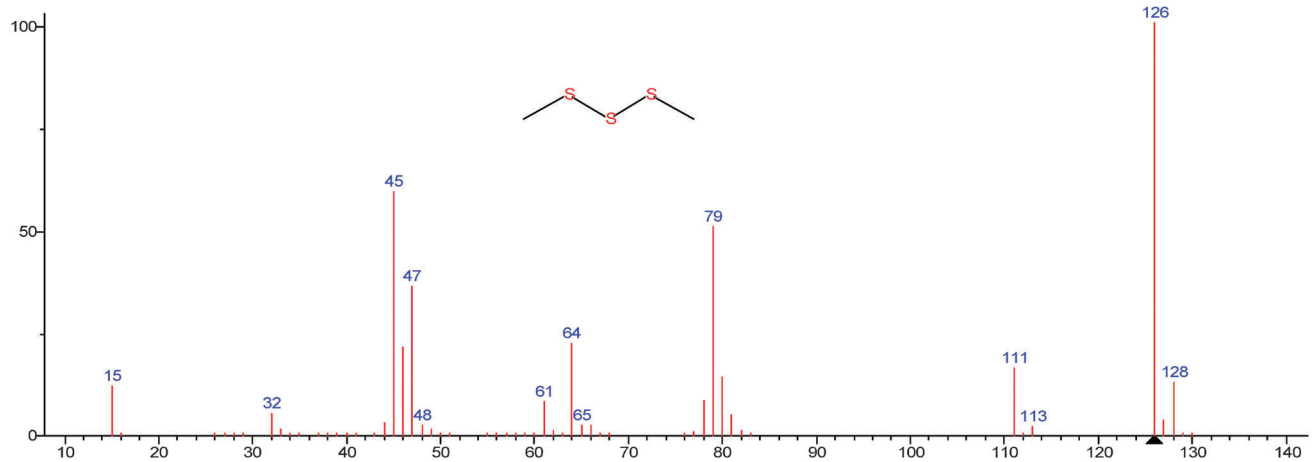

Fig. 7 Volatile organic compound-derived MS spectrum of dimethlytrisulfide from *Salmonella typhimurium* contaminated pork from ref. 103.

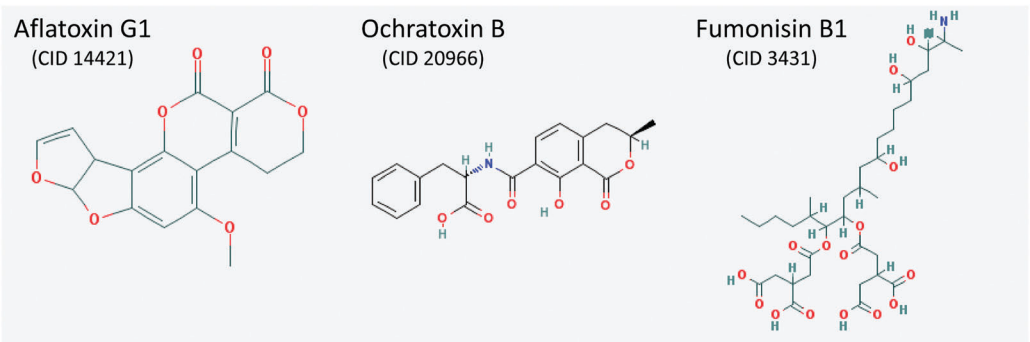

Fig. 8 The chemical structures of three common mycotoxins found to contaminate food after fungal growth. These structures are taken from the PubChem database.

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C_3 and C_4 plants use different photosynthetic pathways which produce different levels of isotopic fractionation and small but different $^{13}C/^{12}C$ ratios. These differences in the carbon isotope ratio are employed to differentiate between foods sourced from C_3 or C_4 plants, similar to that reported above for SNIF-NMR. IRMS studies have been performed to assess fossil fuel-based changes to the carbon isotope ratio of atmospheric CO_2 and how this is affecting the carbon isotope ratio in plants. Temporal changes in atmospheric CO_2 have been shown to correlate with temporal changes in plants.[265] This is important in authentication and adulteration studies to provide accuracy. Adulteration of royal jelly has been detected using changes in carbon and nitrogen ($^{15}N/^{14}N$) isotope ratios, related to adulteration with high fructose corn sugar (using carbon isotope ratio) and yeast powder as a protein source (using nitrogen isotope ratio).[266] Adulteration of natural vanilla flavour with synthetic vanillin can be determined using IRMS for determination of changes in hydrogen ($^{2}H/^{1}H$) and carbon isotope ratios.[267] Inductively coupled plasma-mass spectrometry (ICP–MS) has also been applied to authentication and traceability studies for high value hazelnut products, including the 'Tonda Gentile delle Langhe' (TGL) variety from Piedmont in Italy.[268] Authentication of oysters according to geographic location has been assessed using GC–MS and pyrolysis-MS[269] and adulteration of milk,[270] milk powder,[271] coffee[272] and buffalo mozzarella[270,273] have all been reported. Additionally, pyrolysis-MS has been applied to adulteration studies of milk and orange juice.[274,275]

Another relatively recent development in mass spectrometry has been the introduction of the direct analysis in real time (DART) ion source by Laramee and Cody for the rapid, non-contact analysis of materials at ambient pressure and at ground potential.[276,277] When installed in a time-of-flight MS, the source has been said to provide improved selectivity and the assignment of accurate elemental composition through exact mass measurements, and in addition, is able to detect directly chemicals on surfaces without the need for any sample preparation, such as solvent extraction.[276] DART–MS has been applied across a wide range of areas such as the pharmaceutical industry,[278,279] fragrance industry,[280,281] and forensics[282–284] for example. In terms of food analysis, DART–MS is said to be a rapidly developing technique that can be used for the target and non-target analysis of complex food matrices It is seen as a simple and high-throughput system for the qualitative identification of chemical species, metabolomic fingerprinting/profiling[285] and quantification of low-molecular weight food components such as trace organic contaminants.[286]

Some of the food-related applications of this technique include the rapid screening of food packaging for the presence of additives, including plasticizers, antioxidants, colorants, grease-proofers, and ultraviolet light stabilizers.[287] A related

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study analysed the PVC gaskets of lids to glass food jars, from which additives could migrate into foodstuffs. With a limit of detection of ≤1% DART–MS was able to identify a range of chemicals in PVC plastisols, including phthalates, fatty acid amides, tributol O-acetylcitrate dibutyl sebacate, bis(2-ethylhexyl) adipate, 1,2-diisononyl 1,2-cyclohexane-dicarboxylate, acetylated mono- and diacylglycerides, epoxidised soybean oil, and polyadipates.[288] One study analysed antioxidant curcumins directly from the turmeric plant (*Curcuma longa*) and turmeric containing beverages and curry powder, to assess the capability of DART–MS for real-time analysis of compounds in natural raw materials and compare the efficiency of this technique to the traditional HPLC method. Results showed that DART–MS could be used for semi-quantitative determinations of curcumin from 5–100 μg ml^{-1}, and that the technique could be applied as a chemical profiling and semi-quantitative method for the quality control of a range of medicinal plants as well as food ingredients.[289] Other studies include the rapid and direct screening of wheat for target fungicides (strobilurin residues) in less than 1 min,[290] quantitative analysis of multiple mycotoxins in cereals,[291] authentication of animal fats and minced meat adulteration,[292] beer brand profiling,[293] identification of contaminants in soft drinks,[294] olive oil authenticity[295] and dairy produce,[296] including the detection of the adulterants melamine and cyanuric acid in milk products.[264,297]

Conclusion

The continuing rapid increase in human population means that global demand for food resources will continue unabated for at least another four decades.[298] These demands and competition for resources, whereby global population estimates are in the region of 9–13 billion, will affect the world's ability to produce enough food,[299] leading to very real concerns over future food security.[298] In addition to the fact that potable and irrigation water are also in decline in certain areas, and that fossil fuels are likely to be depleted in the next 70 years.[300] It is also inevitable that some potential food supplies will be diverted towards biofuel production.[301–305] Other potential issues involving food production systems include the threat of deliberate contamination of the food or water supply by bioterrorism[43–45,306] and biotracing of harmful pathogens in food chains.[68,307] All these are in addition to continued concerns regarding quality, authenticity and adulteration, concerns which will doubtless increase concurrent with population pressures. On top of these there are of course the omnipresent potential future impacts of climate change,[308,309] which not only involve the impact of climate change on food production systems (and food security), but also the way food production systems and consumer consumption itself can have an environmental impact[310] and have the potential to further enhance climate change. An often overlooked fact for example is the energy budget used in food production and the huge amounts of energy lost through food waste; in the US alone between one-quarter and one-third of all the food produced is wasted,[311] equivalent to 350 million barrels of oil per annum.[312] If addressed and distributed properly, the amount of food wasted globally would potentially be enough to sustain the undernourished human population on the planet of almost 1 billion people. A significant proportion of this waste is food spoiled prior to it ever reaching consumers, an area of research covered within this review.

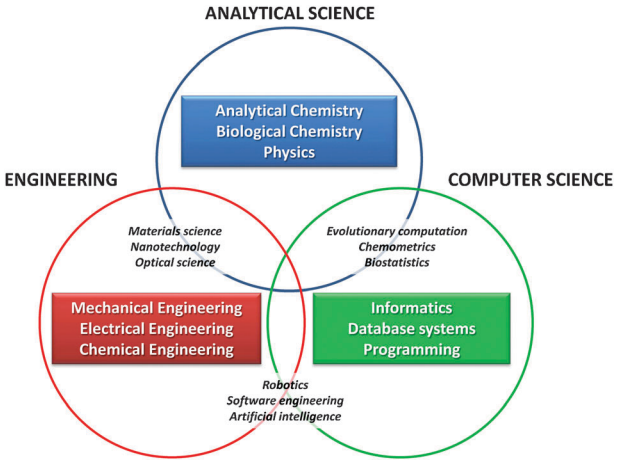

Fig. 9 The interdisciplinary approaches that are typically combined within a multidisciplinary framework for the detection of food authentication, contamination and spoilage.

These concerns readily illustrate the requirement for continued development and refinement of current analytical methods, as well as the development of new technologies (Fig. 9), to allow us to measure, monitor, and analyse food systems at all stages from farm to fork. In addition to the technologies mentioned here, many others of course exist and deserve to be mentioned, such as electrochemical detection,[313–315] electronic noses and tongues,[316,317] ultrasound,[27,318] nanosensors,[319] thin film sensors,[320,321] nanoparticle detection systems,[322,323] and already well-established techniques such as DNA detection[233,324,325] and protein quantification *via* ELISA.[22,326] In this exciting era of systems-level thinking and the resultant interdisciplinary collaborations between the life, engineering, and physical sciences (Fig. 9), it is clear that research and novel developments will continue a pace, to the detriment of those who wish to interfere negatively with our food systems for whatever end.

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