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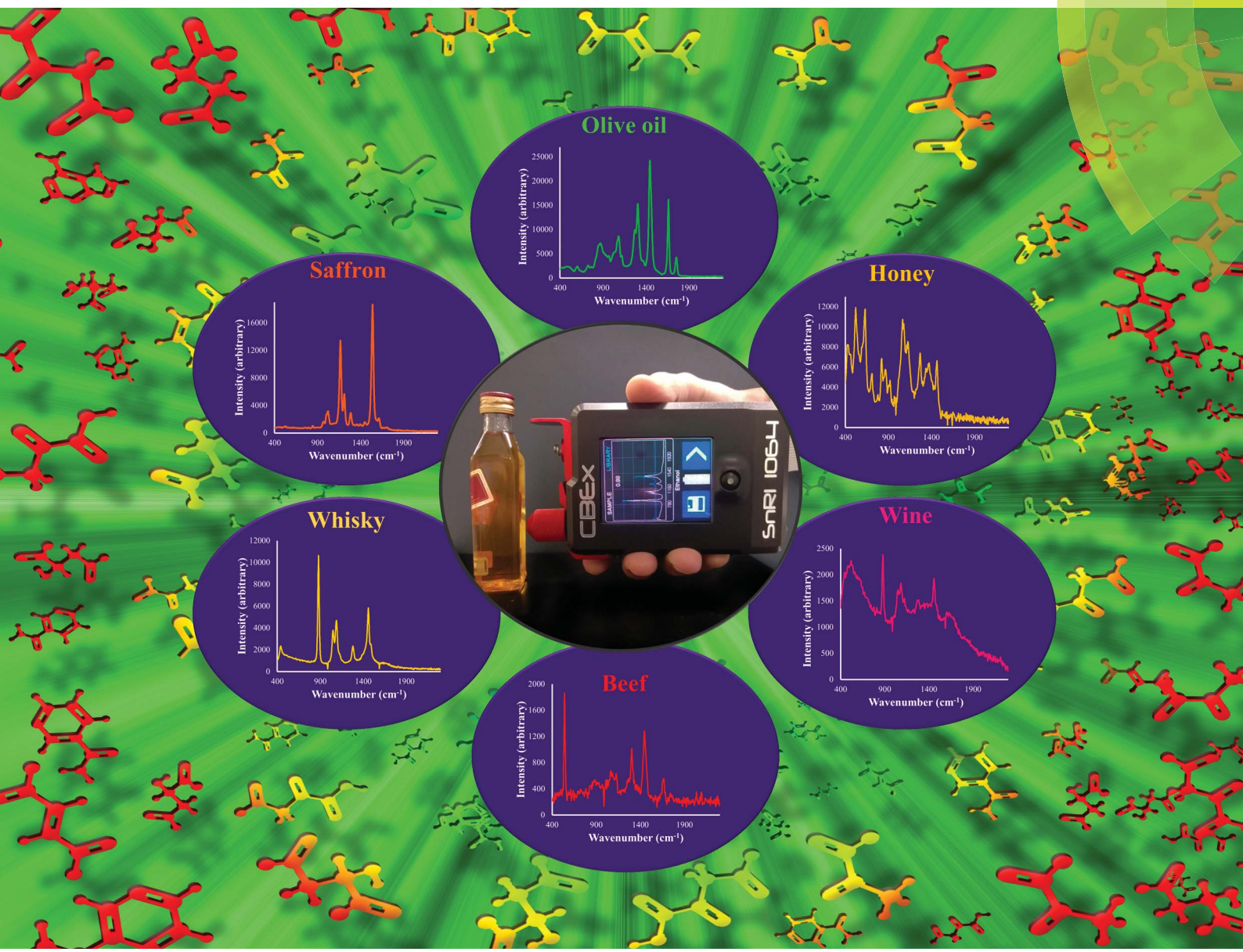

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David I. Ellis *et al.*

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Point-and-shoot: rapid quantitative detection methods for on-site food fraud analysis – moving out of the laboratory and into the food supply chain

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Major food adulteration and contamination events occur with alarming regularity and are known to be episodic, with the question being not if but when another large-scale food safety/integrity incident will occur. Indeed, the challenges of maintaining food security are now internationally recognised. The ever increasing scale and complexity of food supply networks can lead to them becoming significantly more vulnerable to fraud and contamination, and potentially dysfunctional. This can make the task of deciding which analytical methods are more suitable to collect and analyse (bio)chemical data within complex food supply chains, at targeted points of vulnerability, that much more challenging. It is evident that those working within and associated with the food industry are seeking rapid, user-friendly methods to detect food fraud and contamination, and rapid/high-throughput screening methods for the analysis of food in general. In addition to being robust and reproducible, these methods should be portable and ideally handheld and/or remote sensor devices, that can be taken to or be positioned on/at-line at points of vulnerability along complex food supply networks and require a minimum amount of background training to acquire information rich data rapidly (ergo point-and-shoot). Here we briefly discuss a range of spectrometry and spectroscopy based approaches, many of

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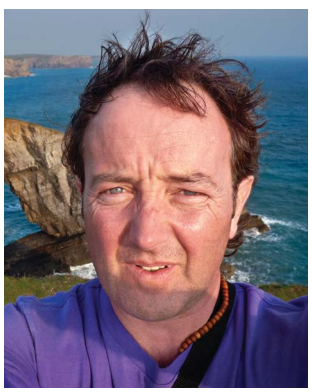

David Ellis was educated on the Welsh coast at the University of Wales, Aberystwyth, obtaining a B.Sc. (Hons) in Environmental Science and a PhD in Analytical Biotechnology/Microbiology. His research involving the rapid and quantitative detection of food-borne bacteria using FT-IR and machine learning has been widely publicised, featuring on BBC TV and radio, the Science Museum in London, as well as the national and international press (e.g. WIRED). He now works at the Manchester Institute of Biotechnology (MIB), as a Senior Experimental Officer undertaking research and managing the labs of Roy Goodacre (http://biospec.net) and Doug Kell (http://dbkgroup.org), in the School of Chemistry, University of Manchester, UK.

Howbeer Muhamadali received first class honours in Microbiology at the Manchester Metropolitan University in 2010. In 2011, he successfully completed an MPhil in geomicrobiology at the University of Manchester, working on the optimisation and scale-up of a batch culture magnetite nanoparticle production bioprocess. He continued with a PhD program (Biotechnology/Metabolomics), in Roy Goodacre's group at the University of Manchester. His project involved the metabolomics investigations of different microbial bioprocesses, such as E. coli, Streptomyces and Geobacter species, using various analytical techniques such as FT-IR and Raman spectroscopies, GC-MS, DIMS and multivariate statistical analysis approaches. Howbeer is currently working as a research associate in Roy Goodacre's labs, on several projects, including metabolomics and fluxomics investigation of recombinant protein production in S. lividans TK24.

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which are commercially available, as well as other methods currently under development. We discuss a future perspective of how this range of detection methods in the growing sensor portfolio, along with developments in computational and information sciences such as predictive computing and the Internet of Things, will together form systems- and technology-based approaches that significantly reduce the areas of vulnerability to food crime within food supply chains. As food fraud is a problem of systems and therefore requires systems level solutions and thinking.

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Chris is currently Professor of Food Safety and founder of the Institute for Global Food Security at Queen's University Belfast. He serves as Pro Vice Chancellor for the university and is responsible for the Medical and Life Sciences Faculty. He has published more than 300 peer review articles, many of them relating to the detection and control of agriculture, food and environmental related contaminants. His main research interests are in the development of innovative techniques to provide early warning of toxin threats across complex food supply systems. Protecting the integrity of the food supply chain from fraud is also a key research topic and Chris led the independent review of Britain's food system following the 2013 horsemeat scandal. Over the years Chris has developed a high level network of collaborators across Europe, the United States and Asia. He co-ordinates and participates in multiple European framework research projects. He is a founding member of the International School for Advanced Residue Analysis in Food based in France. He is also a visiting Professor at the China Agriculture University in Beijing, a recipient of a Winston Churchill Fellowship and is an elected Fellow of the Royal Society of Chemistry, Royal Society of Biology and the Institute of Food Science and Technology.

Background

Major food fraud and contamination events occur with alarming regularity, and are known to be episodic, with the question being not *if* but *when* another large-scale food safety/integrity incident will occur. The increase in scale and spread of these events could be said to be directly related to globalization and rapid distribution systems, with the result that major events can now have international impacts, with far-reaching and sometimes lethal consequences.[1] It is perhaps not surprising then that as the modern phase of globalization is relatively recent (from the latter part of the 20th century), issues related to large-scale food adulteration and contamination events are only now beginning to be realised, discussed and analysed in far more detail, by the food industry, regulators, as well as by consumers. These discussions could be said to include the parts played by the drivers of global population and consumer/supplier demand for an increasingly wide-range of food products year round, regardless of seasonality or local availability, resulting in

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the ever increasing scale and complexity of food supply networks. This not only leads to food supply networks becoming significantly more vulnerable to fraud and contamination (as well as potentially fragmented and dysfunctional[2–4]); it also makes the task of deciding which analytical methods are more suitable to collect and analyse data within the component parts, or targeted points of vulnerability along complex and dynamic supply chains, that much more challenging.

The vulnerabilities currently inherent within complex international food supply chains were very publically demonstrated by the horsemeat scandal (so-called 'Horsegate' scandal) in 2013 centred in the UK and Europe, which also focused the attention of governments, industry, researchers and regulatory bodies across the world onto the subject of food fraud (food crime) and contamination. The events are well documented but primarily involved the large-scale replacement of processed beef products with horsemeat and other undeclared meat products, such as pork, sometimes up to levels of 100% substitution.[5] Of course this form of adulteration (or contamination) of the food supply is nothing new, and is probably as old as the food production systems themselves and continues unabated.[1] Table 1 contains examples of the adulterants found by Accum and Hassall in some of the first studies of food adulteration and contamination in the first half of the 19th century and published in *The Lancet*.[6,7] A short list of relative recent high impact examples that have affected global food security would include: widespread adulteration of milk products with melamine in China in 2008; PCBs and dioxins in pork *via* industrial oil contaminated animal feed in Ireland in 2008 (and Belgium in 1999); carcinogenic Sudan I–IV dyes in chilli powder and tomato-based products leading to EU regulation in 2003; scrapie-infected feed for cattle leading to BSE in the late 1980s/early 1990s in the UK; wine adulteration, *e.g.* by methanol in Italy in 1986; diethylene glycol (used in some anti-freeze products) in Austrian wines in 1985; and Toxic Oil Syndrome in Spain in 1981 which unfortunately killed over 600 people.[8]

Whilst these are just a few of the recent major incidents, the engagement with fraudsters and detection of adulterated and contaminated food is continuous and becoming increasingly more sophisticated, with the leading food categories of reported food fraud including adulteration and mislabelling of dairy produce, meat, seafood, wines, spirits, edible oils, honey, fruit juices, coffee and tea, organic food and products, and clouding agents.[9] More recently, the adulteration of various herbs[10] and spices,[11–13] the so-called gutter oil scandal in Asia,[14,15] and fake rice, for example, are causing significant or potential problems. One recent report stated that in the UK alone, food and drink companies lose an estimated £11.2 billion per annum to food fraud and that tackling fraud within this industry could boost profitability by £4.48 bn (34%).[16] Worldwide, this is a huge and growing problem with sophisticated and well connected networks of fraudsters becoming involved and seeing opportunities in existing and rapidly expanding sectors such as whole meats and fish into newly affluent markets, the burgeoning halal market, where the consumption of haram food is highly undesirable,[17–19] and organic food sectors,[20] through to low-value but very high turnover products such as processed foods, as was the case with beef substitution with horse *etc.* in ready meals.

Spectrometry *versus* spectroscopy

Following the horsemeat scandal, as well as the other food fraud and contamination events mentioned above (in addition to many others not mentioned here), it is evident that those working within and associated with the food industry, such as producers, retailers and regulators, are seeking rapid, user-friendly methods to detect food fraud and contamination, and rapid/high-throughput screening methods for the analysis of food in general (*i.e.* quality indicators). These methods should be portable, ruggedized, and ideally handheld and/or remote sensor devices that can be taken to or positioned on/at/in-line at points of vulnerability along (complex) food supply networks. It is also essential that these approaches require a minimum amount of background training in order to allow the users to acquire information rich and reproducible data rapidly (*ergo* point-and-shoot). These rapid methods could include any one, or a combination of, spectroscopies as well as many other methods (see below). Of course much more sophisticated and sensitive, though considerably more expensive, techniques already exist in the form of mass spectrometry and related hyphenated approaches which incorporate prior chromatographic separations. Here we will briefly discuss a range of spectrometry and spectroscopy approaches.

Mass spectrometry

Mass spectrometry (MS) is a powerful technology which offers a number of advantages and, as inferred above, some current limitations for applications within the food supply chain (though not within food industry and food regulatory laboratories). Targeted analytical methods such as MS offer high chemical specificity and sensitivity for example, enabling the accurate identification and quantification of known analytes within complex food matrices at sub-μg concentrations. Considered to be the gold standard within many industries, and research fields, including the agri-food as well as the pharmaceutical, petrochemical, and defence industries, these methods are usually coupled with chromatographic techniques. The chromatography column chemistry needs to be carefully chosen in order to separate out the complex components of food adequately and thus comes with an additional analytical cost as well as being relatively slow (min–h).

That being said, some forms of MS can be considered as fingerprinting techniques[21] as they involve the direct introduction of samples into the mass spectrometer without the requirement for prior chromatographic separation. Some recent examples of these MS fingerprinting techniques have included direct infusion (or injection) mass spectrometry (DIMS) for the characterization of the foodborne pathogen *Campylobacter jejuni*,[22] desorption electrospray ionisation (DESI) for the analysis of melamine migration into foods from melamine tableware,[23] matrix-assisted laser desorption (MALDI) MS for the detection of hazelnut oil in extra virgin olive oil (EVOO) down to levels of 1% [24] and direct analysis in real-time (DART) MS for the direct swabbing of fruit and vegetables for the detection of pesticides,[25] amongst many others. For a

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Table 1 A range of the adulterants identified by Accum and Hassall in some of the first published studies of food adulteration during the early to mid 19th century[6,7]

	Adulterant	
Food product	To increase the bulk/weight	To alter the appearance/flavour
Cayenne pepper	Bulked out with the addition of a variety of compounds such as ground rice, mustard seed husks, sawdust, and salt	Coloured with red lead, vermillion, venetian red (from ferric oxide, also known commonly as rust), turmeric
Cocoa and chocolate	Arrowroot, wheat, maize, sago, potato, tapioca, flour, chicory were commonly used to increase weight and volume	Venetian red, red ochre, and other iron compounds added to effect the colour
Coffee	Chicory, roasted wheat, rye flour, potato flour, roasted beans, and acorns were added to bulk out the volume	Burnt sugar, which was also referred to as black jack, was used as a darkener
Confectionery	No bulking agents found	Sweets coloured with Gamboge, a Southeast Asian tree sap/resin, traditionally used to dye Buddhist monks robes. White comfits were coloured with clay from Cornwall, red sweets with red lead and vermillion, green sweets were often found to be coloured with copper salts and Scheele's green, a compound which used to be used to colour paints and also known as copper arsenite (a compound famously linked to the death of Napoleon)
Custard powders	Bulked out with wheat, potato, or rice flour	Lead chromate, and turmeric were used to enhance the yellow colour
Gin	Diluted with water	Cayenne, cassia, cinnamon, sugar, alum (aluminium sulfate), and so-called salt of tartar (potassium carbonate) used to change taste
Olive oil	No bulking agents found	Olive oil was reported to contain lead from the olive presses
Pickles	No bulking agents found	Toxic copper salts were used as a green colourant
Porter and stout	Diluted with water	Adulterated with fishberry (also known as Levant nut), a poisonous picrotoxin. And many other adulterants such as brown sugar, capsicum, salt, wormwood, ginger, caraway seeds, highly poisonous Nux vomica seeds from the strychnine tree, brucine, cream of tartar, shavings from the horns of male red deer, treacle, coriander, liquorice and honey
Red cheese	No bulking agents found	Red lead (lead tetroxide), and vermillion (mercury sulfide), used as colourants
Tea	Used tea leaves, as well as a variety of leaves from plants not related to tea. Starch, sand, China clay	The pigment Prussian blue (ferric ferrocyanide) in black tea, turmeric, orpiment (arsenic sulfide), and copper salts for green tea. *Plumbago*, gum, and *Indigofera*
Vinegar	No bulking agents found	Vinegar was found to contain dissolved tin and lead after being boiled in pewter vessels. It could also undergo a process known as sharpening, using sulfuric acid

more technical explanation of these, and other, lab-based MS methods for the authentication and analysis of food adulteration and contamination, such as isotope ratio mass spectrometry (IRMS),[26] the reader is directed to our more comprehensive review on fingerprinting food in *Chemical Society Reviews*,[1] as well as other reviews on the potential of ambient mass spectrometry for high-throughput analyses,[27] and DART-MS for food analysis.[28]

Whilst the MS methods mentioned thus far are all relatively bulky and therefore confined to conventional laboratories, there is obviously huge potential for these techniques outside the lab and out in the food supply chain, with research and development into the portability and miniaturization of ambient MS[29] having been underway for some considerable time[30] (at least two decades[31]). These developments have primarily been based around point-of-care clinical applications (such as the Mini 12 [32]) or in-field chemical detection[33] applications, though the broader potential of 'handheld' MS in other areas such as food analysis has of course been recognised.[32,34,35] Very significant and progressive steps in both portability and the less relative

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term, miniaturization, during the last decade have been achieved with reductions in size to less than 4 kg by Graham Cooks and Zheng Ouyang[36] (and for the purposes of this article, we consider any instrument weighing 4 kg or less to be handheld,[37] and above 4 kg as portable). Cooks and Ouyang have also been at the forefront in a multitude of other areas of broader MS research such as DESI, low temperature plasma, and paper spray handheld/portable mass spectrometry.[38–40] Miniaturization of MS has continued to evolve by addressing technical challenges such as the development of compact low-power pumping systems suitable for miniature MS and the reduction in size of ion traps. These have led to the development of discontinuous atmospheric pressure interface (DAPI), as well as rectilinear ion traps as mass analysers, the optimisation, miniaturization, and simulation of which are still on-going.[41,42]

Whilst these developments are extremely encouraging, to date these systems still require much further optimization for them to be tolerant to and tested in a wide-range of environmental conditions outside of the laboratory, cost-effective, and importantly, the ability to be used and the data presented in a way that is readily interpretable by those not expert or with a background in MS. The development of totally self-sustained, integrated, and truly handheld MS sensors may yet be sometime in the future. Yet this could still be possible with simplified user interfaces, and as some have reported, perhaps with the same MS core but with any number of interchangeable sample cartridges for a variety of on-site applications.[31] Innovations such as these would allow for the true democratisation of MS methods in becoming universal techniques able to be routinely used by non-specialists within a wide range of applications outside of laboratories, such as food supply chains.

Infrared spectroscopy

Spectroscopy includes a wide range of methods which involve the measurement of the interaction of matter with electromagnetic (EM) radiation. Here we will briefly focus on a subset of these methods, specifically those termed vibrational spectroscopies, and their current and potential future use within food supply chains. Infrared spectroscopies include near infrared (NIR) and Fourier transform infrared (FT-IR) spectroscopy, the latter operating in the mid-infrared (MIR) part of the EM spectrum.[43] Both these methods involve measuring the absorption of an infrared beam within a sample, with every sample having its own unique spectral fingerprint.[44] Unlike the predominantly lab-bound MS methods mentioned above, on/at-line NIR instrumentation has been used within the food processing industry for four decades, particularly for the monitoring and control of product and process quality.[1,45]

The use of NIR hyperspectral imaging as an analytical tool for process control, food safety and quality has also been well recognised, more so during the last decade,[46] as well as more recently,[47–49] accompanied by the application of chemometrics for data pre-treatment and analysis[50,51] and multivariate screening and modelling.[52] Other recent reports include the application of NIR to melamine adulteration of soya bean meal[53,54] and non-targeted analysis of the adulteration of milk powders.[55] Even more relevant to our focus here, are reports such as advancements in the miniaturization of these methods using handheld micro-electrical-mechanical-systems (MEMS) based NIR online in abattoirs for the *in situ* classification of several different high-value gourmet meat carcass types on the slaughterhouse line[56] with further reports into the algorithms used for the rapid transfer of large databases from at-line high performance NIR monochromators downloaded directly to handheld MEMS-NIR.[57] These methods have been reported to enable a new approach and confirm the suitability of handheld MEMS-NIR for the rapid, low-cost, on-line/*in situ* analysis of meat products. For a recent review of the applications of portable NIR in the agro-food industry the reader is directed to dos Santos and co-workers.[58]

Whilst not having the on-site history that NIR applications have had within the food processing and related industries over the last four decades, the potential of FT-IR spectroscopy for food analysis (and many other forms of rapid bioanalysis[44,59,60]) has been recognised for some considerable time. As mentioned above, FT-IR operates within the mid-infrared range of the EM spectrum, and along with NIR, it readily presents itself as a rapid, high-throughput at/in/on-line screening technology for food and feed. As well as operating within the mid-infrared, FT-IR (like NIR) uses a broadband source, though the resultant data collected contains fundamental vibrations of the sample under analysis from the entire wavenumber range (unlike NIR which corresponds to vibrational overtones and combination modes, which are consequently broader in nature and not so information rich). Consequently, whilst NIR technology is still improving and is an extremely convenient technology within the agri-food sector (predominantly due to the perceived lack of water interference) for rapid, bulk and high-throughput screening, FT-IR is more sensitive and perhaps more suited to the detection of low-level compounds within complex food matrices and subtle differences between samples from very similar backgrounds.

Within research laboratories FT-IR has a long history of published food-based research applications, such as food and food ingredient authentication,[61] with work by Gerard Downey and co-workers contributing a great deal to this, and indeed, other areas of vibrational spectroscopy for food analysis and authentication.[62,63] The range of applications of food-based FT-IR research are considerably broad (and increasing) and include the rapid detection of food spoilage bacteria (an indicator of food quality as well as shelf-life estimation) at ambient temperatures in meat,[64–67] and detecting food spoilage micro-organisms[68] on meat in different forms of conventional and vacuum packaging,[69] as well as dairy produce.[70] Others include the monitoring of bacterial interactions within milk,[71] speciation in meat and dairy produce,[72,73] and more recently, brand authentication of a range of Trappist beers,[74] adulteration of milk[75] and of highly processed foods with complex chemical and physical matrices, such as fresh/frozen/thawed beef burgers.[76] For a review of FT-IR for rapid authentication and detection of food adulteration, the reader is directed to Rodriguez-Saona and Allendorf.[77]

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Again, as with NIR, the suitability and utility of portable/handheld FT-IR spectroscopy within the food supply chain has become increasingly more evident; with portable and handheld spectroscopy having already been demonstrated for its potential to the move from the confines of the relatively stable and controlled laboratory environment and out into the potentially more challenging and dynamic environs of the food supply chain. Indeed, very recently a considerable body of work by Rodriguez-Saona and co-workers has shown the utility and efficacy of portable and handheld FT-IR for a range of food-based applications. This growing body of work includes monitoring oxidative stability[78] as well as measuring trans fat content in edible oils,[79] showing that handheld FT-IR can be a simple and rapid alternative to MS for on-site analysis of acrylamides in potato chips,[80] and *in situ* discrimination and authentication of conventionally produced and organic butter.[81]

Combined NIR/FT-IR

Interestingly, one study by the Rodriguez-Saona group compared and evaluated the use of both portable mid-IR and handheld NIR for determining the levels of sucrose coatings in infant cereals, and found that superior predictive capability was obtained with their portable mid-IR unit.[82] We consider this evaluation and direct comparison of both NIR and MIR methods of particular interest, as we believe that the ability to *combine* both these methods (and others, see below) into one unit, ideally handheld, would be a very useful tool indeed for a range of applications across the food supply chain (as well as countless other applications). This is due to the fact that both NIR and MIR spectroscopy have their own advantages and limitations. FT-IR is more sensitive to vibrations from liquid, bound and atmospheric water than NIR, which can be overcome to some extent *via* the use of very narrow path lengths or attenuated total reflectance (ATR).[83,84] Conversely NIR, whilst less sensitive to water than FT-IR (and the resultant data less information rich), is able to penetrate much deeper into the surface of samples.

Lab-based benchtop combined mid-IR/NIR spectroscopy already exists and allows for the selection of the most appropriate range to be chosen according to context, what is fit-for-purpose, allowing for a broader and more diverse range of samples to be analysed rapidly by a single instrument. It is only a matter of time before such benchtop innovations are significantly reduced in size and available on/at-line, and handheld combination single package MIR/NIR instruments can be used within the food supply chain. These would be simple to use, truly democratised analytical technology much closer to development and commercialisation than handheld MS for use in the food supply chain, with the ability to switch to reduced wavenumber ranges when and if required and generate highly reproducible and easily interpretable data.

Raman spectroscopy

Raman spectroscopy is another vibrational technique, which has to a large degree been made portable by many manufacturers (*vide infra*) and we consider it to have exceptional potential for use within food supply chains. Related and complementary to both forms of infrared spectroscopy discussed above, in simplistic terms, whilst infrared spectroscopy measures the *absorption* of energy, Raman spectroscopy involves the measurement of the *exchange* of energy with EM radiation of a particular wavelength, which is usually provided by a monochromatic light source such as a laser of any wavelength from the deep UV (*e.g.* 244 nm) to visible (405–633 nm) and into the NIR (785 nm, 830 nm, or 1064 nm are currently popular).[1] The measurement in the shift of the incident laser light (the Raman shift) is observed, which is also known as the *inelastic* light scattering effect. Infrared and Raman spectroscopy are complementary due to the selection rules, whereby molecules are either infrared or Raman active, with molecules being infrared active only if the vibration induced by infrared light causes a change in the dipole moment, with Raman spectroscopy detecting changes in the polarizability of molecules. Therefore, there is a rule of mutual exclusion meaning that the two methods can provide complementary (bio)chemical information, with bands in Raman typically being a lot sharper and hence more characteristic than in the infrared. Whilst the Raman effect is an inherently weaker process than infrared, and to date, the equipment more expensive to produce, the materials used to construct Raman devices are becoming gradually less expensive. In addition, the detection responses in Raman devices are faster than infrared techniques, and indeed the detectors themselves are charge-coupled devices (CCDs) similar to those found in digital cameras and therefore within every smart phone and home.

In terms of food analysis, Raman spectroscopy also offers other distinct advantages to infrared spectroscopy, with water being a weak Raman scatterer for example, which is always an advantage when the vast majority of foods or feed contain water in some form. It is also a *confocal* method. Being a confocal technique means that Raman spectroscopy measures precisely at the point where the laser is focused on/within a sample, with any out-of-focus signal being eliminated. This in itself is highly significant as it means that as long as the material the laser is passing through is transparent to laser light, conventional Raman spectroscopy can readily analyse samples through glass or plastic bottles/bags and other forms of transparent packaging (used in abundance throughout the food industry), focusing directly on the contents inside (including liquids) and collect a (bio)chemical fingerprint within seconds; this eliminates the need to remove the sample from the container which is very important if the sample is highly hazardous. Therefore, Raman affords the user some advantages over the infrared methods above. Several groups have undertaken direct comparative studies of infrared and Raman spectroscopies for the investigation of food samples including meat speciation,[72] detection of meat spoilage,[85] and the detection, enumeration and growth interactions of bacterial species in milk.[71] The benefits of direct comparative studies of infrared and Raman have also been recognised in other areas more recently.[86] It is interesting to note that as well as these lab-based benchtop comparative studies, a handheld combined FT-IR/Raman spectrometer is already commercially available (see Table 2), in

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addition to a wide-range of the other handheld spectroscopy devices discussed here.

The advantages of portable/handheld Raman spectroscopy are being increasingly recognised by the pharmaceutical, materials, biosecurity[87] and other sectors, as well as their potential applications within clinical settings.[88] In terms of food analysis, relatively recent studies involving portable Raman spectroscopy have included the screening of melamine adulteration in milk powder[89] and in other multiple sample matrices such as infant formula, lactose, whey protein, wheat bran and wheat gluten and povidone (which can have contraindications and severe allergic reactions).[90] Portable Raman devices have been used successfully for the detection of the organophosphate and organothiophosphate pesticides phorate and fenthion on apple skins[91] and the fungicide and parasiticide thiabendazole applied on citrus fruits and bananas,[92] authenticity and origin of vegetable and essential oils,[93] detection of marker compounds for illegal (non-commercial) alcoholic beverages.[94] Detection and discrimination of pathogenic bacteria on food crops *in the field*,[95] detection of offal adulteration in beef burgers;[96] rapid meat spoilage identification,[97] and finally, a similar study to the one above using MEMS-NIR, for prediction of pork quality on a slaughterhouse line, here using a portable Raman device. Fig. 1 shows a commercially available handheld 1064 nm Raman spectrometer (Snowy Range Instruments, Laramie, USA), with a range of spectra acquired by us from several different foods and beverages including extra virgin olive oil, honey, red wine, beef, whisky, and saffron. For a review of infrared and Raman spectroscopy for the verification of food origin, the reader is, perhaps not surprisingly, directed to Downey.[62] In addition, several of the more recent studies have employed surface enhanced Raman scattering (SERS) techniques[98,99] and for a more in-depth review of SERS and its application to food safety, specifically in terms of foodborne pathogen detection and food fraud and contamination, the reader is directed to Craig *et al.*[100]

Another more recent and exciting innovation and variant of Raman spectroscopy is spatially offset Raman spectroscopy (SORS).[101] With SORS, Raman spectra are collected from locations *within* a sample *at depth* that are spatially separate from the point at which the sample is illuminated by the laser on the sample's *surface*. SORS can be undertaken in seconds, by shining a laser light onto a surface/container and detecting the Raman signal at the point of excitation and one or more offset positions, the resultant spectra subtracted using a scaled subtraction, which produce two spectra representing the surface and subsurface of samples.[102] Therefore, SORS enables the user to isolate and retrieve chemically rich spectral information from distinct layers, substructures, and indeed through other barriers, which would not be accessible even *via* conventional Raman spectroscopy, or indeed, any of the other techniques (handheld or otherwise) mentioned thus far. When commenting from the perspective of its potential use for food product analysis, the ability of SORS to penetrate through barriers/packaging and retrieve chemically rich information is especially pertinent and it appears to be a readily transferable technology, and one may even suggest it has the potential to be a highly disruptive technology.

The range of potential SORS applications demonstrated to date include the determination and fast screening of genuine and counterfeit pharmaceuticals (including anti-malarials) through translucent plastic, paper sacks, coloured glass bottles,[103,104] and tablet blister packs,[105] the latter study by Ricci *et al.* combining SORS with ATR. This ability to *see through* and penetrate layers and packaging not transparent to the human eye has led to its use for the screening of liquids, aerosols and gels (LAGs) at multiple international airports,[106] concealed liquid explosives detection,[107] and other concealed substances in sealed opaque plastic and coloured glass bottles and containers several millimetres thick. These are compared with reference libraries of pure materials, to enable the rapid and unambiguous identification of the containers contents,[108] with a reported inherently high probability of detection and low false alarm rate.[106] Concealed contents identification has also included the determination of fake and genuine ivory through paint, plastic, varnishes and cloth.[109] More recent emerging applications of SORS include those within the clinical sciences and the reader is directed to an excellent review of this area by Pavel Matousek (the co-inventor of this technique) and co-workers including the non-invasive diagnosis of bone disease, cancer, and non-invasive monitoring of glucose levels.[110]

Being such a recent innovation, the only food-related SORS applications to date include one to demonstrate the potential utility of subsurface detection of lycopene and product quality through the pericarp of tomato fruit,[111] and more recently, the qualitative and quantitative characterization of quality parameters of salmon through the skin.[112] Whilst there appears to be a paucity of published food-based SORS studies, to date at least, the wide range of applications published thus far in the other areas mentioned above show the specific and seemingly unique combined capabilities of this technique. All of which keenly illustrate that SORS remains an exciting area, ripe for further exploration, development, and detailed investigation within the area of food authenticity, wider food analysis in general within supply chains/networks and its use within other forms of logistic networks.

Future perspective

The emphasis in this short review has predominantly been toward an optics based approach to food fraud and contamination detection (Table 3), due in part to the commercial availability and ubiquitous nature of these methods, but also their ease of use and rapidity, chemical sensitivity, and the continued innovation and development of these spectroscopic devices and their components. In addition to the advantages of portable/handheld spectrometers being taken out into the supply chain, optics/photonic technologies in general also readily lend themselves to be utilized as fixed/embedded on/at-line technologies. Therefore, one must not overlook ongoing technological developments within the whole suite of optical technologies, and the future potential of these within food supply chains, such as the use of vertical-cavity surface emitting lasers (VCSELs) as minute low-power light sources,[113] UV-Vis,[114] and blue LED[115] amongst others. With further innovation and

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Table 2 A snapshot of commercially available handheld Raman and infrared spectrometers, for them to be considered as 'handheld' as opposed to portable devices, the cut-off point was determined as a weight of less than 4 kg[a]

	Company	Product	Spectral range (cm^{-1})	Weight (kg)	Size (cm)	Laser (nm)
Raman	Metro-Ohm	Mira M-1	400–2300	0.54	12.5 × 8.5 × 3.9	785
		Mira M-2*	400–2300	0.82	14.4 × 9.3 × 6.4	1064
	Ocean Optics	ID Raman Mini	400–2300	0.33	9.1 × 7.1 × 3.8	785
	Rigaku	Progeny	200–2500	1.6	29.9 × 8.1 × 7.4	1064
	Thermo Scientific	First Defender RM	250–2875	0.82	4.4 × 19.3 × 10.7	785
		First Defender RMX	250–2875	0.92	19.6 × 11.4 × 6.1	785
		TruNarc	250–2875	0.505	16.3 × 10.4 × 5.1	785
		TruScan GP	250–2875	0.9	20.8 × 10.7 × 4.3	785
		TruScan RM	250–2875	0.9	20.8 × 10.7 × 4.3	785
	Snowy Range	CBEx	400–2300	0.33	9.1 × 7.1 × 3.8	785
		CBEx 1064	400–2300	0.77	11.3 × 7.9 × 5.7	1064
	Sciaps	Inspector 300	175–2875	1.7	19 × 17.5 × 4.3	785
		Inspector 500	100–2500	2.7	20 × 17.5 × 4.3	1030
	Airsense Analytics	LS-ID	ns	0.4	13 × 7 × 4	785
	Chemring Detection	THOR-1064	160–2200	1.5	22.9 × 11.5 × 5.1	1064
	Systems	PGR-1064	ns	1	6.4 × 19 × 16.7	1064
	BWTEK	NanoRam	176–2900	1.2	22 × 10 × 5	785
		TacticID	176–2900	0.9	19 × 10 × 5	785
	Wasatch Photonics	NOVA	200–2500	0.82	16.2 × 13.2 × 3.7	785
	Agiltron	Pin Pointer	200–3000	1.36	21.4 × 10.8 × 6.3	785
	TSI	ASSURX	250–2350	1.9	23.1 × 10.1 × 22.2	785
	Bruker	BRAVO	300–3200	1.5	27 × 15.6 × 6.2	700–1100
FT-IR/Raman	Thermo Scientific	Gemini Analyzer	250–2875 (Raman) 650–4000 (IR)	1.9	25.6 × 14.6 × 6.1	785
FT-IR	Agilent	4300	650–4500	2.2	10 × 19 × 35	Not
		4100 Exoscan	650–4000	3.2	17.1 × 11.9 × 22.4	applicable
	Thermo Scientific	TruDefender	650–4000	1.3	5.3 × 19.6 × 11.2	
	Pyreos	Mid-IR	909–1818 or 2000–4000	0.71	16.5 × 7.4 × 3.5	
	Arcoptix	FTIR-Rocket	1700–5000 or 830–4000	1.2	18 × 16 × 8	
NIR	Sentronic	SentroID	5800–11 000	1.1	23 × 8 × 4.2	
	BWTEK	i-Spec nano	4500–7700	ns	12 × 6 × 3	
	Thermo	microPHAZIR	4100–6250	1.8	26.6 × 25.1 × 10.9	
	JDSU	MicroNIR Pro	6000–11 000	0.06	4.5 × 4.4	
	ASD	QualitySpec	4000–28 500	2.5	31 × 10 × 30	
	Ocean Optics	NIRQUEST256-2.5	4000–11 000	1.18	18.2 × 11 × 4.7	
	Avantes	AvaSpec-NIR256-2.5-HSC	4000–10 000	3.5	18.5 × 14.5 × 18.5	
	Brimrose	Luminar 5030	4300–9000 (others available)	ns	ns	
	Arcoptix	FT-NIR Rocket	3800–11 000	1.7	18 × 12.6 × 7.8	

[a] ns = not specified.

future developments in sensor technologies and computing, such as wired or wireless connectivity (*i.e.* Wi-Fi, Bluetooth) and/or remote access capability[116] built into the portable and handheld devices discussed here, these rapid methods could be networked and thus used to detect trends in the food market (perhaps even before any food security threat/event is acknowledged by regulators) and thus could very easily sit within the umbrella of the Internet of Things (IoT). Which, like cloud computing, will not be one but rather a series of paradigms and platforms which are set to explode and impact on all our lives within the next decade.[117–119]

Indeed, it is worth remembering that the first use of the term the 'Internet of Things' (by the British technology pioneer Kevin Ashton) was for its direct application to supply chains.[120] IoT is comprised of networks of interconnected communicating sensor/actuating physical objects (Things) able to identify each other, and generate, analyse, share and act upon information across common operating platforms and applications. At its current stage of evolution, at the forefront of IoT sensor technologies are radio frequency identification (RFID) tags/togs/labels, characterized by unique identifiers which can be passive, semi-passive and active, as small as an adhesive sticker, and used to monitor objects in real-time;[117] *e.g.*, to track luggage at airports. Within food supply chains RFID approaches can be used to monitor product quality in terms of expiry dates on perishable goods,[121] determine the probability of goods such as RFID-tagged oils as being counterfeit using mathematical algorithms,[122] establish traceability systems,[123] enable low cost and ultra-low power food logistics,[124] low-cost chipless short range ID and temperature/humidity monitoring,[125] and the detection of food freshness and bacterial growth.[126]

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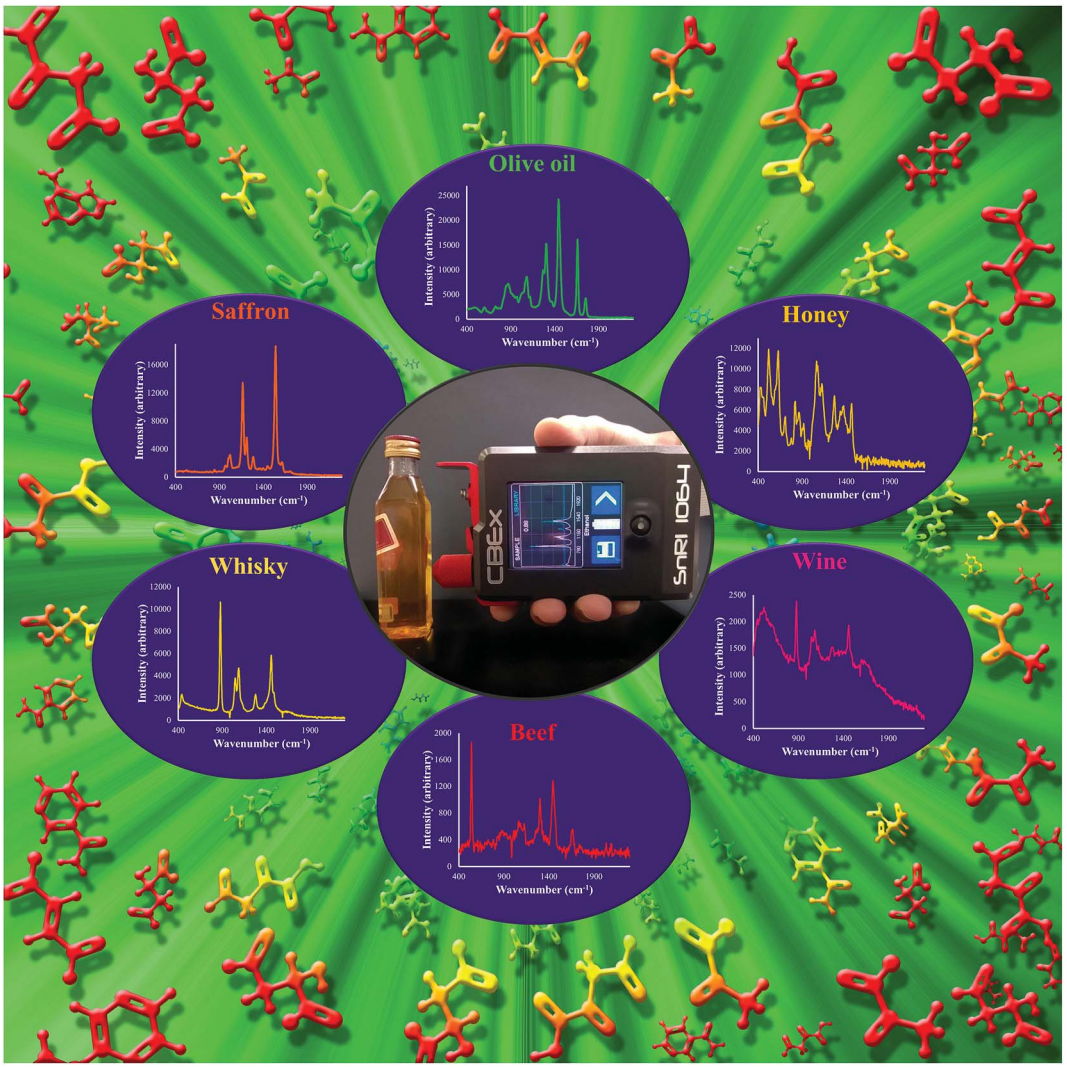

Fig. 1 A commercially available handheld Raman spectrometer (CBEx 1064, Snowy Range Instruments, Laramie, USA) and a range of Raman spectra acquired from this device either directly through plastic packaging, commercial glass and plastic bottles, or from vials. These are from several sample types commonly associated with food fraud, and include extra virgin olive oil, honey, red wine, beef, whisky, and saffron.

However, as the IoT continues to evolve it will be comprised of many more sensor modalities and innovations in addition to RFID and become fully formed *via* a much larger analytical sensor,[127] biosensor[128,129] and computational toolbox.[130,131] These will include machine-to-machine communicating fixed/embedded as well as portable/handheld sensor devices with direct human input such as those discussed here. These people-centric (participatory) sensing platforms are able to acquire rapid, timely, and context specific data associated with predicted or anticipated events, compared to data from fixed sensor networks alone,[118] and particularly so when in the hands of operatives with experience of supply chains and non-specialists in spectroscopy or science in general. This ability to ensure at the developmental stage that handheld detection methods can be used by non-specialists is in itself an extremely important part of the research and development process of these rapid devices. It forms a part of the knowledge exchange process, is an exercise in mutual learning, and allows the translation of research into practical applications, with positive impacts on the food supply chains and therefore society as a whole.

In addition, whilst fixed or benchtop spectroscopic devices could be based at major distribution and transport nodes/hubs within complex food supply networks, the handheld devices can be taken to changing points of vulnerability to fraud within these increasingly complex and dynamic networks. Points of vulnerability in food supply networks that, in the future, may well have been automatically identified/predicted and targeted for further investigation by pervasive and automated computational *systems analysis* embedded within an IoT network. As stated elsewhere, pervasive computing *in conjunction* with sensor technology platforms offers considerable potential for the improvement and efficiency of food supply chains/systems.[117]

Therefore, the future analytical toolbox will also include a combination of an increasingly innovative sensor portfolio,

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Table 3 A summary of definitions of terms used throughout this article, adapted from Annex D of the Elliott Review,[5] the UK Food Standards Agency definition of food fraud*, and Ellis *et al.*[72]

Term	Definition
Food fraud	Committed when food is deliberately placed on the market for financial gain, with the intent of deception of consumers.* Referred to in the USA and occasionally elsewhere as economically motivated adulteration (EMA). Two of the main types include: trading of food which is unfit for consumption or harmful, or deliberately misdescribing or mislabelling food. The latter can include false statements regarding geographical origin, ingredients, or substitution with lower value (*i.e.* myrtle instead of oregano), or sometimes even dangerous contents not intended for human consumption (*i.e.* industrial dyes). The terms food fraud and food adulteration can be used to mean the same thing, when adulteration is intentional
Contamination	Can involve unwanted and usually unintentional physical, chemical, or biological contamination. Examples could include metal or plastic fragments (physical) or chemicals used for cleaning from food processing equipment, or microbial (bacterial/fungal/toxins) from microbes. If on rare occasions any of these are intentional, then it would be food crime, and depending on the intention and extent of deliberate contamination, bioterrorism
Food spoilage	Usually described as any changes in organoleptic characteristics which make a food undesirable for consumption. These may include changes in appearance (discoloration), development of off-odours, slime formation, or changes in taste. In meat and poultry for example it is generally accepted that detectable organoleptic spoilage is a result of decomposition and the formation of metabolites caused by the growth of microorganisms
Food crime	Food crime has been described as the point when food fraud is no longer just random acts caused by so-called 'rogues' within the food industry, but when this activity becomes organised and is undertaken by groups who knowingly set out with the intention to deceive, or injure, those purchasing a food product
Food security	Concerns the food supply, and ensuring access to a secure, sufficient quantity of safe, nutritious food to maintain a healthy and active life
Food authenticity	Is reflective of a reasonable assumption that the description of the labelling, or the menu section, of a finished food product purchased by the consumer is correct. Reasonableness should be a Wednesbury test in that it assumes no specialist knowledge of the food industry
Food integrity	Ensuring that food products that are sold or offered are of the quality, substance, and nature expected by the consumer. To sections of society which eschew certain types of foods, due to religious, medical, or dietary considerations, this can be of particular importance

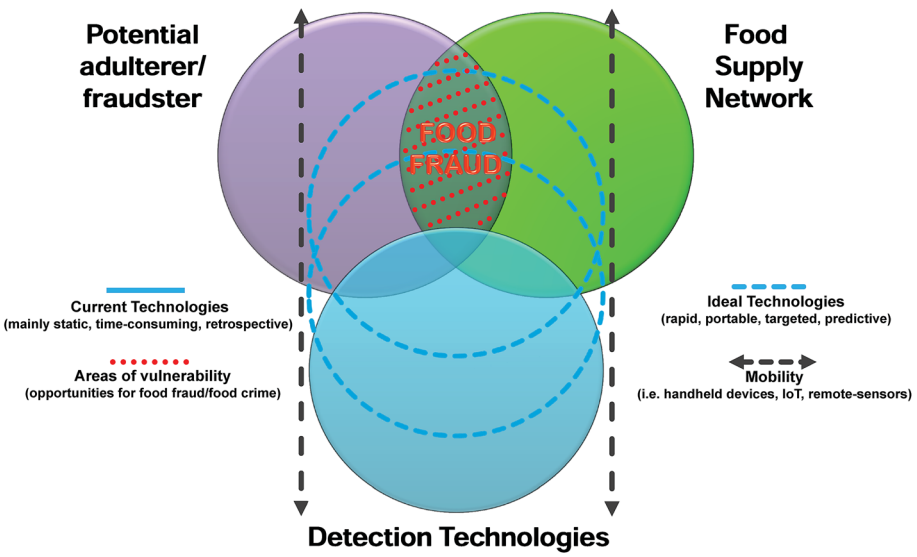

Fig. 2 Adapted from a graphical model of Routine Activity Theory,[138,139] which is based on the three necessary conditions for many forms of crime (such as food fraud) to occur, converging in time and space. These three conditions require: (i) a likely offender (potential adulterer/ fraudster); (ii) a suitable target (food supply network); and (iii) the absence of a capable guardian (detection technologies). The opportunities for, and vulnerabilities to crime (food fraud) occur in the areas where the so-called capable guardian is absent. We propose a technology-based capable guardian system, whereby static and mobile/handheld sensor platforms and technologies and future pervasive, predictive computation will *together* take on this role and assist in significantly reducing the areas of vulnerability to food crime within food supply chains.

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with methods able to track, trace and detect within food supply chains. These could include microfluidic[132,133] and nanofluidic devices such as Nanopore,[134] active and intelligent packaging[135] and containers,[136] DNA barcoding,[137] edible tags,[138] 3D-printed smart caps[139] and novel adaptations to existing technologies, such as turning a handheld personal blood glucose meter into a melamine detector for milk for one very recent example.[140] In addition to computational tools for data analysis, simulation and fusion, as well as visualisation and interpretation of food supply chains and systems.[141–143]

Concluding remarks

In this review we have focussed, and some may say 'shone a light on', one small subset of potentially very useful handheld detection methods for on-site food fraud detection, namely vibrational spectroscopy. It is our sincere hope that, along with the many other methods currently in development, mobile handheld (as well as static, benchtop, fixed at-line) spectroscopy, will play a far greater role within the area of food and feed fraud detection, and indeed food analysis/screening in general, within increasingly complex and globalized food supply chains. As it is our firm belief that the ever expanding portfolio of sensor platforms and technologies and future pervasive, predictive computation will *together* take on the role of a technology-based capable guardian for food systems.[144,145] Able to increase the resilience of food systems, and reduce the areas of vulnerability within complex food supply chains significantly, as well as the space within which the opportunities for food crime currently exist (Fig. 2). As food fraud has repeatedly been shown to be a problem of systems, and it therefore requires systems level solutions and thinking,[146] holism, as opposed to one-eyed reductionism.

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