L. FIORANI

Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

G. GIUBILEO

Formerly at Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

L. MANGIONE

GenioMan Srl, Roma, Italy

A. PUIU

Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

W. SALEH

ENEA guest, Department of Physics, College of Science,
University of Baghdad, Baghdad, Iraq

FOOD FRAUD DETECTION BY LASER PHOTOACOUSTIC SPECTROSCOPY

ENEA

L. FIORANI

Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

A. PUIU

Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

G. GIUBILEO

Formerly at Fusion and Technology for Nuclear Safety
and Security Department
Frascati Research Centre, Rome

W. SALEH

ENEA guest, Department of Physics, College of Science,
University of Baghdad, Baghdad, Iraq

L. MANGIONE

GenioMan Srl, Roma, Italy

FOOD FRAUD DETECTION BY LASER PHOTOACOUSTIC SPECTROSCOPY

ENEA

FOOD FRAUD DETECTION BY LASER PHOTOACOUSTIC SPECTROSCOPY

L. Fiorani, G. Giubileo, L. Mangione, A. Puiu, W. Saleh

Abstract

The Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) applied for years laser photoacoustic spectroscopy to food fraud detection. After a review of food fraud in the global market, the present instrument has been investigated and characterized. Then, the measurement of some food samples is described, in the framework of the Metrofood project. Finally, the technical requirements for the development of a handheld prototype are briefly outlined.

Key words: *Agro-food chain, Food fraud, Quality control, Fast detection, Laser spectroscopy, Photoacoustic technique*

Riassunto

Il Laboratorio Diagnostiche e Metrologia (FSN-TECFIS-DIM) dell'Agenzia Nazionale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile (ENEA) ha applicato da anni la spettroscopia fotoacustica laser alla rivelazione di frodi alimentari. Dopo una rassegna sulle frodi alimentari nel mercato globale, lo strumento attuale è stato esaminato e caratterizzato. Quindi, è descritta la misura di alcuni campioni di cibo, nel quadro del progetto Metrofood. Alla fine, i requisiti tecnici per lo sviluppo di un prototipo portatile sono brevemente delineati.

Parole chiave: Filiera agroalimentare, Frodi alimentari, Controllo di qualità, Rivelazione veloce, Spettroscopia laser, Tecnica fotoacustica

INDEX

1. Introduction

1.1 Research goal

As it will be described in this introduction, food fraud is an emerging problem of global amplitude. In this framework, the Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) [1] of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) applies laser spectroscopy, in general, and photoacoustic technique, in particular, to the wide field of quality control of agro-food chain [2], focusing mainly on fast detection of food fraud [3] by laser photoacoustic spectroscopy (LPAS) [4].

The research presented in this report is intended to be the basis for the manufacturing of a handheld and sensitive prototype for food fraud fast detection. This device should interface with a database of food types which are most targeted in frauds, in order to compare the sample under test with the spectroscopic fingerprints of standard materials.

1.2 What is food fraud?

Food fraud is the act of purposely altering, misrepresenting, mislabeling, substituting or tampering any food product at any point along the farm–to–table food supply–chain. Fraud can occur in the raw material, in an ingredient, in the final product or in the food's packaging.

"Food fraud" (which has a larger meaning), "food counterfeiting" and "intentional adulteration" are alternative terms: they are intentional substitution, dilution or addition to a raw material or food product, or misrepresentation of the material or product for financial gain (by increasing its apparent value or reducing its cost of production) or to cause harm to others (by malicious contamination).

According to Gary C. Smith: "Food fraud is the deception of consumers through intentional adulteration of food: (a) by substituting one product for another; (b) using unapproved enhancements or additives; (c) misrepresenting something (e.g., country of origin); (d) misbranding or counterfeiting; (e) stolen food shipments and/or (f) intentional contamination with a variety of chemicals, biological agents or other substances harmful to private – or public – health" [5].

David Edwards affirms that: "Due to both its global nature and the fact that most food today no longer follows a straight line from source to fork, it is more like a supply 'network', and tracing an ingredient back to its source has become challenging due to this increasing network of handlers, suppliers and middlemen globally" [6].

1.3 Types of food fraud

John Spink and Douglas Moyer, defines food fraud as: "A collective term used to encompass the deliberate and intentional substitution, addition, tampering, or misrepresentation of food, food ingredients or food packaging; or false or misleading statements made about a product, for economic gain" [7] and identify seven distinct kinds of food fraud (Figure 1 [6] and Table 1 [7]).

Figure 1. What is food fraud?

Food Fraud Incident Type	Definition	Example
Adulteration	A component of the finished product is fraudulent	Melamine added to milk
Tampering	Legitimate product and packaging are used in a fraudulent way	Changed expiry information, product up-labeling, etc.
Over-run	Legitimate product is made in excess of production agreements	Under-reporting of production
Theft	Legitimate product is stolen and passed off as legitimately procured	Stolen products are co-mingled with legitimate products.
Diversion	The sale or distribution of legitimate products outside of intended markets	Relief food redirected to markets where aid is not required
Simulation	Illegitimated product is designed to look like but not exactly copy the legitimate product	"Knock-offs" of popular foods not produced with same food safety assurances
Counterfeiting	Intellectual property rights infringement, which could include all aspects of the fraudulent product and packaging being fully replicated	Copies of popular foods not produced with same food safety assurances

Table 1. Food fraud incident types.

Patrick Pimentel states that: "Food fraud includes economically motivated adulteration, called EMA by some experts. The U.S. Food and Drug Administration (FDA) defines EMA as the 'fraudulent, intentional

substitution or addition of a substance in a product for the purpose of increasing the apparent value of the product or reducing the cost of its production'. […] A 2011 U.S. Government Accountability Office (GAO) report entitled *Food and Drug Administration (FDA): Better Coordination Could Enhance Efforts to Address Economic Adulteration and Protect the Public Health* identified supply chain complexity as a challenge in the detection and prevention of economic adulteration. The report highlights two situations posing significant public health risks: the use of melamine, an industrial chemical, and heparin, a blood thinner, where ingredients were evidently added to products to increase the apparent value or reduce their production costs (e.g., economic adulteration)" [6].

The 15 most problematic ingredients for EMA (based on about 550 scholarly articles from 1980 to 2010) are shown in Figure 2 [8].
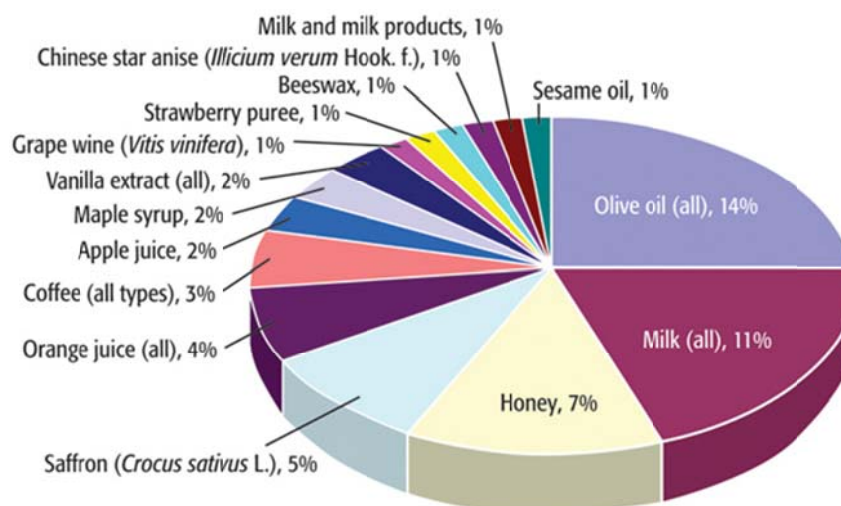

Figure 2. Fifteen most problematic ingredients for economically motivated adulteration.

Jeffrey C. Moore lists the following kinds of EMA:

- milk diluted with water,
- milk extended with melamine,
- wheat extended with urea,
- turmeric extended with lead chromate,
- olive oil diluted with hazelnut oil,

and says that: "Food safety presumes knowledge of composition and, when the next adulterant is unknown, from our perspective, food safety collapses to a singularity, and that is the fraudster. The ethics and the knowledge of the fraudster define the safety of a food product throughout the whole supply chain. Melamine provides a good example. With an LD_{50} of 3.16 g/kg body weight (rat), it isn't particularly toxic. On the

other hand, it caused the deaths of infants and pets. In the case of the pet-food scandal, some fraudsters used inexpensive, scrap-grade melamine that was contaminated with cyanuric acid, which hydrogen-bonds with melamine and creates a toxic co-crystalline complex that precipitates in renal tubules (Dobson et al., 2008). In the case of infant formula, a similar situation prevailed. The melamine complexed with uric acid to form, again, a toxic co-crystalline complex, causing renal failure in infants" [8].

In fact, counterfeiting of rice, adulteration of sugar and contamination of seafood are also critical issues.

Lakshminarayana R. Vemireddy and coworkers state that: "Rice, being a staple food crop for over one third of the world's population, has become a potential target for many unscrupulous traders for mixing with low grade, low cost grains/products and low nutritious adulterants to fetch profits with least efforts. […] As it is difficult to differentiate seeds of various rice varieties based on visual observation accurately, the harvested seeds and subsequent processed products are highly prone to adulteration with look-alike and low quality seeds by the dishonest traders. To protect the interests of importing countries and consumers, several methods have been employed over the last few decades for unambiguous discrimination of cultivars, accurate quantification of the adulterants, and for determination of cultivated geographical area. […] Adulteration is rife in almost all agricultural food products where distinguishing the adulterant with look-alike food products is difficult with naked eye/visual observation. Many of the food products targeted for adulteration are of high commercial value products and/or produced in high tonnage around the world. […] Hence, high quality rices are being adulterated with low quality and low price rices by the traders. For instance, the good quality Basmati rices are being blended with look alike low cost non-Basmati rices" [9].

Sugar is usually adulterated with sodium carbonate (washing soda) or some other insoluble items such as chalk powder. HATTON makes the following points: "There is nothing peculiar about sugar which lends itself to fraud: it is simply one of many commodities and trades which are used in similar fraudulent routines. Recent developments in international markets have increased the vulnerability of the sugar trade, thus raising the profile of frauds. […] With sugar, the fraudulent transaction is almost invariably based on a consignment which does not physically exist. Although surprising at first glance, this potential arises because bureaucracies everywhere have engendered a belief in the authority of paperwork. Just as worthless paper money is accepted as having value, so pieces of paper are accepted as having value, so pieces of paper are accepted as proof that a consignment of sugar exists. […] Sugar is openly traded on all the world's major commodity exchanges and its price is exactly established. There are several long-standing international sugar traders of the highest repute. Offers to sell sugar at less than the ruling market price makes no commercial sense - unless the real motive is fraud" [10].

According to WHO: "Seafood and fish can become contaminated with pathogens such as Vibrio cholera, Salmonella, E. coli, Shigella, Listeria due to human activity or poor hygiene and sanitation during food production and processing. There have been outbreaks of foodborne illnesses and infections linked to consumption of contaminated fish and seafood. In addition, Methyl mercury is formed by bacterial action in

an aquatic environment from dumping of industrial mercury as well as natural sources of elemental mercury" [11].

Ruggero Urbani observes that: "Within the fisheries sector, the issue of heavy metals is particularly relevant to large pelagic fish, such as tuna and swordfish. These fish are at the top of the food chain and therefore tend to accumulate higher quantities of heavy metals, especially mercury, in their muscular tissues. The quantity of heavy metals in these species often exceeds the limits set by the EU. Contamination of fish by heavy metals are closely related to the biology of the specific fish species – in terms of which level of the food chain the fish live in – and in certain geographic areas, this factor is accentuated by the localized environmental pollution. In general, contamination by heavy metals is not due to deliberate adulteration or fraudulent conduct. […] The European market has also introduced stringent measures aimed at protecting the health of European consumers by regulating the quantities of chemical residues admissible in fish and fishery products. One of the most important issues is the presence of heavy metals, particularly cadmium, lead and mercury. In 2006, the European Commission Regulation 1881/2006 established the maximum levels for such contaminants in food products" [12].

The principal cause of border detention in the EU is still quantity of heavy metals (Table 2 [12]).

Another serious threat in fish is histamine. Timothy E. Corden states that: "Histamine fish poisoning is among the most common toxicities related to fish ingestion, constituting almost 40% of all seafood-related food-borne illnesses reported to the US Centers for Disease Control and Prevention (CDC). Histamine fish poisoning results from the consumption of inadequately preserved and improperly refrigerated fish. It resembles an allergic reaction but is actually caused by bacterially-generated toxins in the fish's tissues" [13].

Causes of detentions	2010	2011	2012	2013	2014	2015	Total	%
Gas Freon	0	0	1	0	0	0	1	0.36
Carbon monoxide treatment	5	8	1	0	0	0	14	5.05
Additives	4	4	12	1	4	1	26	9.4
Mercury	4	12	14	18	11	11	70	25.28
Cadmium	8	16	7	3	9	3	46	16.6
Lead	0	1	0	0	0	0	1	0.36
Industrial contaminants	2	0	2	2	3	0	9	3.25
Pesticide residues	0	5	0	0	0	0	5	1.8
Residues of veterinary medicinal products	10	18	9	8	48	7	100	36.1
Radiation	0	5	0	0	0	0	5	1.8
Total	33	69	46	32	75	22	277	

Source: *EU Rapid Alert System*

Table 2. Causes of border detention related to chemical risks in the EU from 2010-2015.

1.4 History of food fraud

Figure 3 [14] shows the timeline of major product safety incident. According to Patrick Pimentel: "As markets have grown from local to global, supply chains have become more complex, and this has opened the door to food fraud on a larger scale. Today, a growing number of leading manufacturers and retailers have endured the consequences either through sourcing and supply challenges, a drop in market share or increasing consumer distrust. Consumers, too, are demanding increased legislative protections, and food companies are responding to protect their reputations" [6].
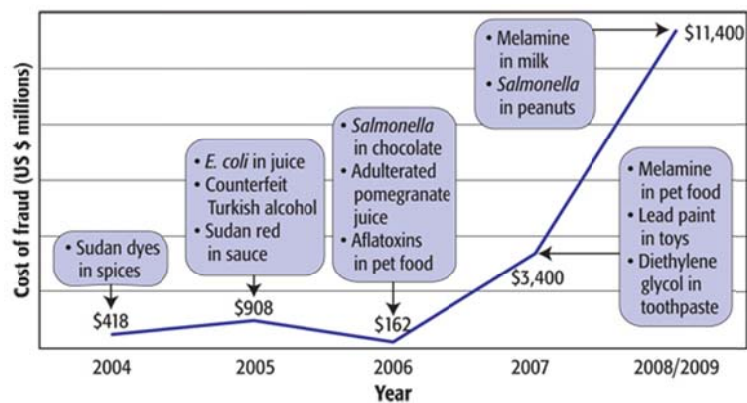
Figure 3. Timeline of major product safety incident.

1.5 Who's responsible?

A greater collaboration between all the actors of the food supply network, mainly government and industry, would certainly help to provide safe products. Patrick Pimentel states that: "Everyone has a role in addressing the threat of food fraud. Suppliers play a crucial role in deterrence and detection of economic adulteration. In addition to implementing strategies similar to manufacturers', suppliers also can consider ways to facilitate appropriate testing procedures, provide increased transparency and timely information and partner with manufacturers in their downstream efforts to reduce fraud" [6].

1.6 Potential solutions

David Edwards affirms that: "As a longer-term strategic approach can be developed by government and industry, the key focus will likely be on: 1) The establishment of an acceptable standard of product testing and analysis that sets out what, where and how often. The UK Food Standards Agency (FSA) is already starting to look into this. 2) More transparency and data sharing between national governments and agencies to create a global database of supply movements, incidents and alerts. New network analysis tools are already appearing to help alert industry and regulators in real time to potential problems. Increased industry

data sharing to the same end, and much closer collaboration between government and the industry. 3) The rapid development of technologies and software tools to facilitate vastly improved analysis that can quickly pinpoint locations and trends in transgressions. 4) The creation of better risk management tools to identify products liable to fraud" [15].

According to Patrick Pimentel, the Food Safety Modernization Act (FSMA): "focuses primarily on the following to minimize or prevent food safety hazards:

- Produce safety
- Imported food safety
- Mandated inspections on a risk-based schedule
- Third-party laboratory testing
- Farm-to-table responsibility
- Ability to require third-party certification for high-risk operations

[…] Implementing a strong food defense plan is another way for food processors, packagers and distributors to limit intentional and malicious food tampering. Food defense plans are also increasingly required for food safety certification and vendor qualification, as well as by FSMA, which requires facilities to identify and evaluate food hazards, including those introduced intentionally, and implement and document preventive controls to provide assurance that food is not adulterated" [6].

1.7 Rapid screening

Jeffrey C. Moore observes that: "Rapid screening methods are particularly important to industry, where an answer is needed within 20 seconds on whether something looks normal. Also required are rapid confirmatory methods; verification of abnormality is crucial, before removal of an ingredient from the supply chain. Methods for checking purity—e.g. for protein as mentioned above—are essential. And, of course, supporting reference materials and spectral libraries are indispensible. […] The analytical method predominantly used at USP [http://www.usp.org] to develop standards is the compendial approach, i.e. using identity and purity tests to verify the integrity, the authenticity of an ingredient. The concept is to detect EMA by looking for a decrease in the purity of an ingredient and by examining a fingerprint for an ingredient to check that it matches the known fingerprint. The advantage of this approach is that it can detect both known and unknown adulterants. For example, if melamine is present at a significant level, the specific assay for protein will reveal a decrease in purity, and the melamine will be detected in an ID test. It's a powerful approach, although its development is challenging. […] Liquid chromatography triple quadrupole tandem mass spectrometry (LC-MS/MS) and gas chromatography/mass spectrometry (GC-MS)—relatively simple methods—have been developed to test for presence of melamine. […] Figure 4 shows data from Fourier transform near-infrared (FT-NIR) spectral analysis, a rapid technique that picks up almost every organic compound and some inorganic compounds. These are data from a number of authentic skim-milk-

powder samples as well as samples that have been spiked with adulterants, melamine, cyanuric acid, urea, or combinations, between 500 ppm and 1%. A spectrometrist may be disappointed that stronger differences are not seen in these data. However, chemometrics teases out subtle differences in the spectral fingerprints; Figure 5 shows these data analyzed by principle component analysis (PCA), successfully differentiating authentic from adulterated materials down, again, to 500 ppm, much lower than we thought would be possible using this approach. We are looking at other non-targeted analytical methods (Figure 6), including Raman spectroscopy, matrix-assisted laser desorption/ionization mass spectrometry, NMR [(nuclear magnetic resonance)] and LC-high-resolution mass spectrometry" [8].
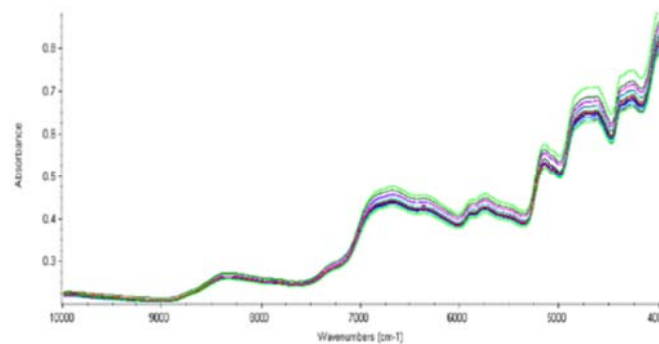
Figure 4. FT-NIR of skim-milk powder, pure and adulterated with 500 ppp to 1% melamine, cyanuric acid, and/or urea.
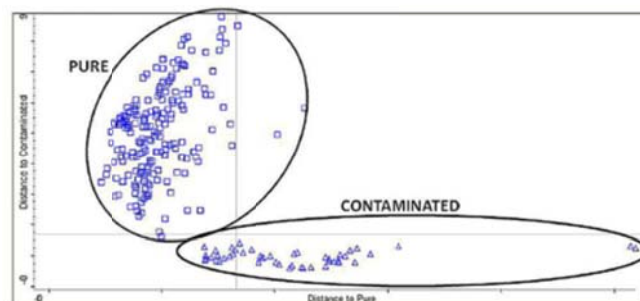

Figure 5. Principle component analysis of the data in Figure 4.

Figure 6. Skim-milk-powder project: authentication.

Adulterant	Analytical solution
Sudan dyes in spices	Chromatography
Melamine in milk powder	Chromatography
Horsemeat in beef	PCR (polymerase chain reaction)
Gelatine in chicken breast	Proteomics
Misdescription of fish species	PCR, DNA bar coding
Conventional food/organic food	HPLC (high-performance liquid chromatography), stable isotopes, etc.
Seed oils in olive oil	Chromatography
Cow's milk added to sheep's milk	Electrophoresis
Adulteration of fruit juices	Chromatography, stable isotopes, SNIF-NMR (site-specific natural isotope fractionation-NMR)
Adulteration of wine	NMR, stable isotopes

Table 3. Adulterants and analytical solutions.

Instrument	Description
Mass Spectrometers	Enable to conduct quantitative and qualitative analysis across a wide range of applications.
SWATH	SWATH Acquisition on a SCIEX TripleTOF® system has rapidly become one of the premier mass spec acquisition strategies for identification and quantitation of analytes complex samples. No other technique can do what SWATH can do. SWATH is the only data independent acquisition (DIA) technique that allows comprehensive detection and quantitation of virtually every detectable compound in a sample (MS/MS^{ALL}). This provides confidence in your quantitative results and virtually eliminates the risk of missing a critical component. SWATH Acquisition strategy can only be achieved through the power and speed of SCIEX TripleTOF® and QTOF technology
SelexION	The SCIEX SelexION device is an innovative achievement in differential ion mobility spectrometry (DMS). This DMS tool delivers highly-selective, robust and powerful ion separation that significantly enhances your quantitative and qualitative performance. Designed to be simple to install without the need to break vacuum on your MS, and compatible with UHPLC timescales, this separation device can help you address your biggest analytical challenges: • Overcome co-eluting matrix interferences and improve data quality in complex samples • Separate isobaric compounds for increased confidence in detection • Detect and quantify isobaric lipid molecular species for more accurate biological insights • Reduce background noise that may be limiting your LOQ • Save time with simplified sample preparation
Microflow LC-MS	SCIEX microflow LC-MS can transform the way you work and take your lab to a superior level of productivity. This innovative technology delivers the perfect combination of robustness, sensitivity and flexibility. Microflow LC-MS offers the best compromise between sensitivity and robustness—more sensitive than traditional analytical flow LC and more flexible and more robust than nanoflow LC — giving you the potential to optimize your biopharma or proteomics workflows, today and into the future.
NMR Spectroscopy	Nuclear magnetic resonance (NMR) spectroscopy is a method that is gaining ground in food analysis, and has been successful in characterizing products such as beer, juice and infant formulas. It has the advantages of being able to reveal multiple components of a foodstuff on a single spectrum and, with the help of automation, can deliver rapid throughput analysis. NMR spectroscopy did not just provide qualitative information. By correlating NMR data with that from gas chromatography. Screening with NMR may provide an advantage over other screening procedures for food fraud and contamination.
FT-NIR	Today well established for quality control applications in all industries including food, agriculture and chemical sector.

Table 4. Integrated solutions with their descriptions.

A list of adulterants and analytical solutions has been recently provided by Franz Ulberth (Table 3 [16]). An example of list of integrated solutions with their descriptions is given in Table 4, filled in with information provided by SCIEX [17].

2. Instruments and methods

The instrument has already been described elsewhere [3] (a block diagram is given in Figure 7 [18]). Here we report on some preliminary tests.
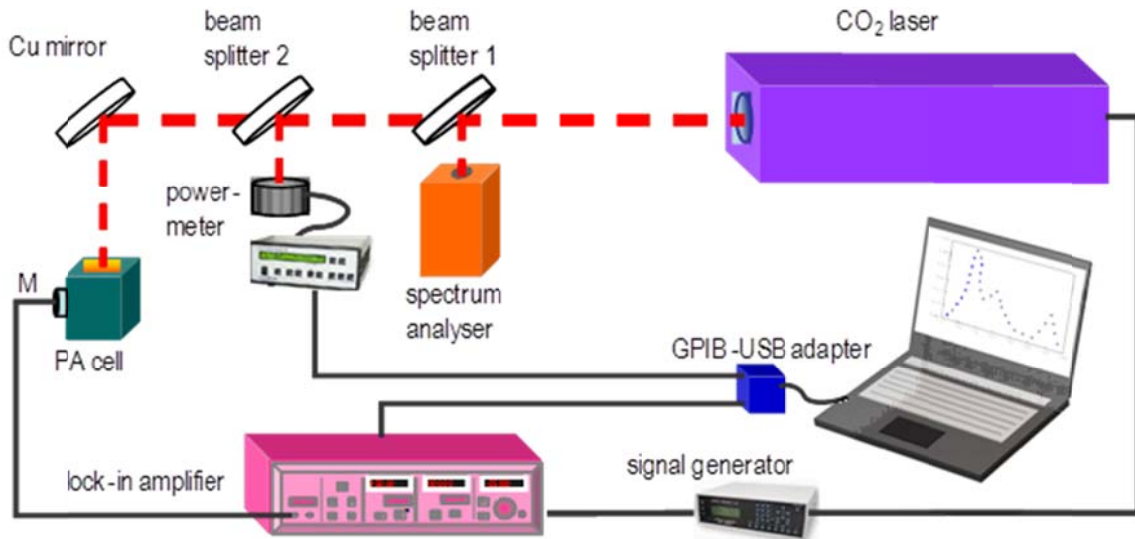

Figure 7. Block diagram of the instrument (M: microphone).

2.1 Stepper motor calibration

The relation between the stepper motor position (step) and the wavelength transmitted by the CO_2 laser (wavelength) has been checked for 61 lines. The step has to correspond to: i) a local maximum of transmitted power; ii) a good beam shape (Gaussian), and these criteria have been carefully checked.
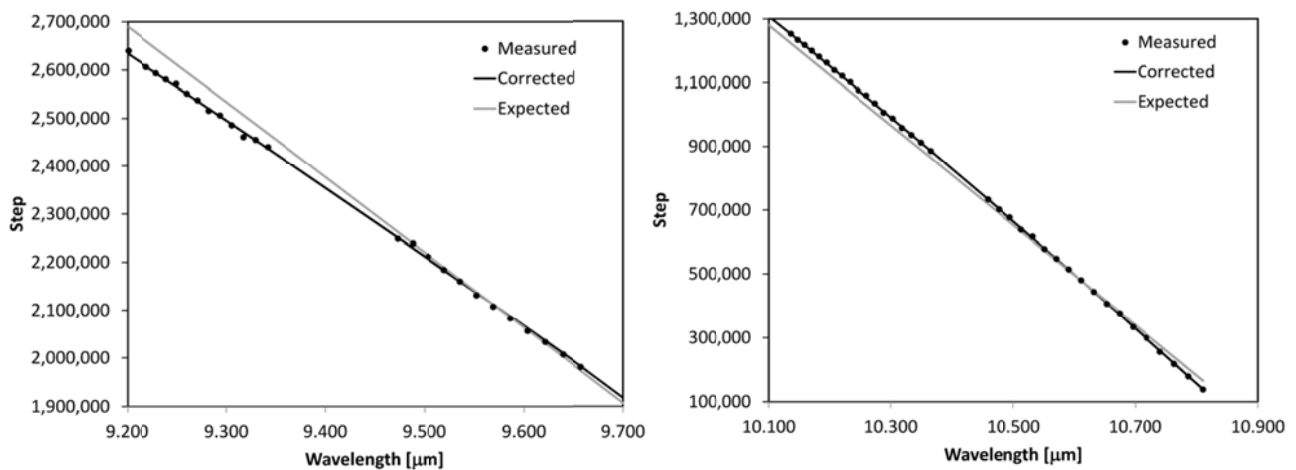
Figure 8. Relation between step and wavelength as measured and modeled by linear ("expected") and second order ("corrected") fit.

One could expect a linear relation between step and wavelength (Figure 8). In fact, the difference between measured points and linear fit is 2.3% on average. Fortunately, this deviation can be easily modeled with a parabola (Figure 9) and the difference between measured points and second order fit is 0.27%.
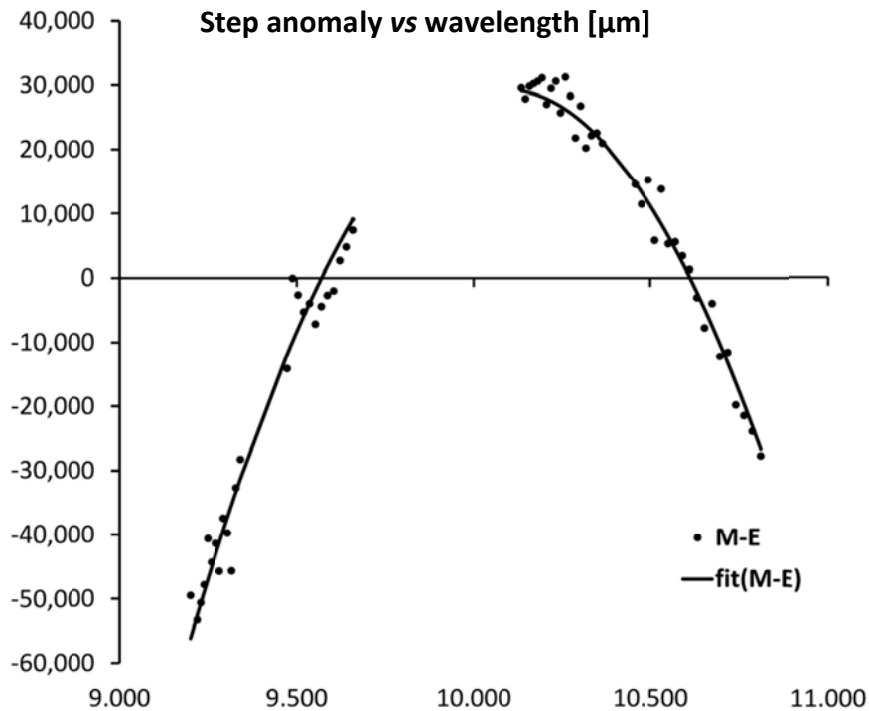

Figure 9. Difference between step measurement (M) and estimation by linear fit (E).

2.2 Cell frequency response

The cell frequency response has been determined measuring the photoacoustic signal (V/W) as ratio between the microphone signal (V) and the laser power (W, measured by the power meter[1]) The empty cell and a sample of charcoal activated granules (Carlo Erba, Batch Number Q1D099281F) have been irradiated at the 10p26 CO_2 laser line (10.653 μm) (Figure 10). A 10× amplifier has been interposed between microphone and analog to digital converter (ADC). Each point represents the average of 10 measurements. Each measurement lasts 1 s. Similar results have been obtained with rice flour (Metrofood, see section 3)

As expected, the response of the empty cell is almost flat and zero, while a clear resonance at about 1700 Hz can be observed with the sample. Although the laser power is not maximum at 1700 Hz (Figure 11 left), the peak of microphone signal (Figure 11 right) is not significantly different from that of photoacoustic signal. The maximum is 1690 Hz and the full width at half maximum (FWHM) is 1000 Hz (Figure 11 right).

---

[1] The laser power measured by the power meter comes from the reflection of a beam splitter and is about 3% of the actual power at the laser output.
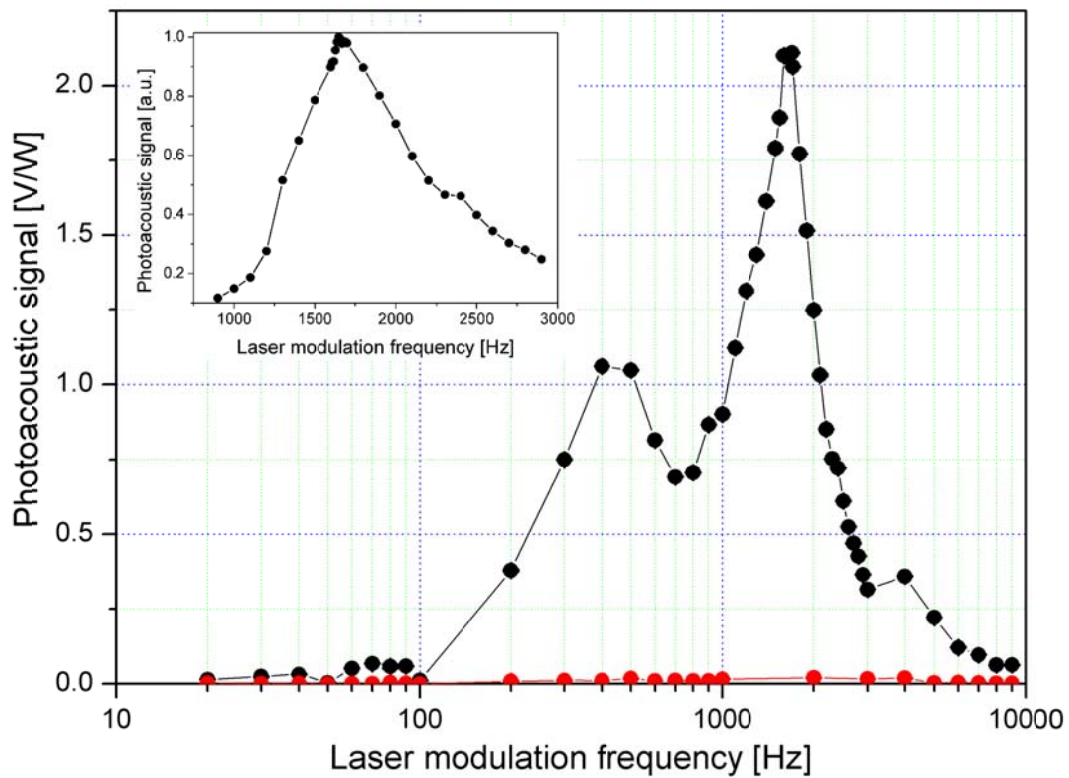
Figure 10. Photoacoustic signal for the empty cell (red points) and a sample of charcoal activated granules (black points) vs the laser modulation frequency. A zoom of the peak is visible in the inset.
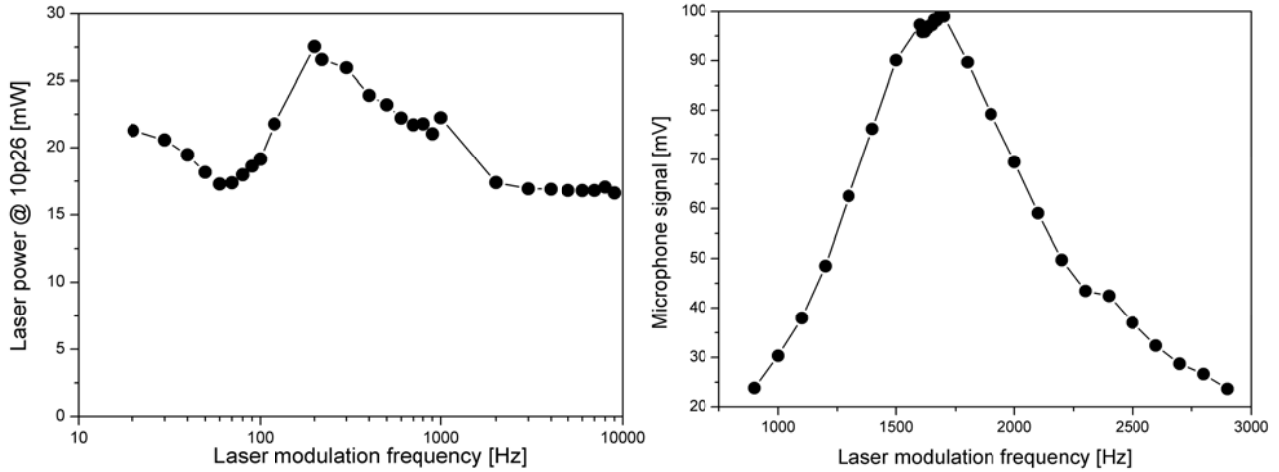

Figure 11. Laser power (left) and microphone signal (right) vs laser modulation frequency.

2.3 Signal linearity test

The linearity between the microphone signal and the laser power (measured by the power meter) has been tested at the 10p26 CO_2 laser line irradiating a sample of rice flour (Metrofood, see section 3) and charcoal activated granules (Carlo Erba, Batch Number Q1D099281F) (Figure 12). Each point represents the average of 10 measurements. Each measurement lasts 1 s.
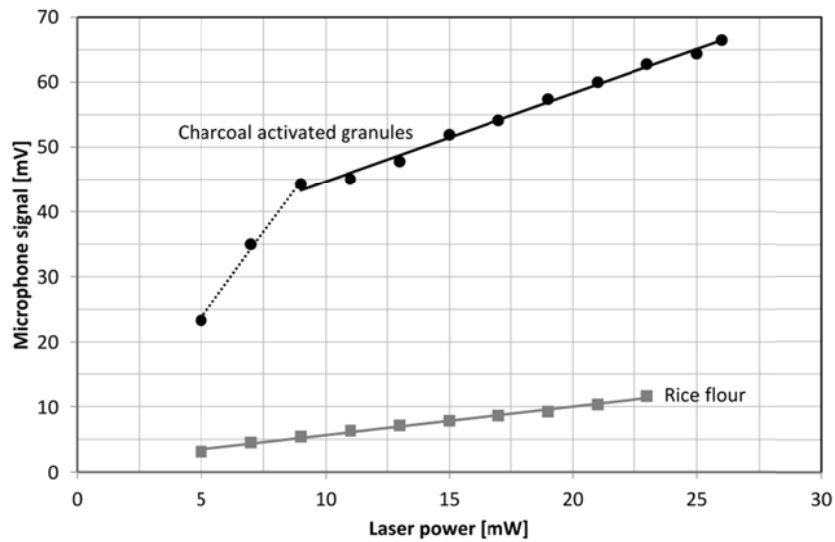
Figure12. Photoacoustic signal vs laser power for rice flour and charcoal activated granules.

In case of low signal (due to low absorption and/or low laser power) the microphone signal is proportional to the laser power, then – above 45 mV – a knee is observed but the trend remains linear (of course with non-zero intercept and different slope). This phenomenon has been ascribed to microphone saturation.

In all practical cases the microphone signal is lower than 45 mV or can be reduced to that level by lowering the laser power. A 10× amplifier has been interposed between microphone and ADC: without amplifier, the knee will occur at about 4.5 mV.

3. Results and discussion

In the framework of the EU project Metrofood [19], some samples were analyzed: oyster tissue powder, rice flour and rice grains. The measurement procedure was as follows:

- Sample preparation of rice:
    - no preparation, grains were directly measured, or
    - grains were grinded some minutes and pressed (12-15 tons) in a pellet of 2 mm thickness and 20 mm diameter (about 1 g).
- Sample preparation of oyster tissue powder and rice flour:
    - powder or flour was pressed (12-15 tons) in a pellet of 2 mm thickness and 20 mm diameter (about 1 g).
- The pellet is put on the sample holder.
- The laser power (measured by the power meter) for the 10p26 CO_2 laser line is set at 6 mW and the measurements at the 10 μm bands are carried out, the laser power is set to maximum (of the order of 10 mW) and the measurements at the 9 μm bands are carried out.
- The LPAS spectrum of each sample has been acquired at 56 CO_2 laser lines (1 s per each acquisition).

Care has been taken to:

1. Center the laser footprint in the sample holder.
2. Fill the sample holder.
3. Check that the grain size of the flour and powder was smaller than the laser footprint.
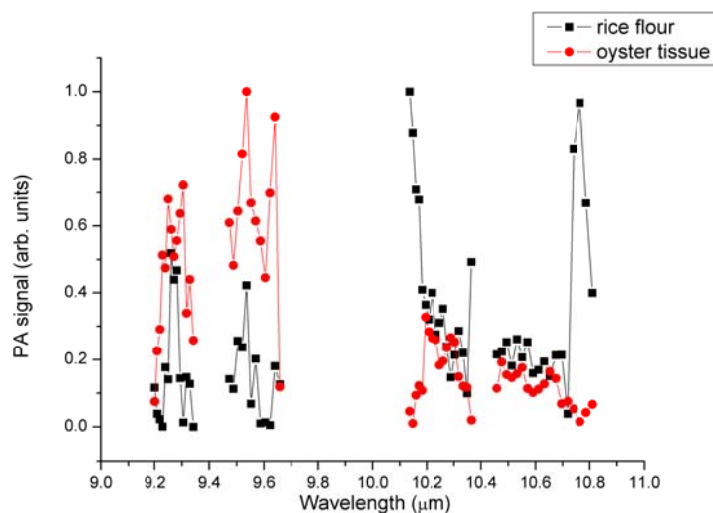

Figure 13. Normalized spectrum of rice flour and oyster tissue provided by Metrofood.

The task assigned to our lab was to discriminate between samples. In case of oyster tissue and rice, this can be easily accomplished looking directly at the LPAS spectrum of the samples (Figure 13): the photoacoustic signal is clearly different at about 10.15 and 10.8 μm.

The damage threshold of oyster tissue is lower, so it has been decided to set the laser power (measured by the power meter) for the 10p26 CO_2 laser line at 5 mW and to carry out all the measurements, both at the 10 and 9 μm bands. Moreover, the irradiation at the sample has been further reduced by the absorption of two ZnSe windows (if one tries to set the power below 5 mW the laser becomes unstable).

The discrimination of different types of rice is difficult looking at the LPAS spectrum but, fortunately, principal component analysis (PCA) [20] can easily perform this task for flours (Figure 14) and grains (Figure 15).
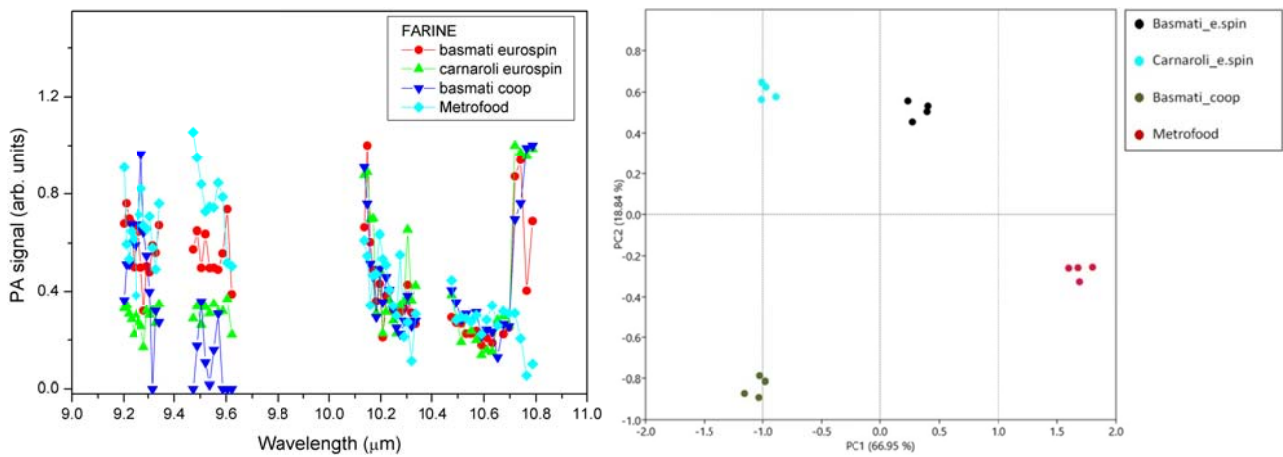

Figure 14. Normalized spectrum (left) and PCA (right) of different rice flours.
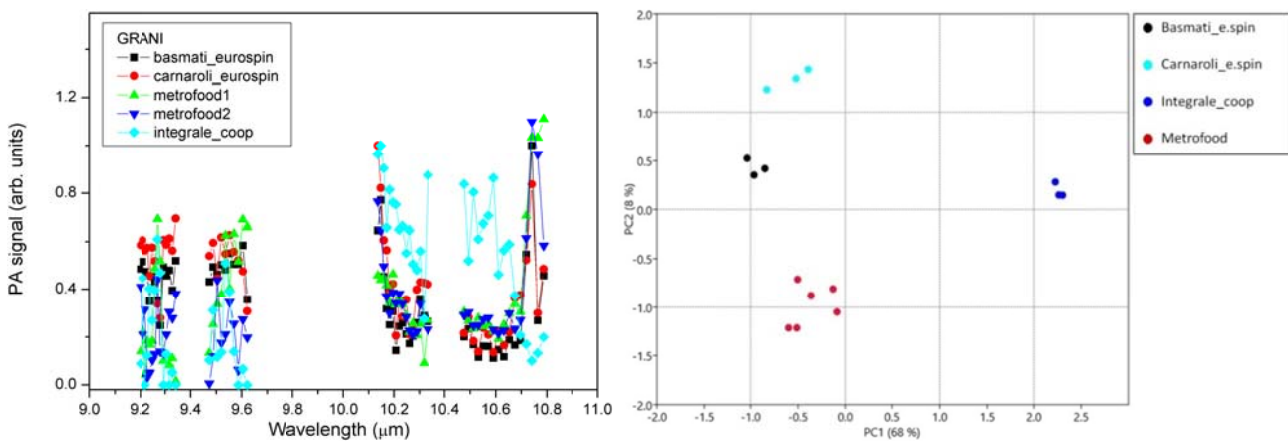

Figure15. Normalized spectrum (left) and PCA (right) of different rice grains.

The following samples of rice flours have been examined:

1. Basmati sold by Eurospin,
2. Basmati sold by Coop,
3. Carnaroli sold by Eurospin,
4. Metrofood.

Each sample has been measured four times (1 s per each measurement). In the spectra, each point has been obtained averaging the four measurements.

The following types of rice grains have been examined:

1. Basmati sold by Eurospin,
2. Carnaroli sold by Eurospin,
3. Whole grain sold by Coop,
4. Metrofood (two samples).

Each sample has been measured three times (1 s per each measurement). In the spectra, each point has been obtained averaging the three measurements.

4. Conclusions

At first, the LPAS instrument has been carefully examined: stepper motor, frequency response and signal linearity have been characterized. The conditions for optimum operation have been determined.

Then, some food samples have been measured and the LPAS instrument demonstrated its discrimination capability in the case of different types of rice, both as flour or grains.

As far as the improvement and the miniaturization of the actual system are concerned, the following technical notes can be drafted:

1. Replace the CO_2 laser with a smaller size and more stable source, such as a quantum cascade laser (QCL) with small cooling system (e.g. electronic cooling).
2. Reduce the size of the platform holding the samples, e.g. including only two sample holders instead of ten: this will allow the elimination large platform, electronic circuit, motor and fan.
3. Miniaturize all the electronic circuits.
4. Add a digital switch for the microphone.
5. Avoid cooling fans or replace them with electronic cooling (saving space and minimizing ripple noise).
6. Arrange all the connections (with short wires) on one board.
7. Reduce the distances between the subsystems of the instrument.
8. Replace laser detector and beam steering mirrors/windows with smaller ones.

Acknowledgements

References

[1]   A. Palucci (ed.), 2016 Activity Report. Diagnostic and Metrology Laboratory, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Frascati (2017)

[2]   G. Giubileo, A. Lai, D. Piccinelli, A. Puiu, Laser diagnostic technology for early detection of pathogen infestation in orange fruits, Nuclear Instruments and Methods in Physics Research A, 623 (2010) 778-781

[3]   G. Giubileo, I. Calderari, A. Puiu, High resolution spectroscopy of sweeteners, in P. A. Ribeiro, M. Raposo (eds.), Proceedings of the 3rd International Conference on Photonics, Optics and Laser Technology, Scitepress (2015) 91-95

[4]   C. Haisch, Photoacoustic spectroscopy for analytical measurements, Measurement Science and Technology 23 (2012) 012001 (17 pp.)

[5]   G. C. Smith, What is food fraud?, http://fsns.com/news/what-is-food-fraud

[6]   P. Pimentel, Trends and solutions in combating global food fraud, https://www.foodsafetymagazine.com/magazine-archive1/februarymarch-2014/

[7]   J. Spink, Douglas C. Moyer, Backgrounder: defining the public health threat of food fraud, http://foodfraud.msu.edu/wp-content/uploads/2014/07/food-fraud-ffg-backgrounder-v11-Final.pdf

[8]   J. C. Moore, Food fraud: public health threats and the need for new analytical detection approaches, http://nabc.cals.cornell.edu/Publications/Reports/nabc_23/23_5_3_Moore.pdf

[9]   L. R. Vemireddy, V. V. Satyavathi, E. A. Siddiq, J. Nagaraju, Review of methods for the detection and quantification of adulteration of rice: Basmati as a case study, Journal of Food Science and Technology, 52 (2015) 3187-3202

[10]   HATTON, Sugar fraud protection, http://www.hattongrp.com/sugar-fraud-protection

[11]   WHO, Food safety: what you should know, http://www.searo.who.int/entity/world_health_day/2015/whd-what-you-should-know/en/

[12]   R. Urbani, EU protection of public health: metal contamination detention issues at borders, http://www.fao.org/in-action/globefish/fishery-information/resource-detail/en/c/456789/

[13]   T. E. Corden, Histamine toxicity from fish, https://emedicine.medscape.com/article/1009464-overview

[14]   GMA, ATKEARNEY, Consumer product fraud: deterrence and detection,
        http://www.gmaonline.org/downloads/research-and-reports/consumerproductfraud.pdf

[15]   NSF International, The growing global epidemic of food fraud,
        https://www.newfoodmagazine.com/wp-content/uploads/NSF-Whitepaper.pdf

[16]   F. Ulberth, Detection of food fraud: the analytical challenge,
        https://ec.europa.eu/jrc/sites/jrcsh/files/esof-2014-food-fraud-ulberth.pdf

[17]   https://sciex.com

[18]   G. Giubileo, A. Puiu, I. Calderari, Spettroscopia ad alta risoluzione di zuccheri, Technical Reports of
        the Italian National Agency for New Technologies, Energy and Sustainable Economic Development
        (ISSN 0393-3016), Rome, Italy, RT/2015/4/ENEA (2015)

[19]   http://www.metrofood.eu

[20]   K. V. Mardia, J. T. Kent, J. M. Bibby, Multivariate Analysis, Academic Press, London (1979)