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Status quo and future research challenges on organic food quality determination with focus on laboratory methods

Johannes Kahl,^{a*} Marija Bodroza-Solarov,^b Nicolaas Busscher,^a Jana Hajslova,^c Wolfgang Kneifel,^d Maria Olga Kokornaczyk,^e Saskia van Ruth,^f Vera Schulzova^c and Peter Stolz^g

Abstract

Organic food quality determination needs multi-dimensional evaluation tools. The main focus is on the authentication as an analytical verification of the certification process. New fingerprinting approaches such as ultra-performance liquid chromatography–mass spectrometry, gas chromatography–mass spectrometry, direct analysis in real time–high-resolution mass spectrometry as well as crystallization with and without the presence of additives seem to be promising methods in terms of time of analysis and detecting organic system-related parameters. For further methodological development, a system approach is recommended, which also takes into account food structure aspects. Furthermore, the authentication of processed organic samples needs more consciousness, hence most of organic food is complex and processed.

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Keywords: organic; food; quality; methods

INTRODUCTION

Organic food quality and its production involve a consumer-oriented approach having ethically relevant recognition. This occurs through underlying paradigms,¹ principles² as well as a regulatory framework.³ The quality characteristics of food are expected by and/or acceptable to consumers following a total food quality model.⁴ Melzer *et al.*⁵ structured these expected properties in direct visible properties (e.g. shape, colour, size), easily recognizable properties (e.g. flavour, taste, consistency) and properties, which are less easily detected (such as nutritional quality or sustainability). Regarding organic food, the term 'vitality' describing a food property seems to be important for some consumers.⁶ Consumers generally expect a difference in organic food quality compared to food from non-organic production.^{6,7} The differences are mainly identified in pesticide use (and residues), type of fertilization, range of food additives, genetic manipulation and selection of technologies. Consumers expect natural, healthy organic food with less environmental impact and enhanced animal welfare during production.^{6,7} Following the total food quality model, as it is described for some food in general,^{4,8} the quality of the food can be described with a multi-dimensional approach⁸ to different food properties, e.g. as given by Melzer *et al.*⁵ Kahl *et al.*,^{9,10} who described the organic food quality model as being based on principles coming from various sources (e.g. Codex 2010, EC 834/2007, national and private standards) and a multi-dimensional approach for evaluation, using aspects, criteria, indicators and parameters.⁹ Based on this, methods for the analysis of criteria-linked parameters can be selected or need to be developed. McGorin¹¹ described these kinds of parameters as tools for different actions in food science and

production. These fields of application of methods are new product development, quality control, regulatory enforcement and problem-solving. Cifuentes¹² gave an overview on different approaches and future developments in food analysis using laboratory methods mainly concentrated on the detection and quantitation of food constituents, where methods, parameters and targets of analyses are structured and evaluated according to the different actions.¹¹ The FAO¹³ summarizes methodological approaches measuring food energy. Moreover, approaches in food authentication (including the method of farming) with a focus on traceability are described.¹⁴

* Correspondence to: Johannes Kahl, Department of Organic Agricultural Sciences, University of Kassel, Nordbahnhofstr. 1a, D-37213 Witzenhausen, Germany. E-mail: kahl@uni-kassel.de

a Department of Organic Agricultural Sciences, University of Kassel, Witzenhausen, Germany

b Institute of Food Technology, University of Novi Sad, Novi Sad, Serbia

c Department of Food Analysis and Nutrition, Institute of Chemical Technology, Prague, Czech Republic

d Department of Food Science and Technology, University of Natural Resources and Life Science, Vienna, Austria

e Department of Agricultural Sciences, University of Bologna, Bologna, Italy

f Wageningen University (WUR), Wageningen, The Netherlands

g KWALIS Quality Research GmbH, Dipperz, Germany

However, one of the major questions is whether and to what extent organic food is different from food from non-organic production and what parameters can be used to determine any difference. Unfortunately, several recently published reviews on this issue do not give a clear picture. Whereas some antioxidants (such as polyphenols) show the statistical probability to be higher in fruits and vegetables from organic produce¹⁵ than in conventionally produced ones, major food constituents seem not to display different levels.^{16,17} For example, milk and dairy products may show some higher content of selected unsaturated fatty acids,¹⁸ probably depending on feeding strategies, but grain samples originating from different agricultural practices cannot be distinguished according to parameters such as amino acids or selected antioxidants.^{19–21} This would mean that other influencing factors may play some role if a proper distinction is envisaged. Other reports give some indication of differences, such as those based on protein composition,²² variables of crystallization²³ and carotenoids²⁴ or on sensory attributes.²⁵

In general, targeted and non-targeted methods of analysis are applied to organic food authentication but still need further research investigations.²⁶ A wide range of techniques and methods exist to determine food quality regarding different targets: single compounds or even compound classes such as nutrients like proteins, sugars, vitamins, health-promoting compounds such as polyphenols, or, on the other hand, toxins (e.g. mycotoxins), residues and, finally, criteria like energy, rheological properties (e.g. texture and structure) as well as sensory properties. For example, descriptions and protocols of these methods for food analysis can be found in CCMAS documents²⁷ or in various scientific textbooks and journals such as *Trends in Food Science*, *Trends in Analytic Chemistry*, *Food Analytical Methods*, *Food Quality and Preferences*, and are further discussed in *status quo* reports.²⁶ Until now, there has been no satisfactory review of methods applied to organic food quality determination. Therefore, it is the aim of this paper to give a status quo report on technologies and analysis methods used to find answers to the various questions related to the field of organic food. Most of the reported findings were presented within the Second International Conference on Organic Food Quality and Health Research in Warsaw, June 2013. Based on the discussion during this conference, gaps and future research challenges were identified.

ORGANIC FOOD QUALITY DETERMINATION

The model of organic food quality given by Kahl *et al.*⁹ identifies several criteria describing organic food. The product-related criteria will be followed in this article, whereas the process-related criteria are discussed elsewhere.²⁸ There are criteria already linked to indicators and parameters such as nutrition, health and enjoyment (sensory attributes), although new parameters can be added. Other criteria such as organic integrity, vital qualities and true nature are not linked to parameters and therefore techniques or methods for determination are scarce.²⁹ Regarding quality control and regulatory enforcement, methods for organic food authentication as well as for detection of residues with a focus on metabolites are needed.²⁶ New product development, aiming at organic processing, also requires food quality determination in relation to the organic food quality model, with a focus on parameter/method development.^{9,29}

In the last decade, public interest in the production technologies of foods has increased. This aspect has an impact on the sensory properties of foods, their nutritional value and safety. This development, in turn, has boosted organic food production.

Due to higher production costs, organic produce tends to retail at a higher price than their non-organic counterparts. However, as a consequence of the premium price, organic produce is susceptible to fraud. Analytical verification of organic food quality parameters based on intrinsic markers would be useful in complementing and underpinning a certification process. However, such an aim requires more than a simple analytical test. Traditional analytical strategies for guaranteeing the quality and uncovering any adulteration are usually based on the determination of the levels of selected marker compounds and a subsequent comparison of the value(s) obtained with those established for equivalent conventional material. The authentication of organic produce is a complex approach and very much depends on the product examined. Therefore, it is rather unlikely that a single marker allows the discrimination between organic and conventional produce. More and more fingerprinting approaches have been developed, which take into account a range of intrinsic (naturally present) components, in combination with advanced chemometrics. The various techniques have been illustrated with exemplary studies and have been discussed in view of their potential and limitations by Capuano *et al.*²⁶

Fingerprinting strategies are a more comprehensive method for the characterization of the metabolome, a set of low-molecular-weight (<1500 Da) primary and secondary metabolites occurring in food commodities. In general terms, it is assumed that not only the genotype of particular living organisms but also the external factors such as the method of farming may influence characteristic metabolome compositions. High-resolution mass spectrometry coupled with ultra-performance liquid chromatography (UPLC) and/or gas chromatography (GC) represent challenging analytical tool options. To avoid adverse effects caused by some matrix components, minimal or no sample preparation is required prior to instrumental measurement. These requirements are met, for instance, by the solid-phase micro-extraction (SPME) sampling technique coupled to GC–MS: a volatile metabolite fingerprint is collected in a sample headspace. Similarly, ambient mass spectrometry (AMS) offers a relevant solution in metabolomics studies. In AMS a unique ionization source, direct analysis in real time (DART), coupled with high-resolution mass spectrometer (HR-MS), is employed for fast metabolomic fingerprinting/profiling. Several case studies have demonstrated the potential of these novel approaches in examining the origins of food.³⁰ It should be noted that instead of target analysis of individual ‘quality markers’, metabolomic research is preferably based on non-target analysis; the identification of all compounds occurring in sample metabolome is not necessarily needed in the first phase; the entire data set consisting of instrumental sample ‘signals’ is classified by advanced chemometric techniques.

Kahl *et al.*³¹ discussed validation strategies for several new approaches applied to organic food quality determination. Most of these new methods, including fluorescence excitation spectroscopy (FES),³² biocrystallization^{33,34} and Steigbild³⁵ could be documented and standardized for several food classes, but still lack a theoretical background. Methodological quality parameters such as repeatability or robustness were tested, but reproducibility tests cannot be performed because reference material is still missing.³¹

In contrast to well-known near-infrared (NIR) methods, the excitation and emission of the FES method use the visible range of the optical spectrum and the delay between excitation and emission (‘delayed luminescence’).³² Optical excitation is carried out for a defined time and at constant illumination intensity made

by a 150 W (24 V) tungsten halogen bulb. Spectral sections are filtered out by coloured standard glass filters. The total light emitted by the sample is subsequently measured using photomultipliers (EMI 9202 and PerkinElmer CP1962) after the end of excitation. The measurements have been applied to wheat and carrot authentication. Relevant parameters considered were the different luminescence after excitation with yellow or white light and the yellow/blue ratio.

NEW APPROACHES IN FOOD QUALITY ANALYSIS APPLIED TO ORGANIC SAMPLES

Several new techniques, methods and principles were presented during the conference. It seems that these approaches may be applied to food quality analysis in general, and are not limited to products of organic origin. However, most of them need further effort put into method development, standardization and theoretical underpinning.

During recent years, metabolomics, which is centred around the detection of the broadest possible range of small molecules in complex biological matrices using a single or small number of analyses, has also emerged as a field of interest in food analysis.³⁶ Several approaches relating to different aims can be employed in a metabolome study: (i) *metabolite target analysis* (search for a specific metabolite in a metabolic pathway); (ii) *metabolite profiling* (study of a group of related compounds or metabolites in specific metabolic pathways); (iii) *metabolomics* (analysis of all metabolites present in the sample – a comprehensive ‘snapshot’ of metabolism at a particular point in time); and (iv) *metabolic fingerprinting* (rapid, global analysis aimed at identification of sufficient metabolites enabling one to classify unknown samples into identifiable groups – identification of patterns.³⁷ It should be noted that metabolome analysis is a rather difficult task (metabolites unavoidably differ widely in structure, functional groups, physicochemical properties and concentrations) that requires not only sophisticated instrumental equipment enabling various applications but also highly qualified personnel designing experimental conditions and data evaluation. Chromatography coupled to MS is probably among the most common instrumental methods.³⁸ In addition to procedures in which separation of sample components is included, a novel MS-based approach allowing the omission of chromatographic separation of sample components has also been introduced. Among ambient ionization techniques DART HR-MS represents the most challenging option since minimum sample preparation is required; moreover, standardization of ‘fingerprints’ (mass spectra of respective samples) and thus building of sample databases is more feasible. HR-MS also facilitates the identification of many compounds occurring in samples. DART’s relative insensitivity to contamination and the lack of carry-over between samples make it possible to analyse many materials. In this way, the workload is reduced while analysis speed is significantly increased.³⁹

A new approach to quality analysis based on the evaporation of droplets^{40,41} has been successfully tested for the quality analysis of wheat seeds.⁴² The experimental design applied consists of the evaporation of sessile droplets of a solution prepared from the sample in question placed on microscope slides; taking photographs of the droplet residues under an optical microscope; detailed description of the structures formed during solvent evaporation; and, finally, computer-based image analysis.⁴² The findings archived up to now indicate that the evaporation of sessile droplets might constitute an interesting tool for quality

analysis of foods and agricultural products. Moreover, this simple approach might contribute to a better understanding of the underlying phenomenon involved in evaporation-induced pattern formation.^{43,44}

This kind of testing of food samples by crystallization is more or less comparable with the biocrystallization method.^{45–47} The method has been applied to milk,⁴⁷ raw and processed carrots^{34,48} and wheat samples,²⁴ and seems to link a systemic approach to food quality. It uses a complex system as an indicator for systemic properties of food samples in an aqueous solution. The results obtained are patterns that then can be evaluated by different methods. The concept behind the pattern formation is based on structure formation related to physics, chemistry and biology. Structure formation can be explained by different concepts: entropy export, dissipative structure and, with some limitations, self-organization. A dissipative system creates an ordered structure while emitting heat. The precondition for a dissipative structure is an entropy exporting system in self-organization processes. The applied crystallization is not an ordinary bulk crystallization but a highly dynamic process called dendritic growth. It starts with a chaotic, self-amplifying process which is limited by heat and CuCl_2 transport, and builds a tree-like structure (the pattern). Crystallization is a dissipative process. The overall design is entropy exporting due to the evaporation of water in the CuCl_2 solution. An additive (in this case a complex food sample in the form of a juice or an extract) modulates the branching and growth behaviour of the dendritic process.

MAIN DISCOVERIES IN LABORATORY METHODS APPLIED TO ORGANIC FOOD QUALITY DETERMINATION

The different methods can be clustered into three different approaches: (i) a wide range of non-target chemical and physical fingerprinting methods used for organic food authentication;²⁶ the newly described fluorescence excitation spectroscopy seems to be part of this group of methods; (ii) analytical techniques used for the identification of biomarkers (profiling of compounds and compound classes), also allowing one to examine factors influenced by processing and applied to the entire organic food chain;²⁶ (iii) a new approach – testing the effect of the sample on crystallization systems either in the presence of an inorganic salt or during evaporation of the watery phase. For all three different approaches, a combination of laboratory techniques and chemometric tools seems to be essential, because large amounts of data have to be analysed.

IDENTIFIED GAPS AND FUTURE RESEARCH CHALLENGES IN ORGANIC FOOD QUALITY DETERMINATION

Cifuentes¹² identified several new areas where the development of techniques and methods for food quality analysis is challenging. Among these, nano-materials, allergens and epigenomics can be named as examples. Nano-materials and allergens are currently under scientific investigation, also in the context of organic food.^{49,50} Epigenomics is considered as an interesting new tool supporting product development and quality control of organic food, as this approach may be related to terms such as organic integrity and true nature. Furthermore, matrix effects and the

structure of parts and food samples seem to pose another research challenge. Also, these properties may be considered in terms of organic food product development. Regulatory reinforcement in terms of describing properties like vital qualities also needs further development of applicable parameters.²⁹ Importantly, new approaches such as systems biology and the levels of molecules, cells and organisms, as well as the optimization of the different 'omics' approaches, are identified as future methodological requirements for the characterization of organic food (for general criteria see Cifuentes).¹² A major gap in organic food authentication is due to the fact that reliable methods are needed for tracing back processed foods; hence 80% of the organic food available on the market is processed. In this context, not only techniques for quality assessment are needed, but also further specification within regulations (e.g. the use of nano-materials, specification of processing technologies) are of importance. From a holistic viewpoint, the interpretation of the obtained results, e.g. related to the physiology of the plant or impact on the consumer, is essential. This needs some well-defined meaning which has to be substantiated by scientific evidence. Taking the systemic approach in using laboratory methods as one of the newest innovations, the crystallization approach definitely needs some further scientific underpinning and validation. One of the main problems and most urgent questions relates to the validation of chemometric tools used to perform the laboratory techniques.

Therefore standard protocols for all multivariate methods regarding the authentication of raw materials need to be developed and verified *in situ*. The limitations of various approaches have to be clearly identified and discussed regarding their application in routine analysis. This is valid for non-target as well as for target analysis methods. Target methods require a multidisciplinary approach to understand and to interpret the results in terms of sample quality, treatments or effects. One of the major future research challenges is the application of a systemic approach in developing new food quality testing methods.

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REFERENCES

- Levidow L, Birch K and Papaioannou T, Divergent paradigms of European agro-food innovation: the knowledge-based bio-economy (KBBE) as an R&D agenda. *Sci Technol Human Values* **38**:94–125 (2013).
- Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999). Codex Alimentarius: Rome, Italy, 2010; Adopted 1999, Revisions 2001, 2003, 2004 and 2007, Amendments 2008, 2009 and 2010.
- Council Regulation (EC) No 834/2007. [Online]. Available: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:189:0001:0023:EN:PDF> [3 July 2013].
- Grunert KG, Food quality and safety: consumer perception and demand. *Eur Rev Agric Econ* **32**:369–391 (2005).
- Meltzer HM, Kaernes U and Ydersbond TA, Human nutrition research: past, present and future. *Scand J Nutr* **36**:119–124 (1992).
- Torjusen H, Sangstad L, O'Doherty-Jensen K and Kjaernes U, European consumers' conceptions of organic food: a review of available research. Project Report 4-2004 for National Institute for Consumer Research, Oslo, Norway (2004). [Online]. Available: <http://orgprints.org/2490/1/haccprapport.pdf> [22 October 2013].
- Pino G, Peluso AM and Guido G, Determinants of regular and occasional consumers' intentions to buy organic food. *J Consum Aff* **46**:157–169 (2012).
- Giusti AM, Bignetti E and Cannella C, Exploring new frontiers in total food quality definition and assessment: from chemical to neurochemical properties. *Food Bioprocess Tech* **1**:130–142 (2008).
- Kahl J, Baars T, Bügel S, Busscher N, Huber M, Kusche D et al., Organic food quality: a framework for concept, definition and evaluation from the European perspective. *J Sci Food Agric* **92**:2760–2765 (2012).
- Kahl J, Załęcka A, Ploeger A, Bügel S and Huber M, Functional food and organic food are competing rather than supporting concepts in Europe. *Agriculture* **2**:316–324 (2012).
- McGorin RJ, One hundred years of progress in food analysis. *J Agric Food Chem* **57**:8076–8088 (2009).
- Cifuentes A, Food analysis: present, future, and foodomics. *Anal Chem* Article ID 801607 (2012).
- FAO, Food energy: methods of analysis and conversion factors. *FAO Food and Nutrition Paper* No. 77 (2002).
- Lees M, ed. *Food Authenticity and Traceability*. CRC, Woodhead Publishing Ltd., Cambridge (2003).
- Brandt K, Leifert C, Sanderson R and Seal CJ, Agroecosystem management and nutritional quality of plant foods: the case of organic fruits and vegetables. *Crit Rev Plant Sci* **30**:177–197 (2011).
- Dangour AD, Dodhia SK, Hayter A, Allen E, Lock K, Uauy R, Nutritional quality of organic foods: a systematic review. *Am J Clin Nutr* **90**:680–685 (2009).
- Smith-Spangler C, Braneau ML, Hunter GE, Bavinger JC, Pearson M, Eschbach PJ et al., Are organic foods safer or healthier than conventional alternatives? *Ann Intern Med* **157**:348–366 (2012).
- Palupi E, Jayanegara A, Ploeger A and Kahl J, Comparison of nutritional quality between conventional and organic dairy products: a meta-analysis. *J Sci Food Agric* **92**:2774–2781 (2012).
- Mäder P, Hahn D, Dubois D, Gunst L, Alfeldi T, Bergmann H et al., Wheat quality in organic and conventional farming: results of a 21 year field experiment. *J Sci Food Agric* **87**:1826–1835 (2007).
- Stracke BA, Eitel J, Watzl B, Mäder P and Rüfer CE, Influence of the production method on physicochemical concentrations in whole wheat (*Triticum aestivum* L.): a comparative study. *J Agric Food Chem* **57**:10116–10121 (2009).
- Zörb C, Niehaus K, Barsch A, Betsche T and Langenkämper G, Levels of compounds and metabolites in wheat ears and grains in organic and conventional agriculture. *J Agric Food Chem* **57**:9555–9562 (2009).
- Zörb C, Betsche T and Langenkämper G, Search for diagnostic proteins to prove authenticity of organic wheat grains (*Triticum aestivum* L.). *J Agric Food Chem* **57**:2932–2937 (2009).
- Szulc M, Kahl J, Busscher N, Mergardt G, Doesburg P and Ploeger A, Discrimination between organically and conventionally grown winter wheat farm pair samples using copper chloride crystallization method in combination with computerized image analysis. *Comput Electron Agric* **74**:218–222 (2010).
- Roose M, Kahl J and Ploeger A, Influence of the farming system on the xanthophyll content of soft and hard wheat. *J Agric Food Chem* **57**:182–188 (2009).
- Arncken CM, Mäder P, Mayer J and Weibel FP, Sensory, yield and quality differences between organically and conventionally grown winter wheat. *J Sci Food Agric* **92**:2819–2825 (2012).
- Capuano E, Boerrigter-Eenling R, van der Veer G and van Ruth S, Analytical authentication of organic products: an overview of markers. *J Sci Food Agric* **93**:12–28 (2013).
- CCMAS, Report of the thirty third session of the codex committee on methods of analysis and sampling, CL 2012/4-MAS, Rome (March 2012).
- Halberg N, Assessment of the environmental sustainability of organic farming: definitions, indicators and the major challenges. *Can J Plant Sci* **92**:981–996 (2012).
- Beck A, Kahl J, Liebl B, Analysis of the current state of knowledge of the processing and quality of organic food, and of consumer protection Final report BÖLN 10OE096 2012, Frankfurt. [Online]. Available: <https://www.fibl.org/fileadmin/documents/shop/1584-analysis-quva.pdf> [25 July 2013].
- Novotná H, Kmiecik O, Galazka M, Krtková V, Hurajová A, Schulzová V et al., Metabolomic fingerprinting employing DART-TOFMS for authentication of tomatoes and peppers from organic and conventional farming. *Food Addit Contam A* **29**:1335–1346 (2012).

- 31 Kahl J, Busscher N and Ploeger A, Questions on the validation of holistic methods of testing organic food quality. *Biol Agric Hort* **27**:81–94 (2010).
- 32 Strube J and Stolz P, The application of fluorescence excitation spectroscopy of whole samples for identification of the culture system of wheat and carrots – method, validation, results. *Biol Agric Hort* **27**:59–80 (2010).
- 33 Busscher N, Kahl J, Doesburg P, Mergardt G and Ploeger A, Evaporation influences on the crystallization of an aqueous dihydrate cupric chloride solution with additives. *J Colloid Interface Sci* **334**:556–562 (2010).
- 34 Busscher N, Kahl J, Andersen J-O, Huber M, Mergardt G, Doesburg P *et al.*, Standardization of the biocrystallization method for carrot samples. *Biol Agric Hort* **27**:1–23 (2010).
- 35 Zalecka A, Kahl J, Doesburg P, Pyskow B, Huber M, Skjerbaek K *et al.*, Standardization of the Steigbild method. *Biol Agric Hort* **27**:41–57 (2010).
- 36 Wishart DS, Metabolomics: applications to food science and nutrition research. *Trends Food Sci Technol* **17**:482–493 (2008).
- 37 Fiehn O, Combining genomics, metabolome analysis, and biochemical modelling to understand metabolic networks. *Comp Funct Genom* **2**:155–168 (2001).
- 38 Kind T and Fiehn O, Advances in structure elucidation of small molecules using mass spectrometry. *Bioanal Rev* **2**:23–60 (2010).
- 39 Hajslova J, Cajka T and Vaclavik L, Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis. *Trends Anal Chem* **30**:294–218 (2011).
- 40 Morozov VN, Vsevolodov NN, Elliott A and Bailey C, Recognition of proteins by crystallization patterns in an array of reporter solution microdroplets. *Anal Chem* **78**:258–264 (2006).
- 41 Kokornaczyk MO, Dinelli G and Betti L, Approximate bilateral symmetry in evaporation-induced polycrystalline structures from droplets of wheat grain leakages and fluctuating asymmetry as quality indicator. *Naturwissenschaften* **100**:111–115 (2013).
- 42 Kokornaczyk MO, Dinelli G, Marotti I, Benedettelli S, Nani D and Betti L, Self-organized crystallization patterns from evaporating droplets of common wheat grain leakages as a potential tool for quality analysis. *Sci World J* **11**:1712–1725 (2011).
- 43 Deegan RD, Bakajin O, Dupont TF, Huber G, Nagel SR and Witten TA, Contact line deposits in an evaporating drop. *Phys Rev E* **62**:756–765 (2000).
- 44 Yakhno TL, Yakhno VG, Sanin AG, Sanina OA and Pelyushenko AS, On the existence of regular structures in liquid human blood serum (plasma) and phase transition in the course of its drying. *Techn Phys* **49**:1055–1063 (2004).
- 45 Gallinet JP and Gauthier-Manuel B, Wetting of a glass surface by protein adsorption induces the crystallization of an aqueous cupric chloride solution. *J Colloid Interf Sci* **148**:155–159 (1991).
- 46 Shibata T, Matsumoto S, Kogure M, Iguchi T, Tanaka A, Nagano T *et al.*, Effects of diabetic human blood addition on morphology of cupric chloride dendrites grown from aqueous solutions. *J Cryst Growth* **219**:423–433 (2000).
- 47 Kahl J, Busscher N, Doesburg P, Mergardt G, Huber M and Ploeger A, First tests of standardized biocrystallization on milk and milk products. *Eur Food Res Technol* **229**:175–178 (2009).
- 48 Seidel K, Kahl J, Paoletti F, Birlouez I, Busscher N, Kretzschmar U *et al.*, Quality assessment of baby food made of different pre-processed organic raw materials under industrial processing conditions. *J Food Sci Technol* doi:10.1007/s13197-013-1109-5 (2013).
- 49 Zagon J, Jansen B, Dahl L, Holzhauser T, Vieths S and Broll H, Comparative study on the quality of vegetables derived from conventional and organic farming using the example of carrots 2006, Bundesinstitut für Risikobewertung (BfR), Berlin. [Online]. Available: <http://orgprints.org/13546/> [7 January 2014].
- 50 Soil Association, Organic standards farming and growing (2012). [Online]. Available: <https://www.soilassociation.org/LinkClick.aspx?fileticket=I-LqUg6illo%3D&tabid=353> [7 January 2014].