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Analytical methods to identify irradiated food—a review

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Abstract

The ability to analytically identify irradiated food—complementary to certification—helps to enhance consumers confidence. It makes it possible to check compliance with existing regulations (e.g. enforcement of labelling, control of prohibition) and to facilitate international food trade. An enormous effort—both at the world-wide international level (ADMIT) and at European (BCR)/national level—has led to several validated and even standardized (CEN) detection methods for a large number of different food products. In this short review, the present methods are summarized, limitations and new developments drafted. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Food irradiation detection; Irradiation identification

1. Introduction

Treating foods with ionizing radiation results in a large reduction in microbial contamination and insect pests but only in minute changes in the food components responsible for its nutritional value. Although certification of irradiated food—just as food processed according to religious belief, e.g. Halal or Kosher—would facilitate trade, it was recognized at the international conference on 'The Acceptance, Control of and Trade in Irradiated Food' (Geneva, 1988) that consumer acceptance and confidence could be enhanced by the availability of reliable and sensitive detection methods. This impetus led to a strong increase in research and to the introduction of a session dealing with identification of irradiated food at the 7th IMRP 1989, and since then at each IMRP the progress in detection methods for irradiated food has been discussed. Today, at the 12th IMRP, again a large number of reports about food irradiation detection are being presented.

Particularly in Europe, consumers have remained sceptical about food irradiation, and it was, therefore, not surprising that Europe took the lead in developing detection methods. An enormous effort—both on a world-wide international level (ADMIT, McMurray et al. (1996)) and on an EU (BCR, Raffi et al. (1994))/ national level—resulted in a big step forward in the ability to identify whether or not a food product has been treated with ionizing radiation. The dogma that irradiation could not be detected and that no radiation-specific compounds were formed, was succeeded by the recognition that several changes occur in irradiated food which could be utilized for detection purposes. Subsequently, more than 30 interlaboratory blind trials were carried out to validate proposed detection methods (Delincée, 1999).

2. Present status

Nowadays, in Europe, due to the activities of the European Committee for Standardisation (CEN), several validated and standardized detection methods are available for a large number of different food products (Table 1).

In addition to validation by intercomparison tests for some selected foods, other studies have demonstrated that most methods are applicable to a large variety of foodstuffs. Since interlaboratory tests cannot be carried out for every kind of food product, in-house validation may be performed on the food item under investigation. In fact, in the last few years in a number of laboratories

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Table 1
European standards for detection of irradiated food (including recent proposals)

Standard no.	Method	Validated products
EN 1784	Gas chromatographic (GC) analysis of hydrocarbons	Chicken, Pork, Beef Avocados, Mangoes, Papayas, Camembert
EN 1785	GC/MS analysis of 2-alkylcyclobutanones	Chicken, Pork, Liquid whole egg
EN 1786	ESR spectroscopy of bones	Chicken, Fish, Frog legs
EN 1787	ESR spectroscopy of cellulose	Paprika powder, Pistachio nut shells, Strawberries
EN 1788 (being revised)	Thermoluminescence of silicate minerals	Herbs and Spices, Shrimps, (to be added in revised version: Shellfish in general, Fresh or dehydrated Fruits and Vegetables, Potatoes)
prEN 13708	ESR spectroscopy of crystalline sugars	Dried Papayas, Dried mangoes, Dried figs, Raisins
prEN 13751	Photostimulated luminescence	Herbs and Spices, Shellfish
prEN 13783	Microbiological screening using direct epifluorescent filter technique/aerobic plate count (DEFT/APC).	Herbs and Spices
prEN 13784	DNA comet assay screening	Chicken, Pork, Plant cells, e.g. seeds

worldwide, the standardized methods have been applied on a wide variety of foods. One example may be the activities in Korea, where many detection methods have been tested (Yang et al., 1999; Chung et al., 2000). It should also be mentioned that the five already standardized methods (EN 1784–1788) are now endorsed by the Codex Committee on Methods of Analysis and Sampling and proposed for adoption as general Codex Methods.

Thus, the compliance of labelling of irradiated food can now be enforced by food inspection authorities, and consumers can rest assured that they are getting what they desire, both consumers who would like to purchase irradiated foods for their safety and those consumers who prefer to abstain from irradiated food.

Surveillance results in Europe in recent years show a very low incidence ($<1\%$) of wrongly labelled irradiated foods (Delincée, 1998, 1999). At present, the EU in its Directive 1999/2/EC requires the results of checks carried out at the product marketing stage, employing standardized analytical methods whenever possible. EU Member States are required to forward to the European Commission every year these detection results together with the results of checks carried out in the ionizing irradiation facilities, regarding the categories and quantities of products treated and the doses administered. This information is then published by the commission in the Official Journal of the European Communities, creating more transparency for consumers.

3. Further development

In order to ensure that detection methods exist for all products, the European Commission and the Member States will encourage the further development of standardized or validated methods of analysis, which aim to verify whether or not foodstuffs have been treated by ionizing radiation. As already noted in Table 1, a number of further detection methods will be adopted as European Standards in the near future. Some of these techniques are screening tests only, which will need confirmation by a validated method to specifically prove the radiation treatment. A number of further detection tests have been proposed in various laboratories, but have not yet been validated in interlaboratory studies. One example is the detection of *o*-tyrosine (Krach et al., 1999), which may be used for protein-rich food. In addition, a number of further improvements aimed at either simplifying the procedure and/or enhancing detection sensitivity are taking place. Some examples are shown in Table 2 (in this short review, only a limited amount of space is available. Apologies to those authors who are not cited here).

For the detection methods relying on changes in the lipid part of the food, alternative extraction procedures are being proposed, e.g. supercritical fluid extraction (Horvatovich et al., 2000) or accelerated solvent extraction (Hartmann et al., 1997a). Both procedures have not only the advantage of a more selective extraction, they also decrease the demand for organic solvents. Increasing detection sensitivity has been achieved by use of 'silver ion chromatography' both for hydrocarbons (Hartmann et al., 1997b) and 2-alkylcyclobutanones (Ndiaye et al., 1999). Fluorometric detection of e.g. 2-alkylcyclobutanones (Mörsel, 1998) has also been suggested to increase sensitivity. A promising approach is still the use of immunochemical techniques to arrive at a simple dip-stick assay (Nolan et al., 1998). Multiple coupled chromatographic techniques have also been successfully used to improve selectivity and sensitivity (Meier et al., 1996; Rahman et al., 1996; Schulzki et al., 1997). This increased sensitivity can be utilized to detect products irradiated at lower doses or to detect minor

Table 2
Improvements in detection methods for irradiated food

'Lipid' methods (EN 1784, EN 1785)
Improved extraction
Supercritical fluid extraction
Accelerated solvent extraction
Improved selectivity and sensitivity
Argentation chromatography
Fluorometric detection
Immunochemical detection
Coupled chromatographic techniques
LC-GC-(MS), LC-LC-GC (-MS)
TLC-HPLC, TLC-GC-MS
ESR—methods (EN 1787)
Alcoholic extraction of fruit pulp
Different heat sensitivity of radicals
Spin probes
Thermoluminescence (EN 1788)
Various radiation sources for normalization
Emission spectra
Comet Assay
Neutral vs. alkaline protocols
More sensitive stains
Microbiological tests
Turbidimetric methods
Emerging methods
'Electronic Nose'
Surface plasmon resonance

amounts of irradiated ingredients in otherwise non-irradiated foods (Schulzki et al., 1995; Ndiaye et al., 1999; Horvatovich et al., 2000).

Developments in ESR measurements of the 'cellulosic signal' involve improved detection sensitivity using alcoholic extraction of fruit pulp (de Jesus et al., 1999) or the different heat sensitivity of the central signal in irradiated vs. non-irradiated samples (Yordanov and Gancheva, 2000). The use of spin probes offers another principle of detection (Sünnetçioglu et al., 1999).

Employing thermoluminescence, the choice of various radiation sources to provide a normalizing dose prior to the second glow curve measurement has been strenghtened (Soika and Delincée, 2000). The recording of thermoluminescence emission spectra may yield useful information (Correcher et al., 1998).

The application of an array of gas sensors ('Electronic Nose') together with pattern recognition was successful in detecting irradiated red pepper (Kim and Noh, 1999). This development had been already expected after the restricted success of only a few gas sensors (Delincée, 1996). The new technique of surface plasmon resonance has been applied to characterize protein conformational changes after irradiation (Masuda et al., 2000) and may possibly be used to detect radiation specific changes. Detection of irradiated food is, thus, in an advanced state of development and new techniques are still emerging. The presence of multiple tests greatly increases confidence in results.

4. Limitations

Analytical detection methods cannot, however, control whether correctly labelled products have been irradiated within proposed dose limits, or whether good manufacturing practices (GMP) have been followed. For the latter purpose other checks and probably also an international and recognized system of certifications are indispensable. For some food products, e.g. egg-white, casein, or blends of spices in which only a very small part is irradiated, problems regarding adequate detection methods still occur. On the other hand, detection of all kinds of irradiated food products and minute amounts of irradiated ingredients should not be overstressed, since it should be kept in mind that irradiated food is safe and wholesome. Detection of hazardous food contaminants or residues should have a higher priority.

5. Outlook

Consumers can now be confident that most irradiated food can be detected and that abuse can be prevented. Since consumers to-day and in the future will want to know what they are consuming, it seems highly unlikely that labelling of irradiated food will become superfluous, even if food irradiation gains world-wide acceptance. Labelling ensures consumers' freedom of choice. Analytical detection methods will, therefore, be needed also in the near future. Applied in the right context, their availability and regular use could even help to facilitate international trade in irradiated food.

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