

Detection of irradiation of fat-containing foods by on-line LC-GC-MS of alkylcyclobutanones

Autor(en): **Meier, Werner / Artho, Anna / Nägeli, Paul**

Objektyp: **Article**

Zeitschrift: **Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene = Travaux de chimie alimentaire et d'hygiène**

Band (Jahr): **87 (1996)**

Heft 1

PDF erstellt am: **29.06.2024**

Persistenter Link: <https://doi.org/10.5169/seals-982074>

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern.

Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden.

Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

Detection of Irradiation of Fat-containing Foods by On-line LC-GC-MS of Alkylcyclobutanones

Key words: Irradiation, Alkylcyclobutanones, Meat, Cheese, LC-GC-MS-coupling

Werner Meier, Anna Artho and Paul Nägeli
Kantonales Laboratorium Zürich, Zürich

Introduction

In some countries, certain foods (e.g. meat, seafood, spices, dried fruits, and vegetables) are legally irradiated. Since such products might be exported into countries, which do not accept such treatment, analytical methods are needed to determine whether or not irradiation has been applied. These methods serve to prevent illegal imports, multiple irradiation of foods and should help to control compliance with labelling regulations.

Two chemical methods, i.e. the determination of volatile compounds (1) and of o-tyrosine, (2) as well as two physical methods, i.e. ESR-spectroscopy (3) and thermoluminescence, (4) are ready for routine analysis.

Irradiation of fat-containing foods forms volatile compounds useful as markers for the detection of irradiation. During irradiation, breaking occurs mainly in the α and β position with respect to the carbonyl groups resulting in the alkanes C_{n-1} and alkenes $C_{n-2:1}$. Also the acyloxygen bond is cleaved and this reaction results in the formation of 2-alkylcyclobutanones and aldehydes, containing the same number of carbon atoms as the parent fatty acid. Methods exist for the analysis of alkanes and alkenes, (5, 6) aldehydes, (5) and alkylcyclobutanones (7). As the previous method for determining alkylcyclobutanones was time-consuming (Soxhlet extraction during 6 hours, Florisil clean-up with 300 ml of solvent), a more rapid and specific method was developed for detecting dodecylcyclobutanone (DCB) formed from palmitic acid and tetradecylcyclobutanone (TCB) from stearic acid. HPLC isolated the alkylcyclobutanones from the raw fat extract. The fraction of interest was transferred on-line to GC. Because of the low concentrations, detection occurred by mass spectrometry (MS), using multiple ion detection (MID) of masses 98 and 112.

Experimental

Extraction of fat

To 30–50 g of homogenized tissue, mixed in a mortar with the same amount of anhydrous sodium sulfate, 100 ml of hexane were added in a 300 ml Erlenmeyer flask. After adding glass beads as boiling aids, the mixture was refluxed for 1 h, then cooled, the hexane decanted and filtered through anhydrous sodium sulfate. The hexane was removed on a rotary evaporator.

LC-GC-MS analysis

A fully automated LC-GC, Dualchrom 3000, was coupled to a MS QMD 1000, both from Carlo Erba/Fisons (Mailand). 20–50 μ l of a 10% solution of fat extract in hexane were injected into a 100 x 4.6 mm i.d. LC column packed with silica gel Spherisorb SI (Stagroma, Wallisellen). Pentane/5% methyl-*tert.*-butyl ether (MTBE) at 400 μ l/min was the mobile phase. An 800 μ l fraction between 5 and 7 min containing the alkylcyclobutanones was transferred to GC through a loop-type interface. The LC-column was backflushed with 5 ml of MTBE immediately after starting the transfer.

A 30 m x 0.25 mm i.d. fused silica column was used, coated with a 0.12 μ m film of PS-255 (a methyl polysiloxane from Petrarch Systems). The inlet pressure behind the flow regulator was 1.5 bar (helium), the oven temperature during transfer was 65 °C. The flow regulator delivered a flow of 1.5 ml/min. The vapour exit was closed 15 s after the end of eluent evaporation. Then the temperature was programmed at 5 °C/min from 160 to 220 °C. Finally the column was heated out at 280 °C for 5 min.

The MS was operated in the EI+ mode at 70 eV. The masses observed were *m/e* 98 and 112 for 0.5 s each with a span of 0.8 amu. The multiplier was at 700 V, the ion source temperature at 200 °C, and the electron current 100 μ A.

Results and discussion

Figure 1 shows chromatograms of two cheese samples, one unirradiated and the other irradiated with 3 kGy. The detection limit was 0.05 mg/kg alkylcyclobutanone (8).

Chicken and liquid whole egg samples (nine coded samples of both products) from an interlaboratory test were analyzed with this method and gave similar results to those obtained using the proposed official alkylcyclobutanone methodology (9). The method was also used for the control analysis of 10 samples of Camembert imported from France. None of the latter samples was found to be

irradiated (see table 1). The detection limit is 0.05 mg/kg fat, corresponding to 0.5 kGy.

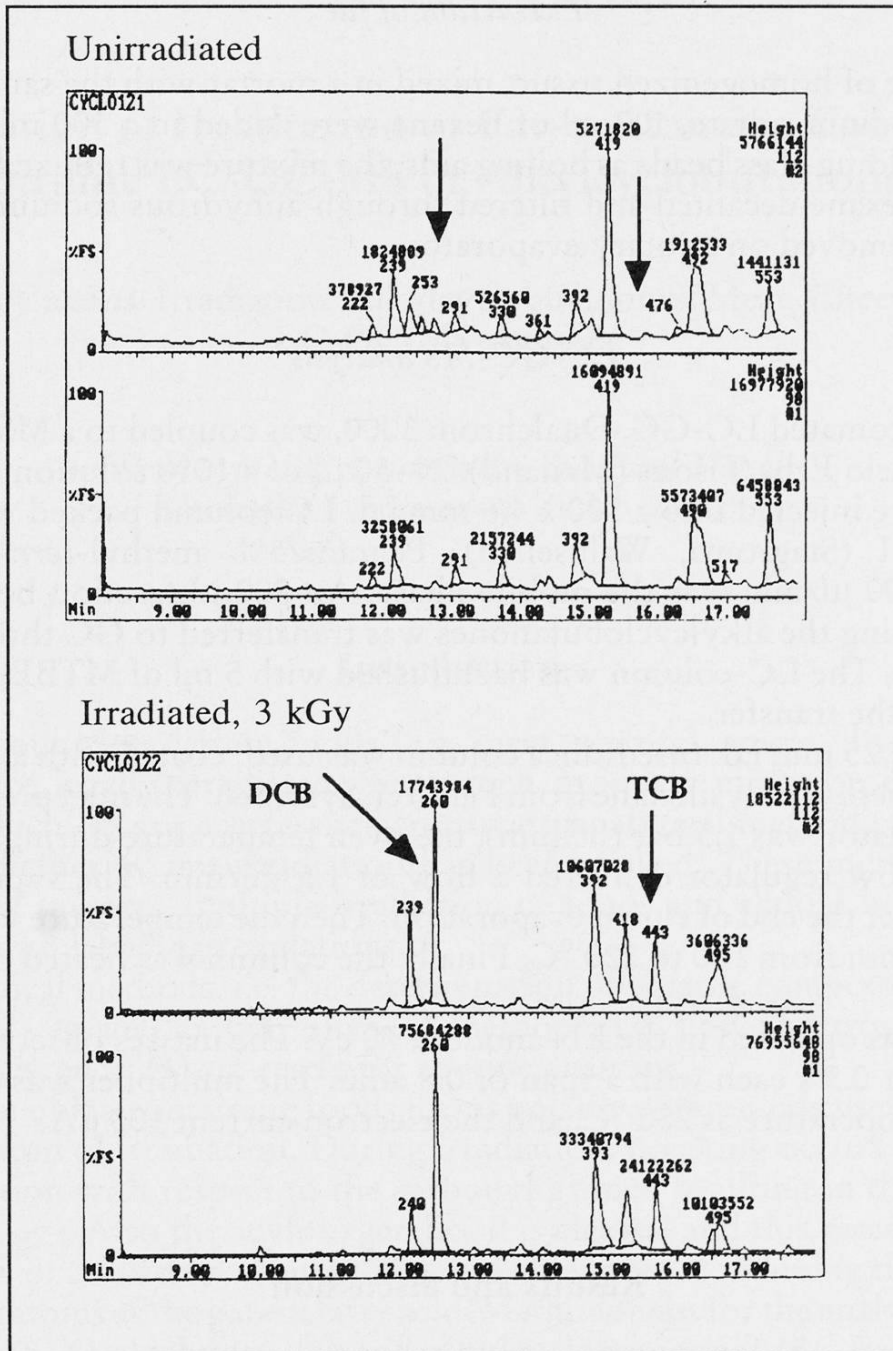


Fig. 1. LC-GC-MS spectra of Camembert

Summary

Alkylcyclobutanones, formed from fatty acids, can be used as markers for the detection of irradiated food. The fat from the food is extracted and injected onto an HPLC column. The fraction containing the alkylcyclobutanones is transferred to GC by concurrent eluent evaporation. The alkylcyclobutanones can then be detected by multiple ion detection (MID)

Table 1. Alkylcyclobutanones found in food in mg kg⁻¹ fat

	Unirradiated	1 kGy	3 kGy
<i>Chicken</i>			
DCB	< 0.05	0.2–0.3	0.5–0.8
TCB	< 0.05	0.05–0.07	0.1–0.2
<i>Eggs</i>			
DCB	< 0.05	0.2–0.3	0.6–0.9
TCB	< 0.05	0.06–0.09	0.1–0.2
<i>Cheese</i>			
DCB	< 0.05	–	1.1
TCB	< 0.05	–	0.4

using the masses m/z 98 and 112. With this method doses of irradiation between 0.5 and 5 kGy, which are normally applied to meat and similar products for conservation, can be detected without any problem. The detection limit is 0.05 mg/kg fat, corresponding to 0.5 kGy, analyzing the alkylcyclobutanones. The method is simpler, faster and less solvent consuming than previous methods.

Zusammenfassung

Alkylcyclobutanone, die aus Fettsäuren gebildet werden, können als Marker für den Nachweis einer Bestrahlung von Lebensmitteln verwendet werden. Das aus dem Lebensmittel extrahierte Fett wird auf eine HPLC-Säule gegeben und die Fraktion, welche die Alkylcyclobutanone enthält, wird mittels simultaner Eluentabdampfung auf die Gaschromatographiesäule transferiert. Die Alkylcyclobutanone werden durch massenspektrometrische Detektion (MID) der Massen 98 und 112 nachgewiesen.

Mit dieser Methode kann eine Bestrahlung zwischen 0,5 und 5 kGy, wie sie üblicherweise für Fleisch und weitere fetthaltige Produkte zur Anwendung gelangt, problemlos nachgewiesen werden. Die Nachweisgrenze für Alkylcyclobutanone beträgt 0,05 mg/kg Fett, dies entspricht einer Bestrahlungsdosis von 0,5 kGy. Die Methode ist einfacher, schneller und benötigt wesentlich weniger Lösungsmittel als bisher beschriebene Methoden.

Résumé

Les alkylcyclobutanones formés à partir d'acides gras peuvent être utilisés comme «marque» (Marker) pour prouver que les denrées ont été irradiées. La matière grasse qui a été extraite des denrées est injectée sur une colonne HPLC. La fraction qui contient les alkylcyclobutanones est transférée simultanément par l'évaporation des éluents sur une colonne de chromatographie en phase gazeuse. Les alkylcyclobutanones peuvent être mis en évidence par la détection multiple de ion (DMI) en utilisant les masses 98 et 112.

Des doses d'irradiation entre 0,5 et 5 kGy appliquées lors d'une irradiation de viande et d'autres produits qui contiennent de la graisse, peuvent facilement être détectées par la présente méthode. La limite de détection pour les alkylcyclobutanones s'élève à 0,05 mg/kg

de graisse; ceci correspond à une dose d'irradiation de 0,5 kGy. La méthode est plus simple et plus rapide et elle nécessite beaucoup moins de solvant que les méthodes précédentes.

Literature

1. Schreiber, G.A., Helle, N. and Bögl, K.W.: Detection of irradiated food – methods and routine applications. *Int. J. Radiat. Biol.* **63**, 105–130 (1993).
2. Meier, W., Bürgin, R. and Fröhlich, D.: Analysis of o-Tyrosine as a Method for the Identification of Irradiated Chicken Meat. *Beta-Gamma*, **1**, 34–36 (1988).
3. Raffi, J. J. and Belliardo, J. J.: European intercomparison on electron spin resonance identification of irradiated foodstuffs. *Int. J. Food Sci. Tech.* **27**, 111–124 (1992).
4. Délincée, H.: Internationale Zusammenarbeit zum Nachweis bestrahlter Lebensmittel. *Z. Lebensm.-Unters. -Forsch.* **197**, 217–226 (1993).
5. Biedermann, M., Grob, K. and Meier, W.: Partially concurrent eluent evaporation with an early vapor exit: Detection of food irradiation through coupled LC-GC analysis of the fat. *J. High Res. Chromatogr. & Chromatogr. Comm.* **12**, 591–598 (1989).
6. Biedermann, M., Grob, K., Fröhlich and Meier, W.: On-line coupled LC-GC and LC-LC-GC for detecting irradiation of fat containing foods. *Z. Lebensm.-Unters. -Forsch.* **195**, 409–416 (1992).
7. Boyd, D.R., Crone, A.V.J., Hamilton, J.T.G., Stevenson, M.H. and Stevenson, P.J.: Syntheses, characterization, and potential use of 2-dodecylcyclobutanone as a marker for irradiated chicken. *J. Agric. Food Chem.* **39**, 789–792 (1991).
8. The alkylcyclobutanone-standards are available from Dr. E.M. Stewart, Food and Agricultural Chemistry Department, The Queen's University of Belfast, Newforge Lane, Belfast BT9 5PX, Northern Ireland.
9. Stevenson, M.H., Kilpatrick, D.J. and Mc Murray, C.H.: FAO/IAEA collaborative blind trial using 2-dodecylcyclobutanone and 2-tetradecylcyclobutanone to detect irradiated chicken, pork and liquid whole egg. FAO/IAEA Report, Vienna, Austria 1994.

Dr. Werner Meier
Anna Artho
Dr. Paul Nägeli
Kantonales Laboratorium Zürich
Postfach
CH-8030 Zürich