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Original Article

The determination of polycyclic aromatic hydrocarbons in smoked fish by gas chromatography mass spectrometry with positive-ion chemical ionization

S. Yurchenko*, U. Mölder

Colloid and Environmental Chemistry, Department of Chemistry, Institute of Physical Chemistry, University of Tartu, Jakobi 2, Tartu 51014, Estonia

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants representing an important group of carcinogens that have been detected in smoked fish. The levels of six PAHs (benzo[a]pyrene, benz[a]anthracene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) were determined in 97 various samples of smoked fish, 11 samples of fresh fish, and 18 olive- and 14 rape-oil samples. For cleaning of the sample, a gel chromatography was used. PAHs were separated by gas chromatography and detected by positive-ion chemical ionization using ammonia as reagent gas. The HP 6890 Plus GC/HP 5973 MSD with positive-ion chemical ionization option was used in the selected ion-monitoring mode. The limit of detection for PAHs using this method was approximately 0.3 ppb with about 75% recovery. The results were confirmed by high-pressure liquid chromatography. The samples of domestic (Estonian) smoked fish was analyzed during 2003–2004, the sum of the average of six PAHs content was found to be 12.37 $\mu g\,kg^{-1}$, and in samples of fresh fish it was not detected.

Keywords: Polycyclic aromatic hydrocarbons; Positive-ion chemical ionization; Gas chromatography; Mass spectrometry; Smoked fish

*Corresponding author. Tel.: +372 5380 6760; fax: +372 737 5264.
E-mail address: sergei.yurchenko@mail.ee (S. Yurchenko).

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are groups of potent carcinogens that are present in the environment; traces of these substances have been found in various food products (Guillen and Sopelana, 2003). The International Agency for Research on Cancer (IARC) categorize benzo[a]pyrene (B[a]P) and benz[a]anthracene (B[a]A) into the group of probably carcinogenic to human, benzo[k]fluoranthene (B[k]F), benzo[b]fluoranthene (B[b]F) and indeno[1,2,3-cd]pyrene (I[cd]P) into the group of possibly carcinogenic to human, and benzo[ghi]perylene (B[ghi]P) into the group of unclassifiable as to the carcinogenicity to human (IARC, 1973).

PAHs are formed in incomplete combustion processes which occur whenever wood, coal or oil are burnt. The possible sources of PAHs in food are environmental contamination, as well as thermal treatment of varying severity which is used in the preparation and manufacturing of foods (Guillen, 1994), the absorption and deposition of particulates during food processing such as smoking, grilling, boiling and toasting, the pyrolysis of fats and the incomplete combustion of charcoal (Larsson et al., 1983; Guillen, 1994; Moret et al., 1997). Regarding food of animal origin, one hypothesis suggests that the lipophilic character of PAHs is responsible for the accumulation into the fat of animals which eat contaminated plants (Guillen et al., 1997).

PAHs occur as contaminants in different food categories and beverages including water (Belykh et al., 1999), fruit, cereals, oils (Dennis et al., 1983; Dennis et al., 1991; Moret and Conte, 2002), smoked meat (Potthast, 1977; Simko, 2002), and smoked fish (Simko, 1991; Akpan et al., 1994; Lodovici et al., 1995; Moret et al., 1999). Non-processed fish contains low PAHs concentration even when it comes from contaminated water because fishes rapidly metabolize PAHs, resulting in low steady-state level in the tissue.

The actual levels of PAHs in smoked foods depend on several variables in the smoking process, including type of smoke generator, combustion temperature, and degree of smoking (Larsson, 1982; Moret et al., 1997). Smoke is generated by thermal pyrolysis of a certain kind of wood when there is limited access of oxygen. Temperature of smoke generally plays a very important role, because the amount of PAHs in smoke, formed during pyrolysis increases linearly with the smoking temperature within the interval 400–1000 °C (Toth and Blaas, 1972). In modern industrial ovens, the smoke is usually generated in a separate chamber cleaned by using various techniques, such as electrostatic filters or smoke washing, and then led into the smoking chamber. This, together with the control of some important parameters such as temperature, humidity, smoke concentration, and circulation rate, can contribute to the minimization of PAHs contamination (Moret et al., 1999).

In literature, methods for sample preparation of PAHs are based on liquid-liquid extraction (Grimmer and Böhnke, 1975), thin-layer chromatography (Daisey, 1983; Menichini et al., 1991; Moret and Conte, 2000), supercritical fluid extraction (Järvenpää et al., 1996) or solid phase extraction (Nazarkina et al., 2001). The determination of PAHs in food has been carried out by different analytical methods, including fluorometric (Simko et al., 1992; Moret et al., 1999; Moret and Conte, 2000) and spectrofotometric (Moret et al., 1997; Moret and Conte, 2000) high-performance liquid chromatography, gas chromatography mass spectrometry (GC-MS) or gas chromatography with flame ionization detector (Larsson, 1982; Larsson et al., 1990; Moret and Conte, 2000). Separation and identification of PAHs is an important analytical problem. The electron impact mass spectra of PAHs are, unfortunately, almost always indistinguishable.