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Determination of chlordane in foods by gas chromatography

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Abstract

Chlordane comes under the group of persistent organic pollutants, which, according to the Stockholm Convention, should be completely prohibited or widely limited. Within the Environmental and Health Monitoring Programme the National Institute of Public Health in Prague, Centre for the Hygiene of Food Chains in Brno, is involved in a project, which explores the dietary exposure of the population of the Czech Republic to chemical substances. In order to meet the demands it is necessary to obtain data which would contribute to a comprehensive description of exposure doses of the priority persistent organic pollutants based on the Stockholm Convention.

Hence alpha- and gamma-chlordane and oxychlordane were incorporated into the project in 2002. Chlordane was monitored in food samples of the so-called food basket of the Czech population. After culinary treatment the food samples underwent extraction, were purified (GPC, Florisil) and analysed (GC-ECD). The method for determination of chlordanes in food was developed in our laboratory and was validated. Internal standards were used to determine the recovery of the analytical procedure. The limits of quantification depended on the type of the matrix and ranged between 0.002 and 0.05 $\mu g\,kg^{-1}$. CRM 598 BCR and proficiency testing (FAPAS) are used to assure that the method provides data of required precision and accuracy. The method is accredited by the Czech Accreditation Institute. In the majority of analysed samples the content of chlordane was below the limit of quantification. The highest amount of chlordanes was found in freshwater fish (2.78 $\mu g\,kg^{-1}$), butter and vegetable fat. The results of monitoring are used for estimation of the dietary exposure of the population of the Czech Republic to these substances.

Keywords: Chlordane; Food; Gas chromatography; Analysis; Dietary exposure

1. Introduction

Chlordane belongs to the group of persistent organic pollutants (POPs), the use of which should, under the Stockholm Convention, be either completely prohibited or limited to a large extend (Blaha, 2001a, 2001b; Rice, 2003).

1.1. Chlordane properties

Chlordane is a broad-spectrum contact insecticide that has been applied to agricultural crops including vegetables, maize, other oilseeds, potatoes, sugarcane, sugar beet, fruits, nuts, cotton and jute. It has also been used extensively to eradicate termites. In the Czech Republic chlordane has never been produced or officially registered for use. The reason why it is found in foodstuffs in the Czech Republic is primarily due to the import of the above commodities (Persistent Organic Pollutants, 2003).

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Chlordane is almost insoluble in water and soluble in organic solvents; it is highly stable and semi-volatile. It is easily bound to water sediments and its bioconcentration takes place in the fat of organisms. These chemical properties of chlordane enable its transport to long distances (Persistent Organic Pollutants, 2003).

Technical chlordane is synthesised by Diels–Alder reaction of hexachlorocyclopentadien and cyclopentadien. The resulting compound is chlordene, with 6 atoms of chlorine, which is further chlorinated into technical chlordane. It is a mixture of more than 140 compounds. The main components of technical chlordane are alpha- and gamma-chlordane (8 atoms of chlorine), *cis* and *trans* nonachlor, and heptachlor; the latter is used separately as a pesticide. In the majority of organisms these compounds are metabolised into 2 persistent epoxides, i.e. heptachlorepoxide (with 7 chlorines) and oxychlordane (with 8 chlorines). There are however great differences in the rate of metabolism; for instance fish does not metabolise these compounds as readily as rats (Dearth & Hites, 1991a, 1991b; International Agency for Research (IARC), 2001; Vetter & Schurig, 1997).

Chlordane stimulates the central nervous system. The first symptom of intoxication is a sharper sensitivity to external stimuli. Later on restlessness, tremor, even epileptic spasms are observed. Symptoms of acute poisoning appear 45 min after consumption, although sometimes they appear as late as several hours afterwards. Chlordane damages the parenchyma organs. Cases of fat degeneration of the liver, even necrosis, kidney damage, haemorrhage in the lungs, liver, kidneys, heart muscle and intestine mucous membrane have been reported. Chlordane affects the metabolism and toxicity of a number of simultaneously applied substances by inducing the activity of hepatic microsome enzymes. In the course of metabolic transformation, metabolites which are more toxic than the original compounds, are generated. Analogous to other chlorinated insecticides, these substances are also deposited in the fat tissues of living organisms and are very slowly metabolised and excreted from the body in the stools, urine, and in nursing females also in the milk (Bondy et al., 2003; Campoy et al., 2001; Hirai & Tomokuni, 1991; Marhold, 1986; Vetter, Weichbrodt, Scholz, Luckas, & Oelschlager,; World Health Organization, 1984).

In terms of the hitherto known toxicological properties and existence of exposure limits, alpha-chlordane, gamma-chlordane and oxychlordane, heptachlor and heptachlor epoxide have been recommended for monitoring the human dietary exposure.

Evaluations of the dietary exposure involve estimations of chlordane content as the sum of contents of alpha-chlordane, gamma-chlordane and oxychlordane (Codex Alimentarius; Nakata et al., 2002; Veter et al.).

1.2. Monitoring of chlordane and chlordane-related substances

Unsystematic monitoring of residues of selected chlorinated pesticides and later also of PCBs had been conducted in the Czech Republic as early as the 1970s and 1980s, particularly thanks to the State Veterinary Administration and Public Health Protection Bodies. The reason why this group of substances was included among analytes monitored in the foodstuffs of the so-called food basket within the system of monitoring the health condition of the population of the Czech Republic in relation to the environment, which was initiated by Government Decision 369/1991 and has been implemented on a national scale since 1994 under the guidance of the National Institute of Public Health, was the awareness of the importance of the health issue and the necessity of obtaining integrated information (Cerna & Bencko, 2001).

Within "The Project on Dietary Exposure to Selected Chemical Substances" the National Institute of Public Health in Prague, Centre for the Hygiene of Food Chains in Brno, participates in a project, the objective of which is to describe the dietary exposure of the population of the Czech Republic to chemical substances (Ruprich, 1995). Within the above group of substances, heptachlor and heptachlorepoxide have been monitored in the framework of this project since 1994.

In order to generate data, which would contribute to a complete description of the exposure doses of the priority POPs according to the Stockholm Convention, alpha- and gamma-chlordane and oxychlordane were incorporated into the project in 2002 (Blaha, 2001a, 2001b). Fig. 1 gives the formula of the analytes.

1.3. The possibility of chlordane determination

For the isolation of chlordane from samples of foodstuffs different extraction methods are used, for example liquid–liquid extraction, extraction with hot solvent (Soxtec), extraction with solvent at high speed, solid phase extraction (SPE), solid phase microextraction (SPME), supercritical fluid extraction (SFE), matrix solid phase dispersion (MSPD), semi-permeable membrane diffusion (SPMD), microwave-assisted extraction (MAE), pressurized solvent extraction (PSE) (Baiada-Pereira, Concha-Grana, & Gonzalez-Castro, 2003; Barker, 1998; Bulletin 900B, 1999; Muccio et al., 1997; Jayaraman, Pruell, & McKinney, 2001; Nguyen & Nau, 1996; Page & Lacroix, 1997; Prados-Rosales, García, & Castro, 2003; Tomkins & Barnard, 2002; Wang, Wang, Ma, Wang, & Mo, 2001).

Because chlordane occurs in foodstuffs in trace amounts (about 0.1 $\mu g\,kg^{-1}$), it is necessary to use relatively large amount of the samples for the extraction. Extraction with solvent at high speed is used for the so-