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Autor(en): **Jan, J.**

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Chlorobenzene Residues in Market Milk and Meat

J. Jan
Public Health Institute of Slovenia, Ljubljana

Introduction

Chlorobenzenes (CB) represent a group of chlorinated hydrocarbons and are ubiquitous environmental pollutants (1, 2). Contamination of milk and meat with CB could appear owing to their high production, wide use, lipophilic character and slow degradation in the environment. CB are in minor use as pesticides, while more are used as solvents, heat transfer fluids, flame retardants and in the electro-industry. In the environment they could also be derived from pesticides (e. g. HCH) by metabolic processes (3), and probably during incineration of organic matter and chloro compounds (4). They have been found in water, fish, seeds and man (2, 5, 6, 7).

This investigation reports the data on CB (di-, tri-, tetra-, penta-, and hexa-) residues in milk and meat; of these only information on hexa-CB (8) in milk and meat, and on 1,4-di-CB in pork meat (9) is available. It is important to collect data on CB levels, since they have comparable toxicity and properties to organochloro pesticides and polychlorinated biphenyls (10, 11). The technique of destructive clean-up as described for organochloro compounds (12), was also applied for CB. The presence of CB in milk and meat was quantified by high resolution glass capillary GL chromatography.

Experimental

Samples

The 9 raw milk samples were received as an average daily sample from the city milk distribution in Ljubljana (Yugoslavia) in September–October 1981. The 3 fresh beef meat samples (M.long.dorsi) were purchused on the market.

Reagents

1,2-dichlorobenzene (1,2-DCB); 1,3-dichlorobenzene (1,3-DCB); 1,4-dichlorobenzene (1,4-DCB); 1,2,3-trichlorobenzene (1,2,3-TCB); 1,2,4-trichlorobenzene (1,2,4-TCB); 1,3,5-trichlorobenzene (1,3,5-TCB); 1,2,3,4,-tetrachlorobenzene (1,2,3,4-TeCB); 1,2,3,5-tetrachlorobenzene (1,2,3,5-TeCB); 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB); pentachlorobenzene (PeCB); hexachlorobenzene (HCB) were supplied by Fluka.

To lower the blank value, glassware was rigorously cleaned with methanol and heated at 300 °C for 1 h. All solvents were glass distilled. Florisil, 60–100 mesh, (Fluka) was Soxhlet extracted with benzene for 3 h before activation for 3 h at 550 °C and maintained at 130 °C prior to use. The reagent blank was measured and corrected for in sample analyses. Recoveries of CB added to beef meat were over 80 %.

Instrumentation

A Varian model 3700 gas chromatograph; electron capture detector (^{63}Ni); glass capillary columns (a) i. d. 0.32 mm, length 20 m coated with SE-30 and (b) i. d. 0.30 mm, length 20 m coated with OV-1. Injector temperature 210 °C, detector temperature 240 °C. Temperature programme: initial column oven 60 °C held for 40 s (during the purge activation time) then the temperature raised to 65 °C in 20 s; 65–170 °C temperature programme 5 °C/min 170 °C isothermal; splitless injection, purge activation time 40 s. Sample 1–3 μl. Solvent n-hexane. Nitrogen flow: column 0.9, injector purge 120, and make-up 25 ml/min, respectively.

Procedures

Meat

To 20 g of finely chopped fresh beef meat and 15 ml of n-hexane were added 20 ml of 1:1 (v/v) H_2SO_4-water in an erlenmayer flask and shaken. After half an hour 30 ml of conc. sulfuric acid was added and digested overnight at room temperature. The reaction mixture was put in a separatory funnel, the acid phase discarded and the hexane extract cleaned-up with 20 ml conc. sulfuric acid. The hexane extract was passed through a florisil column 10 cm in height with an i. d. of 1 cm having 0.5 cm of anhydrous Na_2SO_4 on the top, and eluted with 25 ml of 6% diethyl ether in hexane. The eluate was concentrated to 2 ml at 50 °C in a flow of nitrogen, and chromatographed. The chromatogram is shown in figure 1.

Milk

20 g of milk and 10 ml of n-hexane were cooled below 0 °C and 20 ml of conc. sulfuric acid was slowly added with stirring. After 1 h when the mixture reached room temperature, a fresh portion of 10 ml of conc. sulfuric acid was added. After standing overnight, the hexane layer was separated and cleaned with 10 ml of conc. sulfuric acid and through the florisil column, and the eluate evaporated and analysed by GL chromatography.

An additional clean-up could be done with hydrolysis by a modified procedure of *Young* and *Burke* (13): to the hexane eluate evaporated to 1 ml, 1 ml of 2% ethanolic KOH was added, this was then sealed in a glass vial and hydrolysed for 1 h at 95 °C. After cooling, water was added to the reaction mixture, extracted with hexane and cleaned-up through conc. sulfuric acid and florisil as above, and

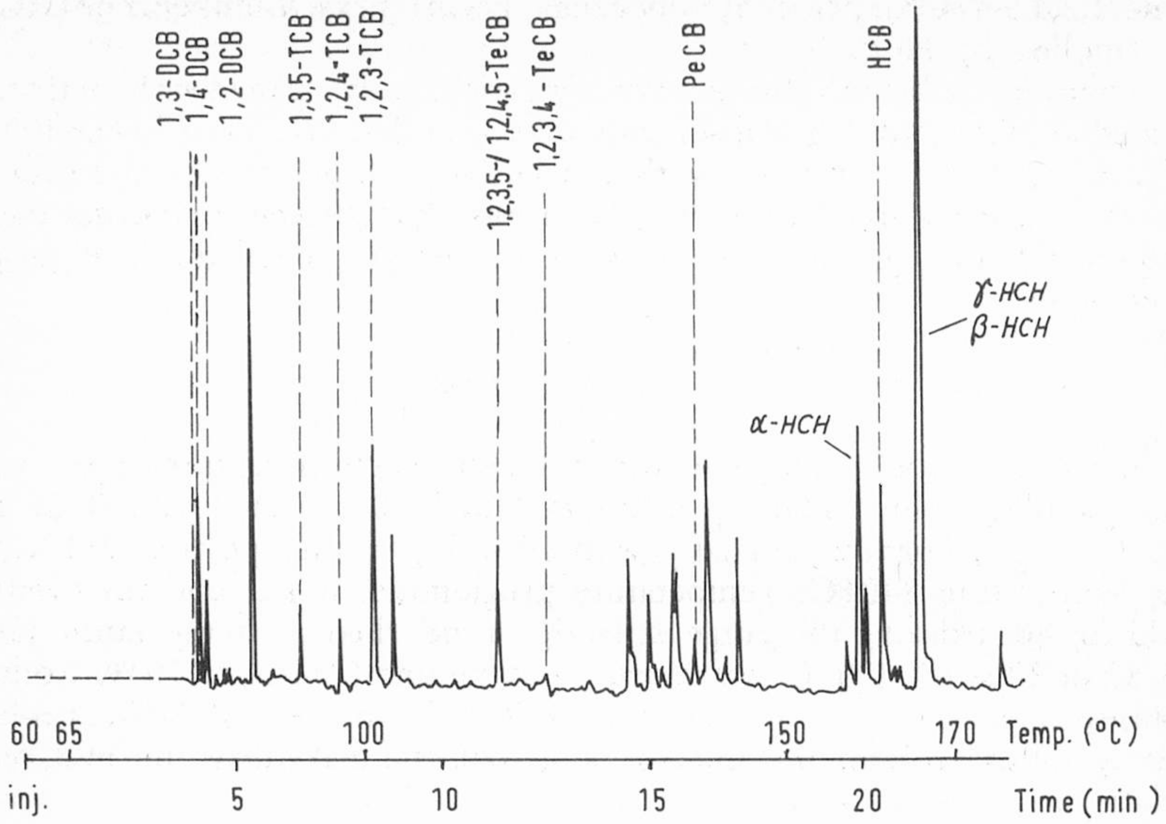

Fig. 1. Chromatogram of the beef meat extract on a SE-30 glass capillary column (for abbreviations, see text)

chromatographed. For quantitative assessment, the increased trichlorobenzene levels produced from hydrolysis of HCH isomers should be taken into consideration.

Results and discussion

In table 1 residue levels of CB and HCH (hexachlorocyclohexane) pesticides in milk and meat are presented. The level in both samples is similar. The total CB (dichloro to hexachloro) in milk falls in the range of total organochloro pesticides (sum of HCH, DDT and cyclodiene groups) as well as polychlorinated biphenyls; the corresponding values are approximately 0.4 (from table 1), 0.1 (8, 14), and 0.3 (from table 2) mg/kg recalculated and expressed on a fat basis, respectively. It is possible to speculate that the contamination of milk and meat with CB could originate through water (5, 20) and cattle feedstuffs prepared on a fish (7) and seed (6) basis, since CB have been found in these sources.

At present there are no available legal tolerances for CB in food except for HCB. *WHO* (10) and *FDA* (11) have proposed some tentative acceptable daily intakes (ADI) and recommended residue limits for organochloro contaminants. In table 2 a comparison of these limits with the average content in milk and the toxicity of CB is presented.

Table 1. Mean levels of chlorobenzenes in cow's milk and beef meat (ng/g «as in» basis)

Compound / Sample	DCB			TCB			TeCB		PeCB	HCH	Total HCH[a]
	1,3-	1,4-	1,2-	1,3,5-	1,2,4-	1,2,3-	1,2,3,5- and/or 1,2,4,5-	1,2,3,4-			
Cow's milk[b]	nd[d]	5.3	2.6	0.9	0.7	1.5	1.10	0.20	0.05	0.35	1.31
Beef meat[c]	nd	5.0	1.0	1.2	1.0	1.8	1.00	0.02	0.05	1.10	2.40

The fat content of the milk was 3.2% and of the meat 2.1%. The GLC analytical technique was not sensitive enough (electron capture detector sensitivity of lower chlorobenzenes is low) to determine DCB and TCB to more than two digits

[a] the sum of alpha-, beta- and gamma-hexachlorocyclohexane isomers

[b] arithmetic means of 9 samples analysed

[c] arithmetic means of 3 samples analysed

[d] not detected

Table 2. Toxicological data, tolerances and residues of some organochloro contaminants in milk

Compound	LD_{50} (mg/kg body weight, rat, orally (15)	ADI (mg/kg body weight) (10)	Residue limit (10) and common content[a] in milk (mg/kg on fat basis)	
Gamma-HCH (lindane)	125	0.0125	0.1	0.02–0.03 (8, 14)
HCB	3 500	0.0006	0.3	0.01–0.03 (8, 14)
1,4-DCB	500	0.014–0.0014	no data	0.16[b]
Polychlorinated biphenyls	4 000 (16)	0.02 (11)	1.5 (17)	0.2–0.4 (8, 14, 18, 19)

[a] in some European contries

[b] calculated from table 1

Results of this contribution illustrate that the CB levels in milk and meat are not so high as to cause concern; however, as the toxic effects of CB are comparable to those of the other organochloro contaminants, it would be advisable in food contamination monitoring to include, besides HCB, CB isomers with less than six chloro atoms on the benzene nucleus.

Acknowledgement

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Summary

Chlorobenzene levels were determined in cow's milk and beef meat samples. Concentrations determined by capillary GL chromatography for some chlorobenzene isomers were from 0.05 to 5 ng/g, original weight basis. The total amount of chlorobenzenes (sum of dichloro to hexachloro), of approximately 10 ng/g, original basis, is found to be in the range of other organochloro contaminants – e. g. organochloro pesticides and polychlorinated biphenyls.

Zusammenfassung

In Kuhmilch- und Rindfleischproben wurden mittels Kapillargaschromatographie die Konzentrationen einzelner Chlorbenzole (Dichlor- bis Hexachlorbenzol) bestimmt. Sie lagen im Bereich von 0,05 bis 5 ng/g (Frischgewicht). Der Totalgehalt an Chlorbenzolen (Summe) betrug ungefähr 10 ng/g und war somit mit den Gehalten anderer chlorierter Kohlenwasserstoffe (Organochlorpestizide, polychlorierte Biphenyle) vergleichbar.

Résumé

Les résidus de chlorobenzènes ont été déterminés dans des échantillons de lait de vache et dans la viande de boeuf. Les concentrations, déterminées par chromatographie gaz liquide capillaire pour quelques isomères de chlorobenzène, varient de 0,05 à 5 ng/g de poids original. La quantité totale des chlorobenzènes (la somme des dichloro- à hexachlorobenzènes) est d'environ 10 ng/g du poids original, elle se trouve dans le domaine des autres contaminants organochlorés – par exemple des pesticides organo-chlorés et des biphényles polychlorés.

Literature

1. *Fishbein, L.:* Potential halogenated industrial carcinogenic and mutagenic chemicals. IV. Halogenated aryl derivatives. Sci. Total Environ. **11**, 259–278 (1979).
2. *Morita, M.:* Chlorinated benzenes in the environment. Ecotoxicol. Environ. Safety **1**, 1–6 (1977).
3. *Engst, R., Macholz, R. M.* and *Kujawa, M.:* Recent state of lindane metabolism. Part II. Residue Rev. **72**, 71–95 (1979).
4. Choudhry, G. G. and *Hutzinger, O.:* Mechanistic aspects of the thermal formation of halogenated organic compounds including polychlorinated dibenzo-p-dioxins. Part V: Hypotheses and summary. Toxicol. Environ. Chem. **5**, 295–309 (1982).
5. *Oliver, B. G.* and *Nicol, K. D.:* Chlorobenzenes in sediments, water, and selected fish from lakes Superior, Huron, Erie, and Ontario. Environ. Sci. Technol. **16**, 532–536 (1982).
6. *Jan, J.:* Chlorinated benzene residues in some seeds. Chemosphere **9**, 165–167 (1980).

7. *Jan, J.* and *Malneršič, S.:* Chlorinated benzene residues in fish in Slovenia (Yugoslavia). Bull. Environ. Contam. Toxicol. **24**, 824–827 (1980).
8. *Heeschen, W.:* Rückstände von Arzneimitteln, Pestiziden und Umweltchemikalien in der Milch – ein Überblick zur gegenwärtigen Situation. Tierärztl. Umschau **37**, 538–545 (1982).
9. *Watson, A.* and *Patterson, R. L. S.:* Tainting of pork meat by 1,4-dichlorobenzene. J. Sci. Food Agric. **33**, 103–105 (1982).
10. *FAO/WHO:* Pesticide residues in food. WHO technical Report Series No. 574. WHO, Geneva 1975.
11. *US Department of Health, Education and Welfare, Food and Drug Administration:* Polychlorinated biphenyls (PCB's). Fed. Reg. **38**, 18096–18103 (1973).
12. *Veierov, D.* and *Aharonson, N.:* Economic method for analysis of fluid milk for organochlorine residues at the 10 ppb level. J. Assoc. Off. Anal. Chem. **63**, 532–535 (1980).
13. *Young, S. J. V.* and *Burke, J. A.:* Micro-scale alkali treatment for use in pesticide residue confirmation and sample cleanup. Bull. Environ. Contam. Toxicol. **7**, 160–167 (1972).
14. *Venant, A.* et *Richou-Bac, L.:* Contamination des produits laitiers français par les résidus de composés organo-chlorés. Lait **61**, 619–633 (1981).
15. *Christensen, H. E., Fairchild, E. J., Carroll, B. S.* and *Lewis, R. J.* (Editors): NIOSH registry of toxic effects of chemical substances. HEW Publ., Washington D.C. 1976.
16. *WHO:*Polychlorinated biphenyls and terphenyls. Environ. Health Crit. Vol. **2**, WHO, Geneva 1976.
17. *US Department of Health, Education and Welfuce, Food and Drug Administration:* Polychlorinated biphenyls (PCB's); reduction of tolerances. Fed. Reg. **44**, 38330 (1979).
18. *Van Renterghem, R.* and *Devlaminck, L.:* Polychlorinated biphenyl compounds in milk and dairy products. Z. Lebensm.-Unters. Forsch. **170**, 346–348 (1980).
19. *Sümmermann, W., Rohleder, H.* und *Korte, F.:* Polychlorierte Biphenyle (PCB) in Lebensmitteln. Z. Lebensm.-Unters. Forsch. **166**, 137–144 (1978).
20. *Grob, K.* and *Grob, G.:* Organic substances in potable water and its precursor, Part II, Applications in the area of Zürich. J. Chromatogr. **90**, 303–313 (1974).

Dr. J. Jan
Public Health Institute of Slovenia
Trubarjeva 2
61000 Ljubljana
Yugoslavia