

THE PRESENT OF PAH'S IN MEAT PRODUCTS FOUND ON THE CLUJ-NAPOCA MARKET

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Abstract: *This study focuses on the present of 15 PAH's in meat products found on the market in Cluj-Napoca. The meat products that were analyzed are: 6 summer salami samples, 1 Hungarian salami sample, 2 pork baloney samples, 2 pork sausages samples and 5 bacon samples. PAH's have been found in all samples in different quantities ranging from 0,0073 to 88,65,25. The samples were analysed using an HPLC with FLD detection.*

Keywords: PAH's, meat products, HPLC-FLD.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds that has been the subject of many studies related to food contaminants (Martena, 2011; Martorell, 2010; Stumpe-Vikсна, 2008; Ishizaki, 2010). The EPA has classified seven PAH compounds as probable human carcinogens: benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene (US EPA, 2001).

PAHs like benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene have carcinogenic, mutagenic and teratogenic effect on laboratory mice (US EPA, 2001; Kummer, 2011; Song, 2011; Shan, 2011; Luch, 2005).

A number of studies has been done in order to determine PAHs level in different food stuff (Martena, 2011; Martorell, 2010; Stumpe-Vikсна, 2008; Ishizaki, 2010). PAH's are found in food due to environmental pollution or are formed during the heat treatment operation that the food suffers in the fabrication process (Martena, 2011; Martorell, 2010; Stumpe-Vikсна, 2008; Ishizaki, 2010). Results indicate that the level of PHAs found depend on the temperature and time of heat treatment that the food suffers, the type of wood used for obtaining smoke, fat content etc (Martena, 2011; Martorell, 2010; Stumpe-Vikсна, 2008; Ishizaki, 2010).

MATERIAL AND METHOD

Reagents and standards

PAH Calibration Mix containing 10 μ g/ml of each compound (Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene, Indeno[1,2,3-cd]pyrene) in Acetonitrile was acquired from Supelco. Florisil (Merck) was used after heating overnight at 120°C. 0,45 μ m filtration cartridge for syringe where acquired from Phenomenex.

Cyclohexane for HPLC (purity $\geq 99.9\%$), Ethanol and potassium hydroxid, Acetonitrile Chromasolv gradient grade for HPLC (purity $\geq 99.9\%$) were acquired from Sigma – Aldrich. The ultra-pure water was obtained with a Milli-Q water purification system from Millipore.

Samples

The meat products were purchase form different shops and supermarkets found in Cluj-Napoca. In total, a number of 16 samples were analyzed: 6 summer salami samples, 1 Hungarian salami sample, 2 pork baloney samples, 2 pork sausages samples and 5 bacon samples. In table 1 is presented the location from which each sample was bought.

Table 1

Location from which each sample was bought

Sample nr.:	Sample name	Sampling location
1.	summer salami	Store from Mănăștur area, Cluj-Napoca
2.	summer salami	Store from Mănăștur area, Cluj-Napoca
3.	summer salami	Store 1 from Gheorgheni area, Cluj-Napoca
4.	summer salami	Store 1 from Gheorgheni area, Cluj-Napoca
5.	summer salami	Store 2 from Gheorgheni area, Cluj-Napoca
6.	summer salami	Store from Grigorescu area, Cluj-Napoca
7.	Hungarian salami	Store from Mănăștur area, Cluj-Napoca
8.	bacon	Store from Mănăștur area, Cluj-Napoca
9.	bacon	Store 2 from Gheorgheni area, Cluj-Napoca
10.	bacon	Store 1 from Gheorgheni area, Cluj-Napoca
11.	bacon	Store 1 from Gheorgheni area, Cluj-Napoca
12.	bacon	Store from Florești area, Cluj County
13.	pork baloney	Store 1 from Gheorgheni area, Cluj-Napoca
14.	pork baloney	Store from Mănăștur area, Cluj-Napoca
15.	pork sausages	Store 2 from Gheorgheni area, Cluj-Napoca
16.	pork sausages	Store from Mănăștur area, Cluj-Napoca

Extraction and analysis

Prior to the liquid/liquid extraction with cyclohexane, the meat samples are saponified using an alcoholic solution of KOH. The samples were purified using a Florosil column and analyzed using a Perkin Elmer 200 Series High Performance Liquid Chromatograph (HPLC) with UV and fluorescent (FLD) detectors. The HPLC parameters are:

- Flow Rate: 1,6mL/min;
- Mobile Phase: A (H₂O);
B (ACN);
- Column Temp: 25°C;
- Injection Volume: 20 μ L;
- Column: ZORBAX Eclipse PAH 5 μ m, 4.6 \times 150 mm column from Agilent Technologies;
 - Wavelength: 254 nm for the UV detector, different wavelengths appropriate for each compound for the FLD detector.

RESULTS AND DISCUSSION

The value obtained for PAHs content after analyzing the 16 meat product samples are shown in table 2.

In table 3 it is shown the average value obtained for each type of meat product.

Table 2

Results obtained for de 16 samples

Comp. name Sample nr.:	Naphthalene	Acenaphthene	Fluorene
1.	13,5569	22,1145	0,0035
2.	14,6092	20,0362	< LQ
3.	12,1857	28,9608	0,0021
4.	13,5568	20,3609	< LQ
5.	11,2253	15,6987	< LQ
6.	10,1141	12,9487	0,0148
7.	15,0674	4,5204	< LQ
8.	8,5623	< LQ	< LQ
9.	9,55329	< LQ	< LQ
10.	7,4765	0,2742	< LQ
11.	5,3326	0,1356	< LQ
12.	4,5523	< LQ	< LQ
13.	11,436	30,1415	0,0021
14.	10,692	29,2169	< LQ
15.	8,249	30,449	< LQ
16.	7,5536	21,685	< LQ

Comp. name Sample nr.:	Phenanthrene	Anthracene	Fluoranthene	Pyrene
1.	18,2689	0,4487	0,2369	10,2384
2.	20,336	1,9603	0,4498	6,983
3.	73,1548	0,8695	0,7147	7,2975
4.	60,5598	2,4781	0,9869	8,998
5.	8,698	1,4489	0,7448	5,0798
6.	0,9186	2,0016	4,6151	9,9395
7.	9,9068	0,4533	0,8962	1,0861
8.	10,2556	0,5521	1,8856	2,009
9.	12,5326	0,2236	2,7145	2,116
10.	11,8504	0,7624	2,3346	2,0237
11.	11,9656	0,2748	4,5021	2,1142
12.	11,2235	0,369	3,0269	2,1178
13.	71,0221	0,7885	0,8495	5,9963
14.	66,539	0,2135	0,7798	4,5478
15.	55,268	0,2219	0,9052	6,326
16.	31,009	0,5589	0,9687	3,5586

Comp. name Sample nr.:	Benz[a]anthracene	Chrysene	Benzo[b]fluoranthene	Benzo[k]fluoranthene	Benzo[a]pyrene	Dibenz[a,h]anthracene	Benzo[ghi]perylene	Indeno [1,2,3-cd]pyrene
1.	4,218	7,2298	51,5874	29,683	2,6698	4,6953	11,3625	< LQ
2.	4,6931	6,0144	30,5966	15,6685	3,014	2,8877	8,2342	< LQ
3.	4,4388	8,6913	65,3264	29,9572	2,5159	3,9244	10,8761	0,0369
4.	3,9801	6,9963	50,2281	30,958	1,975	2,5514	8,3246	< LQ
5.	3,8971	8,5548	30,5587	30,521	3,9681	2,6038	3,559	< LQ
6.	4,0482	1,9711	19,1012	11,4159	0,3969	0,9424	< LQ	< LQ
7.	0,0349	0,1451	7,0258	0,429	1,1381	2,872	2,7365	< LQ
8.	0,9965	0,3265	20,0236	0,9638	0,0852	2,2265	0,1255	< LQ
9.	0,851	0,5023	10,1125	1,254	0,3556	2,3354	< LQ	1,556
10.	1,6018	0,4442	244,2473	1,7543	0,1261	3,2166	< LQ	< LQ
11.	2,0368	0,6158	80,2264	1,5985	0,2241	4,5389	0,9635	< LQ
12.	2,1103	0,7003	55,0136	2,1369	0,5568	5,6635	< LQ	< LQ
13.	4,9638	7,9923	25,3704	31,2447	2,5159	5,0031	9,8635	0,0369
14.	5,6231	6,3258	49,3692	29,0586	1,5986	4,897	11,2344	< LQ
15.	5,7962	7,1128	39,875	29,6638	2,4478	3,8102	10,2249	0,4788
16.	4,2136	5,096	55,216	26,9986	3,9681	3,8209	11,635	< LQ

Table 3

Average values obtained for each type of meat product

Crt nr.	Chemical compound	Summer salami ($\mu\text{g}\cdot\text{kg}^{-1}$)	Hungarian salami ($\mu\text{g}\cdot\text{kg}^{-1}$)	Pork baloney ($\mu\text{g}\cdot\text{kg}^{-1}$)	Pork sausages ($\mu\text{g}\cdot\text{kg}^{-1}$)	Bacon ($\mu\text{g}\cdot\text{kg}^{-1}$)
1	Naphthalene	13.0267	15.0674	8.0875	7.87480581	7,0953
2	Acenaphthene	21.4342	4.5204	7.4812	14.8989	0,0819
3	Fluorene	0.0011	<LQ*	0.0002	0.0003	<LQ
4	Phenanthrene	36.2035	9.9068	25.8693	35.5578	11,5655
5	Anthracene	1.4411	0.4533	0.4525	0.41444	0,4363
6	Fluoranthene	0.6266	0.8962	2.3732	2.03727	2,8927
7	Pyrene	7.7193	1.0861	2.8751	3.70149	2,0761
8	Benz[a]anthracene	4.2454	0.0349	2.4628	3.59074	1,5192
9	Chrysene	7.4973	0.1451	2.1781	3.81737	0,5178
10	Benzo[b]fluoranthene	45.6594	7.0258	74.0003	58.9585	88,6525
11	Benzo[k]fluoranthene	27.3575	0.4291	8.6940	16.3671	1,5415
12	Benzo[a]pyrene	2.8285	1.1381	0.7164	1.53717	0,2695
13	Dibenz[a,h]anthracene	3.3325	2.8721	3.9346	4.40805	3,5961
14	Benzo[ghi]perylene	8.4712	2.7365	2.8005	5.86746	0,2178
15	Indeno[1,2,3-cd]pyrene	0.0073	<LQ	0.2380	0.13311	0,3112
PAHs total average value		179,8521	46.3116	213.6612	188.5553	103.0435

*LQ quantitation limit.

The different types of meat products suffer different heat treatment processes. Table 4 shows the type and temperature of the smoking process that each product suffers.

Table 4

Type and temperature of the smoking process

Name of the product	Type of smoking process	Temperature
Summer salami	Hot and cold	75-95°C and 30-40°C
Hungarian salami	Hot	75-95°C
Pork baloney	Hot	75-95°C
Pork sausages	Hot	75-95°C
Bacon	Very hot	95-110°C

The correlation graphic between the smoking temperature and total the PAH's content is shown in Figure 1. In Figure 2 is shown the values of benzo[a]pyrene in the samples analyses. A comparison between the total level of PAHs found in the meat samples and the benzo[a]pyrene content is shown in Figure 3.

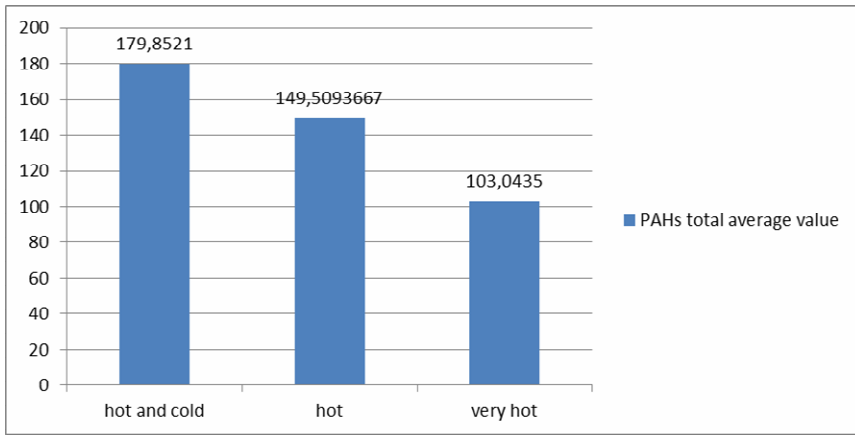


Fig. 1. Average total the PAH's content depending on the smoking type

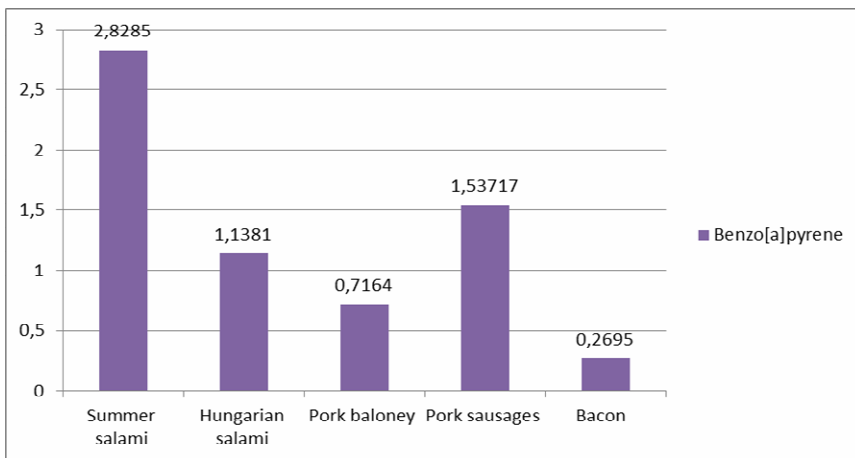


Fig. 2. Benzo[a]pyrene content in the meat samples

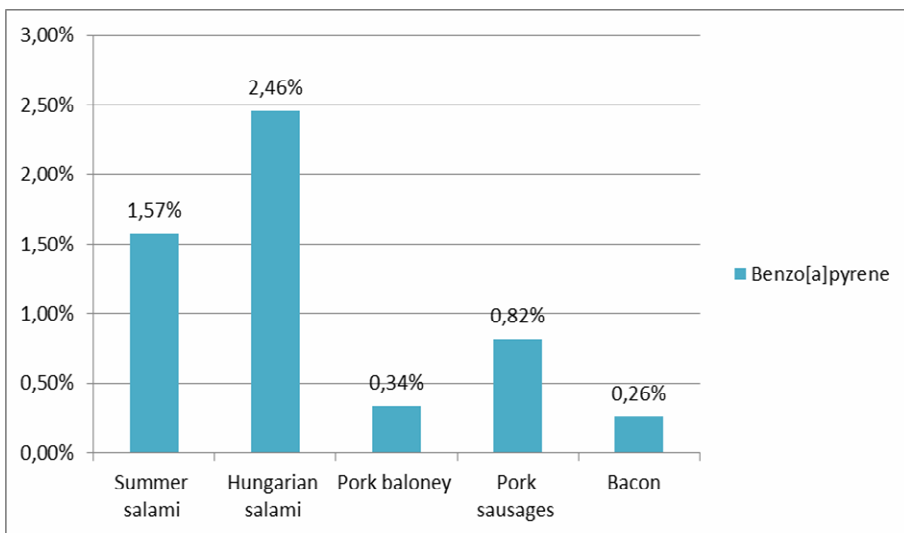


Fig. 3. Percentage of Benzo[a]pyrene form total PAH's in different meat samples

CONCLUSIONS

The highest value of total PAHs was found in the baloney samples. The lowest value of total PAHs was found in the Hungarian salami sample. Bezo[a]pyren, which is the only PAH's that has maximum level legislation, was found in all samples below the maximum limit, 5 µg/kg. Other PAHs that have mutagenic and carcinogenic effect on mice, like Benzo[b]fluoranthene, were found in very high values more than 20 times the value of Benzo[a]pyrene.

Different values of PAHs were found in meat products, made by the same manufacturer but sold in different shops proving that the level of PAH's found in the samples is also due both to the heat treatment and an incorrect storage and transport of the products.

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