codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON FOOD ADDITIVES AND CONTAMINANTS

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The Hague, the Netherlands, 25 – 29 April 2005

DISCUSSION PAPER ON POLYCYCLIC AROMATIC HYDROCARBONS (PAH) CONTAMINATION

Governments and international organizations in Observer status with the Codex Alimentarius Commission wishing to submit comments on the following subject matter are invited to do so **no later than 31 January 2005** as follows: Netherlands Codex Contact Point, Ministry of Agriculture, Nature and Food Quality, P.O. Box 20401, 2500 E.K., The Hague, The Netherlands (Telefax: +31.70.378.6141; E-mail: info@codexalimentarius.nl - ***preferably***), with a copy to the Secretary, Codex Alimentarius Commission, Joint FAO/WHO Food Standards Programme, FAO, Viale delle Terme di Caracalla, 00100 Rome, Italy (Telefax: +39.06.5705.4593; E-mail: Codex@fao.org - ***preferably***).

INTRODUCTION

1. At the thirty-six session of the Codex Committee on Food Additives and Contaminants (CCFAC), the Delegation of Denmark proposed to develop a Code of Practice for the reduction of contamination of food with polycyclic aromatic hydrocarbons (PAH) during food processing. In noting that these substances would be evaluated by JECFA in 2005, the Committee considered it premature to start elaboration of a Code of Practice and agreed that a working group led by Denmark, with assistance of Australia, Brazil, Cuba, European Community, Finland, Poland, Spain and the United States would prepare a discussion paper to set out the issues concerning PAH in foods for circulation, comments and consideration by the 37th session of the CCFAC (ALINORM 04/27/12, para. 217).

SCOPE

2. The general purpose of the Codex Alimentarius (through the Codex Standards) is to protect consumers' health while ensuring fair practice in the food trade.

3. PAHs constitute a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms. Hundreds of individual PAH may be formed and released as a result of incomplete combustion or pyrolysis of organic matter, during industrial processes and other human activities. PAH are also formed in natural processes, such as carbonisation. As some of the polycyclic aromatic hydrocarbons (PAH) are carcinogenic and mutagenic substances, the purpose of this paper is to provide the background for a discussion at the Codex Committee on Food Additives and Contaminants on ways to reduce contamination of foods with PAH during processing.

4. The scope of this discussion paper is restricted to cover contamination of food with PAH from processing and not to cover the contribution from environmental contamination. PAH contamination in the environment as a source of PAH in food should be covered either by source directed measures or good agricultural practice (GAP), when growing crops and selection of appropriate farmland1.

BACKGROUND

5. PAH are contaminants in food. Sources of PAH are contamination2 from processes or from the environment.

6. Most of the Codex Commodity Standards have requirements for contaminants like heavy metals. The Codex Committee on Fish and Fishery Products have discussed a draft standard for smoked fish at their twenty-seventh meeting, 2004 (step 3). However, PAH are not specifically covered by this standard yet, nor from other the existing commodity standards.

SOURCES OF PAH IN FOOD.

7. PAH contamination of food can originate from different sources among which the sources of major importance are the environment and food processing. Processing procedures, such as smoking, drying, and cooking of food are recognized a major source of contamination by PAH.

FOOD PROCESSING, WHICH CAN CONTAMINATE WITH PAH.

8. PAH may be formed during processing and domestic food preparation, such as:

- Smoking,
- Drying,
- Roasting,
- Baking,
- Frying and
- Barbecuing/grilling.

9. Although not precisely known, it is likely that there are several mechanisms of PAH formation such as melted fat that undergoes pyrolysis when dripping onto the heat source and pyrolysis of the food as a result of cooking temperatures at above 200°C.

10. A number of variables, including cooking method (grilling, frying, roasting), time, and fuel, as well as the distance between the food and the heat source and drainage of fat, results in the production in the food of a number of compounds including PAH. For example, a comparison of PAH levels in duck breast steaks undergoing various processing and cooking treatments for 0.5 hour to 1.5 hours, showed that charcoal grilled samples without skin contained the highest amount of total PAH (320 µg/kg), followed by charcoal grilling with skin (300 µg/kg), smoking (210 µg/kg), roasting (130 µg/kg), steaming (8.6 µg/kg) and liquid smoke flavouring (0.3 µg/kg).

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1 Some information on the sources of environmental PAH is provided in Annex I.

2 *Contaminant* is defined as "any substance not intentionally added to food, which is present in such food as a result of the production (including operation carried out in crop husbandry, animal husbandry and veterinary medicine), manufacture, processing, preparation, treatment, packing, packaging, transport or holding of such food or as a result of environmental contamination. The term does not include insect fragments, rodent hair and other extraneous matter".

Smoking

11. Traditional smoking of food such as meat and fish products and some cheeses has been used for centuries in many countries. Originally the purpose was to preserve the food, partly by drying and partly by adding anti-microbiological constituents such as phenols from the smoke to the food. Smoking is now primarily used to achieve the characteristic taste and appearance of smoked food with preservation playing a minor role. However, smoking has an influence on the shelve life of food because the smoke may inhibit growth of some microorganisms depending of the contents of some components like phenols in the smoked food.

12. The traditional smoking process method may differ and as a result, data on PAH in smoked foods are highly variable. The type and composition of wood and herbs used to smoke foods, use of direct3 or indirect smoking, use of a washing procedure after the smoke process and different temperatures, the type of generator used, the accessibility of oxygen; temperature; and smoking time all contribute to its inconsistencies.

13. Data reported in the literature on PAH in smoked foods are highly variable. The main reason for such discrepancies is the differences in the procedures used for smoking. The content of 12 PAH in smoked fishery products from modern smoking kilns with external smoke generation and procedures that remove high-boiling compounds such as PAH and particles potentially containing PAH have been compared with products from traditional smoking kilns where the smoke is generated in direct contact with the product. The average benzo [a] pyrene concentration determined for the traditional kilns was 1.2 µg/kg and 0.1 µg/kg for the modern kilns.

14. The flavour of smoke can also be added to food by the use of smoke flavours. There are different types of smoke flavours, but they can have a content of PAH. As an example, the EU legislation on smoke flavourings has a limit on benzo [a] pyrene in foodstuffs with added smoke flavour4,5.

Direct drying

15. Drying of food can take place either by indirect or direct drying processes. Indirect drying is not regarded as a source of PAH contamination, and will not be addressed with in this paper.

16. In direct heating and drying, combustion products are directly mixed with the process environment (typically process solids and a forced "air" stream). Because radiation transfer is rapid, typically at high temperature, and ceases upon reaching a boundary (the outer layer of process matter), it is often undesirable and unnecessary. Therefore, natural and forced convection heat transfer engineering may dominate the drying processes.

17. In *direct heating (convection drying),* hot drying gases are in direct contact with the food to be dried and is heating it whereby the material to discharges moisture. The heat energy of a system must:

- Heat the dryer feed to the vaporization temperature of the "light" components
- Vaporize and/or free the liquid/by-products above the solids' surface
- Heat solids to the final desired temperature, for the desired duration of time, and
- Heat the vapour to the final desired temperature.

18. Numerous factors, including equipment cost and availability of energy sources often result in similar foods being dried in very different ways. Common direct drying/heating operations and applications include:

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3 *Direct smoking* is the type of smoking process where the smoke is developed in the same room as the food is processed; *indirect smoking* uses smoke generators and the smoke is developed in a separate room and lead into the smoking chamber.

4 *Smoke flavourings* are regulated under the EU Framework directive for flavourings. A new regulation includes a limit for the content in the flavour preparation/condensate on

- benz(a)pyrene on 10 micrograms/kg and for
- benz(a)anthrazene on 10 micrograms/kg

5 Information on the smoking process is found the Council of Europe Publication: Health aspects of using smoke flavours as food ingredients, (Council of Europe, 1992). The publication is enclosed in English and French.

- Drying to remove water (and/or other solvents/chemicals) added, left, or produced during processing
- Starch, stalk and husk dryers, and fruit peel and feed dryers, used in beet and cane sugar manufacturing, grain mill products etc.

6. Barbecuing/grilling

19. Barbecuing or grilling are processes mostly used in the catering sector and in private homes. PAH formation during charcoal grilling is shown to be dependent upon the fat content of the meat, the duration of cooking and the temperature used. For example a heavily barbecued lamb sausage contained 14 µg/kg of the sum of six PAH, considered by European Union Scientific Committee on food (2002) to be carcinogenic and mutagenic.

20. The presence of PAH was studied in several samples of meat and fish that were grilled on two geometrically different gas barbecues. In contrast to a horizontal barbecue, the vertical barbecue prevented fat from dripping onto the heat source, and the PAH levels were 10-30 times lower than with the horizontal system.

LEVELS OF PAH IN SOME FOODSTUFFS

21. Some examples are given on the content of PAH in foods after processing of food (such as drying and smoking) and cooking of foods at high temperatures (grilling, roasting, frying):

- Levels as high as 200 µg/kg food have been found for individual PAH in *smoked* fish and meat
- In *barbecued* meat, 130 µg/kg has been reported whereas the average background values are usually in the range of 0.01-1 µg/kg in uncooked foods
- Contamination of vegetable oils (including olive residue oils) with PAH usually occurs during technological processes, such as during *direct fire drying*, where combustion products may come into contact with the oil seeds or oil. PAH levels in crude edible oils vary widely and refining processes can reduce the levels significantly.

TOXICOLOGICAL CONSIDERATIONS

22. PAH are on the agenda for JECFA is 2005. One of the main purposes of Codex Alimentarius is to ensure the protection of consumers and the safety aspects have to be taken into account in all cases.

23. In the European Union, thirty-three PAH were evaluated by the he Scientific Committee on Food (SCF 2002). Among these, 15, namely benzo[*a*]anthracene, benzo[*b*]-, benzo[*j*]- and benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, cyclopenta[*cd*]pyrene, dibenz[*a,h*]anthracene, dibenzo[*a,e*]-, dibenzo[*a,h*]-, dibenzo[*a,i*]-, dibenzo[*a,l*]pyrene, indeno[1,2,3-cd]pyrene and 5-methylchrysene show clear evidence of mutagenicity/genotoxicity in somatic cells in experimental animals *in vivo*. The most potent PAH appear to be compounds with a bay- or fjord region (Fig.1).

24. Animal's studies have shown that PAH can cause a variety of toxicological effects, such as haematological effects, reproductive and developmental toxicity, and immunotoxicity. The most critical effects, which can occur at very low doses, are carcinogenicity and genotoxicity. The carcinogenic and genotoxic potentials of PAH are largest among the high molecular weight PAH, i.e. compounds with 4 rings or more. For most PAH, the carcinogenic potential constitutes the critical effect for the hazard and risk characterization. A number of PAH, as well as coal tars and various complex mixtures containing PAH from combustion emissions, have shown carcinogenicity in experimental animals and genotoxicity and mutagenicity in vitro and in vivo.

25. In general, the evidence of genotoxicity shows considerable overlapping with carcinogenicity in agreement with the mechanistic link between DNA adduct formation, mutations, and cancer outcome following PAH exposure.

26. With the exception of benzo[*ghi*]perylene the15 genotoxic PAH have also shown clear carcinogenic effects in various types of bioassays in experimental animals. Although only benzo[*a*]pyrene has been adequately tested using dietary administration, these compounds may be regarded as potentially genotoxic and carcinogenic to humans. They represent a priority group in the assessment of the risk of long-term adverse health effects following dietary intake of PAH.

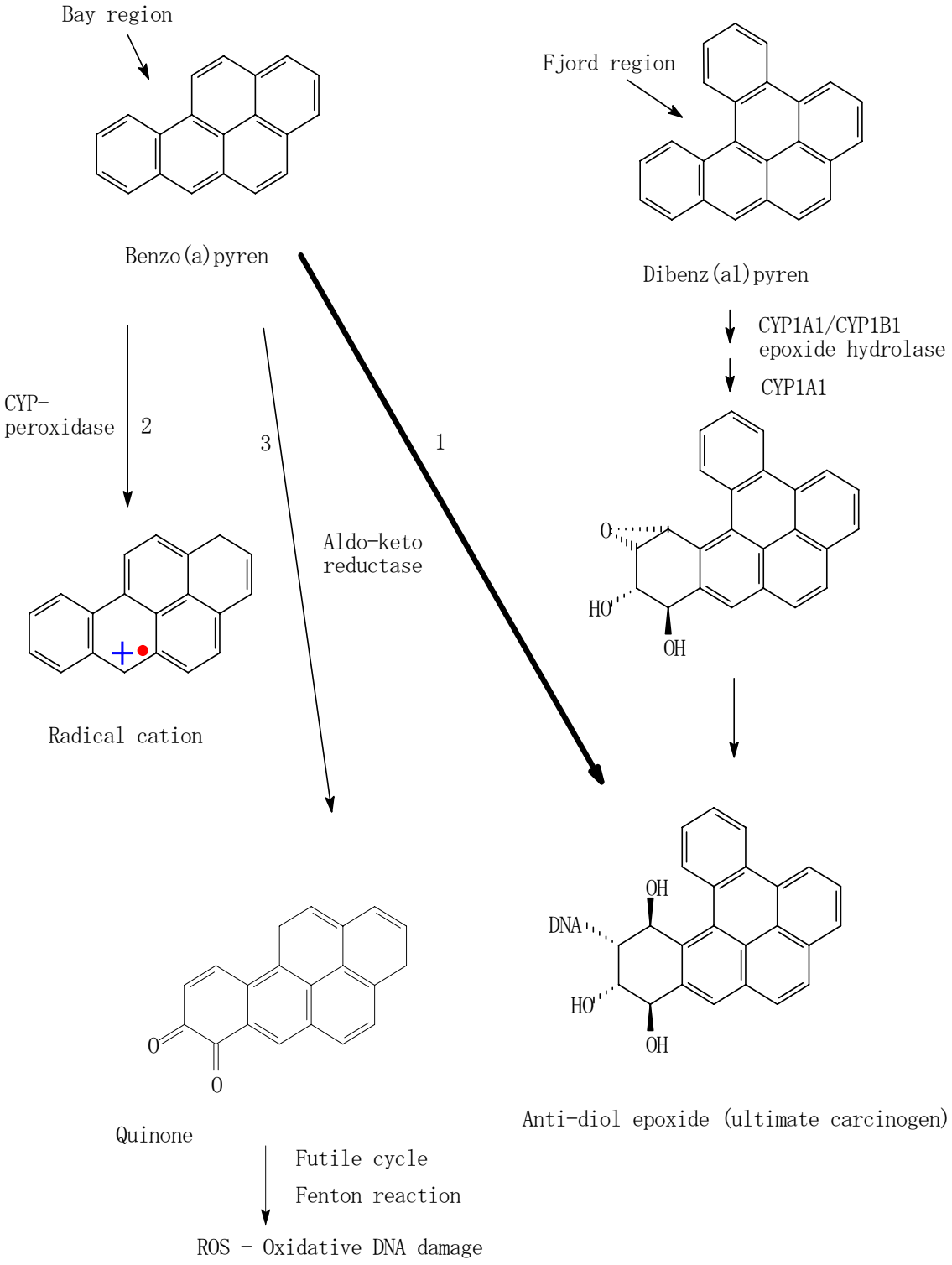

Figure 1. Activation of Bay and Fjord region PAH by phase 1 enzymes (adapted with a few modifications from IPCS, 1998). ROS = Reactive Oxygen Species.

MEASURES TO REDUCE PAH CONTAMINATION OF FOODS AND SOME RISK MANAGEMENT OPTIONS.

27. The amount of PAH formed in foods can be reduce by altering cooking or processing techniques. Some examples are given below.

Drying

28. Direct contact of oil seeds or cereals with combustion products during drying processes has been found to result in formation of PAH and should therefore be avoided.

Smoking

29. PAH contamination of smoked foods can be significantly reduced by replacing direct smoking (with smoke developed in the smoking chamber, traditionally in smokehouses) with indirect smoking. The latter is obtained by an external smoke generator, which, in modern industrialised kilns, is operated automatically under properly controlled conditions, and smoke can be washed before coming into contact with the food.

30. Use of smoke flavourings is generally considered to be of less health concern than the traditional smoking process, as it may minimise PAH contamination

Barbecuing/grilling

31. Simple practices such as

- selecting lean meat and fish
- preventing direct contact of foods with flames,
- using less fat for grilling, and
- cooking at lower temperature for a longer time,

results in a significantly reduced PAH contamination of foods.

32. Broiling can significantly reduce PAH levels. Fat should not drip down onto an open flame, which could send up a column of smoke to increase PAH contamination of the food. The use of medium to low heat and placement of the meat further from the heat source, can greatly reduce formation of PAH.

33. A management option for reduction of the content of PAH in barbecued food can be done via advise to the public like e.g.

- “Use vertical barbecues instead of horizontal barbecues” and
- “Don’t eat barbecued food too often”
- “Limit smoke formation by not letting oil drip on the coal”
- “Don’t eat burned food”.

34. The intensity of flavour is not necessarily associated with the depth of the brown colour of grilled foods. It is therefore not necessary to overcook the food to get the flavour. However, proper cooking temperature should be maintained to destroy food borne pathogens or endogenous toxins.

DISCUSSION

35. The paper describes the sources for PAH during processing: Some information on levels, chemistry and the toxicology. Good manufacturing practice, including choice of processes after evaluation of the potential contamination of the food could reduce the formation of PAH, and well as other contaminants such as heterocyclic amines, and nitrosamines. However, it should be highlighted that in some cases, when conditions for reduced formation of one process contaminants the formation of others may increase.

36. Concerning the smoking process, direct smoking requires less equipped production facilities that indirect smoking. The use of smoke flavours might not be accepted by consumers, even though the contamination of the final food will be less than after traditional smoking, even though the consistency and flavour are equal.

OPTIONS FOR DECISIONS

37. The use of processing should not contaminate food and endanger human health. At the same time, proper processing would reduce the level of microorganisms and improve the variety and shelve life of food. Processes such as the smoking have been used for centuries and smoked food is traditional food in many countries. However, consumer safety is highly important also in this case and the content of PAH formed due to production can be reduced.

38. CCFAC should take initiatives to reduce the content of PAH contamination due to processes in food, taking into account that more information are needed before elaborating on a Code of Practice for reducing PAH contamination in food on

- PAH formation and levels as a result of various food processing (e.g., smoking, drying, grilling), as well as
- JECFA evaluation in 2005.

39. Some options are:

a. CCFAC start to develop a Code of Good Manufacturing Practice for the use of direct drying and/or

b. CCFAC start to develop a Code of Good Manufacturing Practice for the use of the smoking process

c. CCFAC start to develop a Code of Good Manufacturing Practice *both* for the use of direct drying and smoking of food

d. CCFAC start to develop a Code of Good Manufacturing Practice for the use of barbecuing in the catering sector

e. CCFAC develop advice to consumers concerning barbecuing

f. CCFAC examine Codex Standards on smoked and dried food to ensure than GMP in relation to contaminants like PAH is foreseen.

40. During the evaluation in CCFAC of chemicals found as contaminants, the normal procedure would be to consult the risk assessors, JECFA, before any decision is taken.

41. The above-mentioned draft papers should also be sent to CCFAC for endorsement.

REFERENCES

Council of Europe Health aspects of using smoke flavourings as food ingredients,., 1992 (prepared by Fabech, B. & Gry, J., Danish Veterinary and Food Administration).

SCF (2002) Opinion of the Scientific Committee on Food on the risks to human health of polycyclic aromatic hydrocarbons in food. Scientific Committee on Food , European Commission.

Levnedsmiddelstyrelsen: Røgning af levnedsmidler, Fabech, B. & Larsen, J.C, Publ. 135, 1986

Annex I

Sources of environmental PAH contamination

Foods can be contaminated by PAH that are present in air (by deposition), soil (by transfer) or water (deposition and transfer). The sources, natural and mostly anthropogenic, of PAH in the environment are numerous and include:

- Stubble burning and spreading of contaminated sewage sludge on agricultural fields
- Exhausts from mobile sources (motor vehicles and aircrafts)
- Industrial plants (e.g. aluminium foundries, incinerators
- Wood preservation, use of tar coated
- Domestic heating with open fireplaces
- Burning of coal for thermal and electric energy
- Oil pollution of surface waters and soils
- Forest fires and volcanic eruptions

The contribution from some of these sources could be reduced if the potential problems are covered by good agricultural practice, e.g. spreading of contaminated sludge.

Vegetables may be contaminated by the deposition of airborne particles or by growth in contaminated soil. Meat, milk, poultry and eggs will normally not contain high levels of PAH due to rapid metabolism of these compounds in the species of origin. However, some marine organisms, such as mussels and lobsters are known to adsorb and accumulate PAH from water, which may be contaminated, for example by oil spills.

Example of a management option

The waxy surface of vegetables and fruits can concentrate low molecular mass PAH mainly through surface adsorption. The concentrations of PAH are generally greater on plant surface (peel, outer leaves) than on internal tissue.

Consequently, washing or peeling may remove a significant proportion of the total PAH. Particle bound high molecular mass PAH which remain on the surface are easily washed off whereas low molecular mass compounds which are in the vapour phase can penetrate the waxy layer of fruits and vegetables and are less efficiently removed by washing.

Annex II

Polycyclic aromatic hydrocarbons included in the EU Risk Assessment opinion

Common name	CAS name	CAS Registry No.	Abbreviation
Acenaphthene	Acenaphthylene	83-32-9	AC
Acenaphthylene	Acenaphthylene, 1,2-dihydro-	208-96-8	ACL
Anthanthrene	Dibenzo[def,mno]chrysene	191-26-4	ATR
Anthracene	Anthracene	120-12-7	AN
Benz[α]anthracene	Benz[α]anthracene	56-55-3	BaA
Benzo[α]fluorene	11 H-Benzo[α]fluorene	238-84-6	BaFL
Benzo[b]fluorene	11 H-Benzo[b]fluorene	243-17-4	BbFL
Benzo[β]fluoranthene	Benz[e]acephenanthrylene	205-99-2	BbFA
Benzo[ghi]fluoranthene	Benzo[ghi]fluoranthene	203-12-3	BghiF
Benzo[j]fluoranthene	Benzo[j]fluoranthene	205-82-3	BjFA
Benzo[k]fluoranthene	Benzo[k]fluoranthene	207-08-9	BkFA
Benzo[ghi]perylene	Benzo[ghi]perylene	191-24-2	BghiP
Benzo[c]phenanthrene	Benzo[c]phenanthrene	195-17-7	BcPH
Benzo[a]pyrene	Benzo[a]pyrene	50-32-8	BaP
Benzo[e]pyrene	Benzo[e]pyrene	192-97-2	BeP
Chrysene	Chrysene	218-01-9	CHR
Coronene	Coronene	191-07-1	CoR
Cyclopenta[cd]pyrene	Cyclopenta[cd]pyrene	27208-37-3	CPP
Dibenz[a,h]anthracene	Dibenz[a,h]anthracene	53-70-3	DBahA
Dibenzo[a,e]pyrene	Naphtho[1,2,3,4-def]chrysene	192-65-4	DBaeP
Dibenzo[a,h]pyrene	Dibenzo[b,def]chrysene	189-64-0	DBahP
Dibenzo[a,i]pyrene	Benzo[rst]pentaphene	189-55-9	DBaiP
Dibenzo[a,l]pyrene	Dibenzo[def,p]chrysene	191-30-0	DBalP
Fluoranthene	Fluoranthene	206-44-0	FA
Fluorene	9H-Fluorene	86-73-7	FL
Indeno[1,2,3-cd]pyrene	Indeno[1,2,3-cd]-pyrene	193-39-5	IP
5-Methylchrysene	Chrysene, 5-methyl-	3697-24-3	5-MCH
1-Methylphenanthrene	Phenanthrene, 1-methyl	832-69-9	1-MPH
Naphthalene	Naphthalene	91-20-3	NA
Perylene	Perylene	198-55-0	PE
Phenanthrene	Phenanthrene	85-01-8	PHE
Pyrene	Pyrene	129-00-0	PY
Triphenylene	Triphenylene	217-59-4	TRI