Phthalates in Food – Risk Assessment and Risk Management

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PHTHALIC-ACID ESTERS - basic structure
« A chemical used to make plastic soft and flexible has been detected in a number of food products made in Taiwan.

Sports drinks, juices, tea, fruit jams or syrups produced by 10 Taiwan based companies would be banned from entering China, said the General Administration of Quality Supervision, Inspection and Quarantine. **DEHP – di(2-ethylhexyl) phthalate was found in many items.**”
“The quality watchdog has issued a temporary ban on such food, the China Daily reported. Taiwan’s health authorities have also announced that DEHP was found in some bottled beverages and dairy products and have ordered 168 processing companies to recall over one million tainted items.”
Taiwan authorities suspect at least one food manufacturer added DEHP to an emulsifier as a cheap substitute for palm oil. The resulting product, called cloudy agent, which stabilizes emulsions, is often found in fruit jelly, yoghurt, juice based drinks, sport drinks and other beverages. »
Origin of DEHP? - China Post Press Flash (June 7)

“...The company, blamed for the circulation of plasticizer-contaminated clouding agents, was found to have sold similarly-contaminated fruit flavours and flavoured syrups to distributors supplying bakeries, confectioners, and soda makers. Sport Drinks and Fruit Jellies were found to contain levels ranging from 11 mg/L to 43 mg/L.”
“The Ministry of Health (MoH) of the P.R. China has issued an internal control document establishing limits for the presence of DEHP, DINP (di-isononyl phthalate) and DBP (di-n-butyl phthalate) in finished food and food additives of:

- 1.5 mg/kg (DEHP)
- 9.0 mg/kg (DINP)
- 0.3 mg/kg (DBP).”
“The MoH has instructed quality inspection services to carry out analytical work on food and food additives. Samples are taken from food producers and food ingredient suppliers, including flavour houses, for testing against the limits.”
P.R. China- Maximum Permissible Levels in Food - IOFI Letter (June 27)

“No distinction is currently made between final food and food ingredients including flavourings. The fact that flavourings cannot be consumed as such is not recognized by the authorities”
Components of Flavourings

- Chemically-identified substances (single substances)
Components of Flavourings

- Essential Oils (EOs) and extracts (complex substances of natural origin, also called natural complex substances)
Components of Flavourings

- Folded (concentrated) EOs
Components of Flavourings

- Other non-flavour ingredients (e.g. solvents, preservatives, antioxidants, emulsifiers…….)
Use of Compounded Flavourings (CFs)

• Typically added at low levels to food to optimize taste and aroma

  – CFs added to food
    • up to 5000 mg/kg ( < 0.5%)

  – More concentrated CFs (folded EOs) are added at lower levels
    • up to 1000 mg/kg ( <0.1%)
Use of Compounded Flavourings (CFs)

- Variation in application levels is based on concentration of the material
Use of Compounded Flavourings (CFs)

- Objective is to achieve a certain flavour impact in line with «expectation»
Use of Compounded Flavourings (CFs)

- CFs are intended only to be used/consumed in diluted form!
IOFI ‘PHTHALATES’ PROJECT: DEHP in CFs

- Objective: establishing the ‘typical’ phthalic-acid ester (PAE) level in flavour materials
- Focus on DEHP
IOFI ‘PHTHALATES’ PROJECT: DEHP in CFs

- DEHP levels actually measured in over 1100 flavourings
- Sources included China, Japan, Europe, USA
IOFI ‘PHTHALATES’ PROJECT: DEHP in CFs

- DEHP detection limits < 0.01 mg/kg (CFs) to > 0.1 mg/kg (Folded EOs)
- 90th, 95th and 99th percentiles of DEHP in flavourings
Levels of DEHP in Flavourings

- Chemically-identified substances
  - 90th and 95th %; < 0.1 mg/kg and 2.90 mg/kg

- Essential Oils
  - 90th and 95th %; 10.2 mg/kg and 34.3 mg/kg

- Folded Essential Oils
  - 90th and 95th %; 46.9 mg/kg and 100.4 mg/kg
  - 50 samples: < 3.1 mg/kg
Levels of DEHP in Flavourings

- Overall levels of DEHP in flavourings
  - 95th and 99th %; 4.08 mg/kg and 12.22 mg/kg

- Conclusion: levels in flavourings are comparable to levels found in fatty foods
  - < 1 to 16.9 mg/kg (Clark et al (2003))
Examples: Levels of DEHP migrating into food from addition of
flavouring

95\textsuperscript{th}%

Flavouring added at 5000 mg/kg

Flavouring

DEHP level = 4.08 mg/kg

DEHP concentration added to food at 95\textsuperscript{th}%

0.020 mg/kg

Food

Example 1: 75 times less than DEHP Limit

P.R. China limit of DEHP into food = 1.5 mg/kg
Examples: Levels of DEHP migrating into food from addition of flavouring

95th%

Flavouring added at 5000 mg/kg

DEHP concentration added to food at 95th%

0.020 mg/kg

Example 1: 75 times less than DEHP Limit

99th%

Flavouring at 5000 mg/kg

DEHP concentration added to food at 99th%

0.061 mg/kg

Example 2: 25 times less than DEHP Limit

P.R. China limit of DEHP into food = 1.5 mg/kg
Unintended Sources of PAE in CFs

- Environmental sources during growing
- Enters during manufacture, from packaging, and during transport
- Extent of migration into flavouring depends on extent and type of processing and the chemical nature of flavouring materials and compounded flavourings
Unintended Sources of PAE in CFs

To Note:

- Intended addition of PAE is forbidden
- Intentional addition of significant amounts of PAE damages flavouring properties!
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

• IOFI Guidelines for PAE reduction in raw materials and compounded flavourings during production, storage and transportation

  – Sources of PAE Contamination

  ▪ Raw Materials (essential oils, folded oils, absolutes, etc.)

  ▪ Processing (extraction solvents, extraction and distillation equipment, filter sheets and aids, etc.)

  ▪ Transportation & packaging (storage tanks, flexible hoses, packaging, etc.)
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- Protocols for testing potential PAE release from polymeric materials used in processing equipment, storage, transportation and packaging
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

• PAE Analysis - Method Evaluation

  ➢ Gas chromatography - mass spectrometry in selected-ion monitoring (SIM) mode

  ➢ Particular recommendations:
    ➢ use of labelled internal standard(s)
    ➢ injector temperature at least 300 °C

  ➢ Sample dilution and direct injection
IOFI ‘PHthalates’ Project: Additional Actions

• PAE Analysis - Method Evaluation

- 4 PAE examined which are the most frequently observed in flavourings, usually at trace levels:
  - di-isobutyl phthalate (DIBP)
  - di-n-butyl phthalate (DBP)
  - di-(2-ethylhexyl) phthalate (DEHP)
  - di-isononyl phthalate (DINP)

- Blank runs are essential - PAE are everywhere!
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

• PAE Analysis - Method Evaluation

- 3 samples
  - cold-pressed lemon oil, straight
  - cold-pressed lemon oil, 5-folded
  - vanilla extract

- as such and spiked with DIBP, DBP, DEHP, and DINP

- spiking levels from approximately 5 to 200 mg/kg, up to 500 mg/kg for DINP (mixture of isomers)
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- PAE Analysis - Method Evaluation

- 13 industry laboratories located in Europe, North America and Asia

- Sample management, dispatching and data collection and analysis entrusted to a professional laboratory proficiency-testing organization (BIPEA, France)
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

• PAE Analysis – Results

- Generally satisfactory for DIBP, DBP, and DEHP in essential oils (lemon as example):
  - Reproducibility RSDs 5-11 %
  - Recoveries 92-102%
  - Observed pragmatic limit of quantification ca. 5 mg/kg
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- Cold-pressed lemon oil – spiked (initial PAE < 5 mg/kg)

<table>
<thead>
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<th></th>
<th>DIBP</th>
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<th>DEHP</th>
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<tr>
<td>Robust mean, mg/kg</td>
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<tr>
<td>RSD R</td>
<td>8%</td>
<td>5%</td>
<td>8%</td>
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<td>Spike, mg/kg</td>
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<td>Recovery</td>
<td>102%</td>
<td>96%</td>
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IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- Cold-pressed lemon oil x5

<table>
<thead>
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<th>as such</th>
<th>DIBP</th>
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<th>DEHP</th>
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<tr>
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<tr>
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<td>RSD R</td>
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<td>N° of results used</td>
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<td>12</td>
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<tr>
<td>Robust mean, mg/kg</td>
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<tr>
<td>RSD R</td>
<td>10%</td>
<td>11%</td>
<td>8%</td>
</tr>
<tr>
<td>Spike, mg/kg</td>
<td>25</td>
<td>8.7</td>
<td>110</td>
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<tr>
<td>Recovery</td>
<td>96%</td>
<td>94%</td>
<td>92%</td>
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IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- PAE Analysis – Results

  - issues with matrices which are not completely volatile, e.g. vanilla extract:
    - highly concentrated
    - presence of fat
    - not completely soluble in dilution solvents
    - material in suspension

  - further work is under way (sample preparation)
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

• PAE Analysis – Results

➢ issues with DINP - a special case !

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<td>EINECS Nr</td>
<td>271-090-9</td>
<td>249-079-5</td>
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<tr>
<td>Substance name (IUPAC)</td>
<td>1,2-Benzenedicarboxylic acid, di-C8-10 branched alkylesters, C9 rich</td>
<td>Di-iso’nonyl phthalate</td>
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<td>Molecular formula</td>
<td>$C_{9+2x}H_{3+4x}O_4$ with $x = 8$ to $10$ ($x = 9$ as main constituent), average $C_{26}H_{42}O_4$</td>
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<tr>
<td>Molecular weight</td>
<td>Average 420.6</td>
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Note: “iso” denotes a mixture of isomers and does not refer to IUPAC definition!
IOFI ‘PHTHALATES’ PROJECT: ADDITIONAL ACTIONS

- issues with DINP - a special case!
CONCLUSIONS

• SAFETY
  – gross contamination (adulteration!) as in Taiwan is hopefully in the past
  – trace levels in flavourings of the order of those in fatty foods
  – 200-1000 fold dilution produces negligible contribution, BUT:
  – flavour industry will continue efforts to reduce exposure to ALARA levels

• ANALYTICAL
  – establish clean-up for partially non-volatile matrices
  – establish marker compound(s) for DINP (cf. case of PCBs etc.)
  – further inter-laboratory testing
CONCLUSIONS

• REGULATORY
  – P.R. China Ministry of Health has taken a pragmatic approach in dealing with PAE in flavourings
  – MoH has now established by a new internal order that the total sum of PAE in flavourings should not exceed 60 mg/kg.
  – Flavourings containing PAE up to that level are permitted for use in production, for sale and application, but urges the Industry to develop approaches for continuous PAE reductions
THANK YOU FOR YOUR ATTENTION!