Analytical considerations from scientific point of view

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Context

- Stockholm Convention article 6, para 2c "… concentration levels of the chemicals listed in Annexes A, B and C in order to define the low persistent organic pollutant content";
- Low persistent organic pollutant content is given by a number and a unit; *e.g.,* 50 mg/kg;
- Analytically, we have to know:
  - Which chemical should be determined?
    (group such as PCB, POP BDEs; single chemical (congener) such as hexachlorobenzene (HCB); sum of isomers such as α-HCH, β-HCH, and lindane or PCDD/PCDF, which are 17 congeners to be reported as toxic equivalents (TEQ) (Annex C Stockholm Convention);
  - What should be analyzed? pure POP (chemical) or [consumer] product/article;
- Application referred to in paragraph 1 (d) (ii) "… wastes, including products and articles upon becoming wastes, are: Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed."

Analytical Approaches

All analysis needs experienced staff; uses standard operational procedures; documentation;

1. Targeted analysis (accurate, labor-, time-intensive, and [relatively] expensive *per* sample):
   - Applies instrumentation in a chemical laboratory to identify and quantify given chemicals (analytes);
   - Reports results on numeric basis for each analyte. **Typically used for enforcement.**
   - Examples: POPs pesticides and PCB with GC-ECD, PBDE with GC/MS, PCDD/PCDF with GC/HRMS; PFOS and HBCD with LC/MS-MS.
2. Screening methods (high-throughput, semi-quantitative, faster, less expensive *per* sample):
   - Used to identify few samples from a large number of samples above a given content to be distinguished from those below the threshold;
   - No false negatives allowed. Often followed by a confirmatory method (see 1. above);
   - Examples of biological methods (bioassays): fluorescence response from receptor binding (CALUX), etc.
   - Examples of chemical methods: direct injection MS, short columns with ECD; simple detectors for sum parameters such as Cl in specific PCB oil tests; bromine determination with XRF.

Mindful of:

- All determination needs clear goal and procedures to follow;
- No deviation permitted (no lower/higher values; not more compounds; no other matrix);
- These are specific to a laboratory and cannot be transferred; respect mandates;
- Determination of low POP content is NOT trace analysis; therefore, lowest detection limit is not the objective of the enforcement laboratory;
- Methods must be robust (accurate enough, repeatable, replicable, QA/QC proven);
- Timeliness/rapid reliable response may be more important than costs;
- In cases of routine disposal operations or accidents (especially remediation), costs for POPs analysis are minor (negligible).

Waste Management Approaches (example)

- E-waste may contain a variety of hazardous chemicals regulated under various regimes, including plastics containing up to % amounts of POPs flame retardants, CRTs, metals;
- For contaminants contained in materials or articles, pretreatment separating them from the matrix is important. Analytically, needs extraction and clean-up of the sample.
- Characterization of potentially POP-containing plastics is done in two ways:
  1. Collection of plastic fraction, shredding followed by separation (wind, flotation, magnetic, etc.) and analysis of these fractions for POPs (European approach), or
  2. Classification of plastics and other components in the major e-waste streams according to product; e.g., printed circuit boards, TV sets (), refrigerators (fluorine extraction), washing machines, computers, telephones – Chinese approach: only material parts below low POP content can be recycled; others are eliminated/destroyed.