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Meeting of the Group of Technical Experts on

Waste Thresholds to be Established Pursuant to

Paragraph 2 of Article 11 of the Convention

Minamata Convention on Mercury

Osaka, Japan, 27-29 May 2019

Information relating to analytical methods of mercury in wastes[[1]](#footnote-1)

Note by the secretariat

1. This note provides information relating to analytical methods of mercury in waste. Annex 1 provides the section relevant to analytical methods of mercury in wastes extracted from technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with mercury or mercury compounds. Annex II provides the submission from one expert.

Annex I: Section relevant to analytical methods of mercury in wastes extracted from technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with mercury or mercury compounds (Revised final version, 15 May 2015)

 III. Guidance on environmentally sound management (ESM)

 D. Sampling, analysis and monitoring

1. Sampling, analysis and monitoring are critical components of mercury waste management. Waste sampling, analysis and monitoring should be conducted by trained professionals in accordance with well-designed programmes using internationally accepted or nationally approved methods and should be carried out using the same methods throughout the lives of such programmes. They should also be subjected to rigorous quality assurance and quality control measures. Mistakes in sampling, analysis or monitoring or deviation from standard operational procedures can result in meaningless data or even programme-damaging data. Each party, as appropriate, should therefore develop standards to ensure that training, protocols and laboratory capabilities are in place for sampling, monitoring and analytical methods and that those standards are enforced.
2. Because there are numerous reasons for sampling, analysing and monitoring and because waste comes in so many different physical forms, many different sampling, analysis and monitoring methods are available. Although it is beyond the scope of this document to discuss them specifically, the next three sections consider key elements that should be included in sampling, analysis and monitoring activities. Waste testing priorities should be set based on existing knowledge (or lack thereof) of the mercury content of different types of waste (e.g., testing waste mercury lamps is unlikely to be a high priority, as significant information about their mercury content is readily available).
3. For information on good laboratory practices, the OECD series on good laboratory practice (OECD, various years) may be consulted; on general methodological considerations, the UNEP/WHO *Guidance for identifying populations at risk from mercury exposure* contains helpful information and may be used.[[2]](#footnote-2)18 Further guidance on global monitoring of mercury is being developed through a UNEP GEF-funded project that is also expected to establish an online databank of operational mercury laboratories.[[3]](#footnote-3)19

 1. Sampling

1. The overall objective of any sampling activity is to obtain a sample that can be used for a targeted purpose, e.g., site characterization, compliance with regulatory standards or determination of the suitability of proposed treatment or disposal methods. This objective should be identified before sampling is started. It is indispensable that quality requirements for equipment, transportation and traceability be met.
2. Standardized sampling procedures should be established and agreed upon before the start of the sampling campaign (both matrix- and mercury-specific). Elements of these procedures include the following:
	1. The number of samples to be taken, the sampling frequency, the duration of the sampling project and a description of the sampling method to be used (including quality assurance procedures put in place, e.g., use of appropriate sampling containers[[4]](#footnote-4)20 and field blanks and of chain-of-custody procedures);
	2. Selection of locations or sites at which mercury wastes are generated and time and date of sample-taking (including description and geographic localization);
	3. Identity of person who took the sample and conditions during sampling;
	4. Full description of sample characteristics – labelling;
	5. Preservation of the integrity of samples during transport and storage (before analysis);
	6. Close cooperation between the sampler and the analytical laboratory; and
	7. Appropriately trained sampling personnel.
3. Sampling should comply with specific national legislation, where it exists, or with international regulations and standards. In countries where regulations do not exist, qualified staff should be appointed. Sampling procedures include the following:
	1. Development of a standard operational procedure (SOP) for sampling each of the matrices for subsequent mercury analysis;
	2. Application of well-established sampling procedures such as those developed by the International Organization for Standardization (ISO), the European Committee for Standardization (CEN), the United States Environmental Protection Agency (EPA), the Global Environment Monitoring System (GEMS) and the American Society for Testing and Materials (ASTM); and
	3. Establishment of quality assurance and quality control (QA/QC) procedures.
4. All these steps should be followed if sampling programmes are to be successful. Similarly, documentation should be thorough and rigorous.
5. Mercury can occur and be sampled in liquids, solids, gases and biota:
	1. Liquids:
		1. Leachate from dumpsites and landfills;
		2. Liquid collected from spills;
		3. Water (surface water, drinking water and industrial effluents);
	2. Solids:
		1. Stockpiles of products and formulations consisting of, containing or contaminated with mercury or mercury compounds;
		2. Solids from industrial sources and treatment or disposal processes (fly ash, bottom ash, sludge, still bottoms, other residues, clothing, etc.);
		3. Containers, equipment or other packaging materials (rinse or wipe samples), including the tissues or fabric used in the collection of wipe samples;
		4. Soil, sediment, rubble, sewage sludge and compost;
	3. Gases:
		1. Air (indoor) of facilities handling mercury wastes;
		2. Mercury releases to the air from treatment of mercury wastes;
		3. Flue gas from waste incinerators;

(d) Biota:

* + 1. Biological materials (blood, urine and hair, especially those obtained through worker health monitoring);
		2. Plants and animals.
1. In environmental and human monitoring programmes, both biotic and abiotic matrices may be included:
	1. Plant materials and food;
	2. Human hair, urine, nails, breast milk or blood;
	3. Air (ambient, wet or dry deposition or, possibly, snow).

 2. Analysis

1. Analysis refers to the extraction, purification, separation, identification, quantification and reporting of mercury concentrations in the matrix of interest. In order to obtain meaningful and acceptable results, the analytical laboratory should have the necessary infrastructure (housing) and proven experience with the matrix and the mercury species (e.g., successful participation in inter-laboratory comparison studies and in external proficiency testing schemes).
2. Accreditation of the laboratory in accordance with ISO 17025 or other standards by an independent body is important. Essential criteria for obtaining high-quality results include:
	1. Specification of the analytical technique used;
	2. Maintenance of analytical equipment;
	3. Validation of all methods used (including in-house methods); and
	4. Training of laboratory staff.
3. Mercury analysis is typically performed in a dedicated laboratory. For screening purposes, test kits are available and can be used in the field.
4. For the analysis of mercury, there is no single analytical method available. Methods of analysing the various matrices for mercury, either for total mercury content or speciation of mercury, have been developed by the International Organization for Standardization (ISO), the European Committee for Standardization (CEN) at the international level, and by EPA and the Japan Standards Association at the national level. Table 4 lists some examples of methods for analysing mercury in wastes, flue gas and wastewater. Most in-house methods are variations of these. As with all chemical analysis, laboratories should use only validated methods and performance should be evaluated through QA/QC programmes.
5. In addition, procedures and acceptance criteria for storage, handling and preparation of the sample in the laboratory, e.g., homogenization, should be established.
6. The individual steps in the analytical determination include:
	1. Extraction;
	2. Purification;
	3. Identification by suitable detectors such as inductively coupled plasma (ICP), atomic fluorescence spectroscopy (AFS), amino acid analysers (AAS) and compact instruments;
	4. Quantification and reporting as required; and
	5. Reporting in accordance with regulation(s).

 3. Monitoring

1. In Article 10 (“International Cooperation”), paragraph 2 (b), the Basel Convention requires parties to “cooperate in monitoring the effects of the management of hazardous wastes on human health and the environment”. Monitoring programmes should provide an indication of whether a hazardous waste management operation is functioning in accordance with its design, and should detect changes in environmental quality caused by the operation.
2. The information obtained through monitoring programmes should be used to ensure that different types of hazardous wastes are properly managed, to identify potential issues relating to possible mercury releases or exposure to mercury and to determine whether amendments to the management approach might be appropriate. By implementing a monitoring programme, facility managers can identify problems and take appropriate measures to remedy them.
3. It should be noted that a number of continuous mercury measurement systems are commercially available for some types of mercury monitoring. Such monitoring may be required under national or local legislation.

**Table 4:** Chemical analysis of mercury in waste, flue gas and wastewater

| **Target** | **Method** |
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| Waste | To determine the mobility of mercury in waste | EN 12457-1 to 4: Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges (CEN, 2002a) |
|  |  | EN 12920: Characterization of waste - Methodology for the determination of the leaching behaviour of waste under specified conditions (CEN, 2006) |
|  |  | EN 13656: Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO3) and hydrochloric (HCl) acid mixture for subsequent determination of elements in waste (CEN, 2002b) |
|  |  | EN 13657: Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements in waste (CEN, 2002c) |
|  |  | TS 14405: Characterization of waste - Leaching behaviour test - Up-flow percolation test (CEN, 2004) |
|  |  | EPA Method 1311: TCLP, Toxicity Characteristic Leaching Procedure (EPA, 1992) |
|  | To determine concentrations of mercury in waste | EN 13370: Characterization of waste - Analysis of eluates - Determination of Ammonium, AOX, conductivity, Hg, phenol index, TOC, easy liberatable CN-, F- (CEN, 2003) |
|  |  | EN 15309: Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence (CEN, 2007) |
|  | EPA Method 7471B: Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) (EPA, 2007d) |
|  | EPA Method 7473: Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry (EPA, 2007e) |
|  | EPA Method 7470A: Mercury in Liquid Waste (Manual Cold-Vapor Technique) (EPA, 1994) |
| Flue Gas | EN 13211: Air quality - Stationary source emissions - Manual method of determination of the concentration of total mercury (CEN, 2001)\*This method determines the total mercury content (i.e., metallic/elemental Hg + ionic Hg). |
| EN 14884: Air quality - Stationary source emissions - Determination of total mercury: Automated measuring systems (CEN, 2005) |
| JIS K 0222: Analysis Method for Mercury in Flue Gas (JSA, 1997) |
| EPA Method 0060: Determination of Metals in Stack Emissions (EPA, 1996)  |
|  | For the speciation of mercury | ASTM D6784 - 02(2008) Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method) (ASTM International, 2008)  |
| Wastewater | ISO 5666: 1999: Water quality – Determination of mercury (ISO, 1999) |
|  | ISO 16590: 2000: Water quality – Determination of mercury - Methods involving enrichment by amalgamation (ISO, 2000) |
|  | 1SO 17852: 2006: Water quality – Determination of mercury - Method using atomic fluorescence spectrometry (ISO, 2006) |

Annex II: Submission from one expert

Analysis of total mercury in waste: available methods and apparatuses

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1) Fast analysis of (multiple) (field) point

* Hand-held or benchtop X-Ray fluorimeter (EN 15309), preferably calibrated for the specific matrix of the analysed waste, usable for all the elements of the periodic table heavier than sulphur, or heavier than sodium with a specific detector.
* Application to the surface of solid waste (wet or not), giving the local surficial mercury concentration; typically, multiple measurements at different locations are performed
* Duration: 30 seconds per spot of about 25 mm²
* Limit of detection (LOD) < 10 mg/kg
* 🡪 **Concentration of total Hg in single or multiple spots of the waste**, and calculation of a mean concentration. Shows the eventual heterogeneity, important for representative sampling. Can be used for sorting waste pieces on-line by their mercury concentration, eventually in automated systems on streams (available on the market).

2) Laboratory analysis of mean representative sample of batch or stream

* Representative sampling on the field from the waste piece, heap or stream to the laboratory sample. The laboratory sample ranges from 0.1 to 100 kg depending on the size and weight of the individual particles composing the material: it should contain about 10 000 particles to measure the 99th percentile of the mercury distribution in the particles if the coefficient of variation of particle analysis is 10% (CEN/TR 15310-1). If the concentration of mercury is dependent of the size of the particles (for instance if mercury is present as a separated mineralogical phase of a given size range), the Gy’s equations (ISO 11648-2) should be used.
* Pre-treatment at the laboratory to obtain a representative test portion of about 1 g to 10 g (drying at temperature < 40°C if necessary, size reduction - crushing, shredding, cutting, milling - if necessary, in one or more steps, mixing, quartering)
* Two methods of measuring concentration:
	+ Extraction/digestion of the test portion (1 g) by hot acids in closed vessels (EN 13657 or ISO 11466), and measurement by laboratory cold-vapor atomic fluorescence (ISO 16772), or
	+ Direct analysis of the test portion (10 g) by hand-held or benchtop X-ray fluorimeter (EN 15309)
* Duration: 1 day – 1 week
* Limit of detection (LOD) < 0.3 mg/kg (acid digestion and cold-vapor measurement) or < 10 mg/kg (direct X-ray fluorescence)
* 🡪 **Mean concentration of total Hg in the waste batch or stream**

Availability of measurement apparatuses

These apparatuses are available on the market.

Hand-held or benchtop fluorimeters are frequently used in mining and metallurgy companies, including secondary metallurgy recycling waste companies, to assess quality of the scraps.

Cold-vapor atomic fluorimeters are frequently used in universities, technical centres and service laboratories analysing industrial and environmental samples.

Standards

CEN/TR 15310-1: 2007. Characterization of waste — Sampling of waste materials — Part 1: Guidance on selection and application of criteria for sampling under various conditions.

EN 13657: 2003. Characterization of waste - Digestion for subsequent determination of aqua regia soluble portion of elements.

EN 15309: 2007. Characterization of waste and soil — Determination of elemental composition by X-ray fluorescence.

ISO 11466: 1995. Soil quality- Extraction of trace elements soluble in aqua regia.

ISO 11648-2:2001. Statistical aspects of sampling from bulk materials - Part 2: Sampling of particulate materials.

ISO 16772: 2004. Soil quality - Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry.

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1. This document has not been formally edited. [↑](#footnote-ref-1)
2. 18 Available at: http://www.unep.org/chemicalsandwaste/Portals/9/Mercury/Documents/IdentifyingPopnatRiskExposuretoMercury\_2008Web.pdf. [↑](#footnote-ref-2)
3. 19 Development of a Plan for Global Monitoring of Human Exposure to and Environmental Concentrations of Mercury (GEF ID 5409). [↑](#footnote-ref-3)
4. 20 Polyethylene bottles are permeable to mercury and should not be used. For details, see Parker et al., 2005. [↑](#footnote-ref-4)