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Screening tests for hazard classification of complex waste materials – Selection of methods

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ABSTRACT

In this study we describe the development of an alternative methodology for hazard characterization of waste materials. Such an alternative methodology for hazard assessment of complex waste materials is urgently needed, because the lack of a validated instrument leads to arbitrary hazard classification of such complex waste materials. False classification can lead to human and environmental health risks and also has important financial consequences for the waste owner. The Hazardous Waste Directive (HWD) describes the methodology for hazard classification of waste materials. For *mirror entries* the HWD classification is based upon the hazardous properties (H1–15) of the waste which can be assessed from the hazardous properties of individual identified waste compounds or – if not all compounds are identified – from test results of hazard assessment tests performed on the waste material itself. For the latter the HWD recommends toxicity tests that were initially designed for risk assessment of chemicals in consumer products (pharmaceuticals, cosmetics, biocides, food, etc.). These tests (often using mammals) are not designed nor suitable for the hazard characterization of waste materials. With the present study we want to contribute to the development of an alternative and transparent test strategy for hazard assessment of complex wastes that is in line with the HWD principles for waste classification. It is necessary to cope with this important shortcoming in hazardous waste classification and to demonstrate that alternative methods are available that can be used for hazard assessment of waste materials. Next, by describing the pros and cons of the available methods, and by identifying the needs for additional or further development of test methods, we hope to stimulate research efforts and development in this direction. In this paper we describe promising techniques and argument on the test selection for the pilot study that we have performed on different types of waste materials. Test results are presented in a second paper.

As the application of many of the proposed test methods is new in the field of waste management, the principles of the tests are described. The selected tests tackle important hazardous properties but refinement of the test battery is needed to fulfil the *a priori* conditions.

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1. Introduction

The Hazardous Waste Directive (HWD, Council Directive 91/689/EC) provides a framework for the hazard classification of waste. For *mirror entries* the classification is based on the hazardous properties (H1–15) of the waste: physical (H1 explosive, H2 oxidizing, H3 flammable) and toxicological hazard criteria (H4 Irritant, H5/6 harmful or toxic, H7 carcinogenic, H8 corrosive, etc.). The hazard assessment is based upon information on the hazardous properties of identified individual waste compounds or – if not all compounds are identified – on results of hazard assessment tests on the waste material itself (direct testing). The recommended methods for the direct testing of toxicological properties of waste (HWD) are the acute and chronic animal tests that are used for hazard assessment of chemicals (CD 67/548/EC (dangerous substances), 726/2004/EC (pharmaceuticals), EC/1907/2006 (REACH), CD 98/8/EG (biocides)). These methods and test strategies are however specifically designed for profound human risk assessment for chemicals in applications where oral uptake, inhalation, skin contact are relevant exposure routes. Not only is human exposure to waste material different, also the waste test strategy is for purposes of hazard *classification* (which is a yes/no decision) and not for risk assessment. Moreover it is not ethical to use animal tests for waste classification. For these reasons at present no direct tests are applied and in practice complex wastes are often arbitrarily classified: chemical

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screening is insufficient to identify *all possible* hazardous compounds in complex mixtures and a sound hazard assessment is therefore not possible.

Industrial companies facing this problem experience how these arbitrary measures can have serious financial consequences and are a threat to competitiveness. Moreover a false classification can have consequences for human and/or environmental health. There is an urgent need for an alternative direct testing strategy.

This study wants to contribute to the development of such an alternative test strategy for hazard assessment of complex matrices. We demonstrate that a lot of methods are available and propose a strategy on how waste classification can be done by alternative methods. Recommendations on the use of alternative tests for direct assessment of waste have already been made by the UK Environment Agency (Hazardous waste, Technical Guidance WM2) and experimental work was already performed in some labs (Krist et al., 2005). Up to now no test strategy is however proposed at the regulatory level.

In this paper the wide range of available test methods that can be useful for direct hazard assessment is described and their potential use in waste assessment is evaluated.

The tools that are reviewed are (a) chemical methods and affinity based biosensors that identify (groups of) toxicants (targeted analyses), (b) *in vitro* methods that originally were developed for screening hazardous properties of pharmaceuticals/chemicals, and (c) ecotoxicity tests (b and c being non targeted analyses). It became clear that the chemical and biological screening methodology is extensive (bv. NATIBO, 2001; Eisenbrand et al., 2002; Krist et al., 2005; Witters et al., 2005; EPA, 2005; Allan et al., 2006) and new applications and techniques are emerging continuously (Riedel et al., 2003; NRC, 2007; Imec-LINC, 2008).

The pros, cons, and needs for additional or further development of test methods are listed to pinpoint the gaps and stimulate research efforts and test development in this direction.

Also the selection of tests that were eventually used for the pilot project is justified. The evaluation is based on the following *a priori* conditions: (a) the classification has to be in accordance with HWD principles i.e. based on *total* concentrations and based on the defined hazardous toxicological properties, and (b) results need to be generated within short time (preferentially 48 h) and at economically feasible prices. The latter conditions are important to allow batch controls, and to prevent large volumes of waste piling up at the plant (occupation of space and/or odour problems). Also (c) a high level of standardization is needed because the test results will be compared to preset limit values. For the pilot test validated and available tests that did not always fulfil the (b) criterion were nevertheless selected for pragmatic reasons, i.e. to cover as many of the toxicological hazard properties as possible, but the needs for new or improved tests is argued.

As the application of many of the proposed tests is new in the field of waste management, the principles of the available tests are described here.

The selected tests were performed in the pilot study on different types of waste material with good results (Deprez et al., under revision).

2. Review of methods and selection of tests for the evaluation of waste

2.1. Extraction methods

HWD limit values are based on *total* concentrations of compounds. The extraction methods therefore have to provide liquids that reflect as much as possible the total content of components that were present in the original sample. For practical reasons it is necessary to provide a universal extraction method to displace as many of the pollutants from the original (solid) waste into a liquid matrix that can be used for both chemical analyses and biological tests.

To achieve this two extraction methods in parallel are recommended: an aquatic extraction to retain the inorganic and ionic organic leachable components and an acetone extraction to retain (most of) the organic components.

2.1.1. Water leachable fraction

In support of the Directive 91/689/EEC on hazardous waste, CEN, the European Committee for Standardization, has set up Technical Committee 292 for the "characterization of waste". CEN TC 292 issued several procedures to determine the characteristics of waste and waste behaviour, as sampling, pre-treatment, leaching properties, determination of total content of species, determination of sum parameters and assessment of ecotoxicity. For the preparation of test portions and water leachable fraction methods described in EN 15002:2006 and EN 12457–4:2002 are referred to.

2.1.2. Organic extract

Acetone is both water soluble and dissolves organic components. It is able to remove also compounds out of porous materials. Aceton is therefore suitable as a worst case extraction solvent.

2.2. Targeted analyses

The most straightforward method to characterize and classify waste is to identify and measure the concentration of hazardous chemical components in waste directly and compare their concentrations to the limit values (HWD). For samples with known toxic components analytical methods should be used to measure their concentrations. For samples of unknown composition screening methods are needed to unravel their composition and/or their hazardous properties.

2.2.1. Targeted chemical analyses of inorganics

CEN TC 292 (in support of the Directive 91/689/EEC on hazardous waste) issued several procedures to determine the characteristics of waste. For inorganic characterization of waste a framework was already designed by CEN TC 292. The applied standardized methods for the chemical characterization of the inorganic species are listed in Table 1.

Most of these analytical methods measure individual elements or species such as anions (e.g. sulphate, chloride) and cations (e.g. metals). This complicates hazard classification, because different speciations of the same element can show very different toxic properties and it is difficult to link the analytical results to the limit values for toxic chemicals, as HWD requires.

The chemical methods for analyses of the inorganic fraction are very practical and fast, and suitable for batch analyses. HWD has to provide guidance on how to deal with the analytical information in terms of toxicity, and results can be used for hazard classification of the inorganic fraction.

2.2.2. Targeted Chemical analyses of organics

Liquid or gas chromatography (LC/GC) and mass spectrometry (MS), infrared spectroscopy, ion mobility spectroscopy (IMS) can be used to screen for a wide variety of organic chemicals.

GC/MS is the best method for substance identification, but also has its limitations: coelution can complicate test results and not all compounds can be identified. LC/MS spectra are not library searchable and cannot be used for general screening. With the more advanced LC-amTOF-MS there is a possibility to obtain the molecular formulas of compounds, but a laborious study of isotope distributions and fragmentation patterns is necessary.

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