



DEFRA

**WR0110 CHARACTERISATION OF RESIDUES FROM
INDUSTRIAL PROCESSES AND WASTE TREATMENT**

ANNEX B - WASTE TESTING

**WRC Ref: Defra7932.2
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B1 INTRODUCTION

This annex provides details of the analytical methods applied to most of the collected waste samples with the exception of the following.

- Bottom ash and air pollution control residues from the gasification of municipal solid wastes (MSW gasification BA and MSW gasification APC residues). Details of sample preparation and testing methodologies are provided in Annex C.
- Cement-stabilised air pollution control residues from incineration of municipal solid wastes with and without other wastes (stabilised wastes). Details of sample preparation and testing methodologies are provided in Annex D.

The remainder of the wastes were prepared for analysis at WRc according to the methods provided in B2 and subsequently analysed as follows.

B2 SAMPLE PREPARATION

Samples were collected as specified in the Sampling Plans or summarised in the Sampling Records presented in Annex A.

B2.1 Organic waste samples

Many of the organic wastes comprised large heterogeneous samples which contained materials other than BMW, particularly samples of MSW derivation. Most wastes were sorted to provide the BMW fraction which then underwent further preparation to provide homogeneous samples for analysis.

B2.1.1 Sorting mixed waste samples to give a separate organic waste fraction

Mixed waste samples such as MSW were manually sorted to separate the organic waste fraction from the other components. The organic waste fraction included all biodegradable fractions including paper, card, cardboard, wood, food waste, greenwaste, textiles. The plastics were excluded from the biodegradable fraction as were inert components such as glass, stones and metal objects.

The biodegradable material content of the mixed waste was recorded as a percentage by wet weight. Further preparation and analysis was only undertaken on the organic waste fraction.

B2.1.2 Size reduction to <10 mm particle size

Where necessary the organic waste samples were then macerated to a particle size of <10 mm. The <10 mm preparations were then well mixed and supplied to the laboratories for further analysis and preparations. Some samples already composed of particles <10 mm were used as received.

The analyses carried out on the <10 mm fraction were the Dry Matter (DM), Loss on Ignition (LOI) and biodegradability tests DR4 and BM100.

B2.1.3 Size reduction for other analysis

For most other analyses the <10 mm material was further prepared by drying and grinding to a particle size <1 mm.

B2.2 Inorganic waste samples

The inorganic samples were homogenised, dried at 30°C and representatively sub-sampled for analysis. The analytical samples were milled to 4mm grain size. Specific sample preparation and stabilisation for the MSW gasification residues are presented in Annex C. Other samples were prepared for analysis in WRC's laboratory facilities, with further preparation for sampling (fine grinding etc.) as appropriate, undertaken at the sub-contractor laboratories.

B3 ANALYTICAL METHODS

B3.1 Organic waste samples

B3.1.1 Dry matter (DM) and loss on ignition (LOI)

DM and LOI determinations were carried out at 103°C and 550°C by using methodologies adapted from standard methods applied to solid recovered fuels (DD CEN/TS 15414-2, DD CEN/TS 15403) and BMW (Environment Agency 2005). Five pre-weighed replicate crucibles of 150 ml volume were filled with the organic waste sample and then dried overnight (minimum 16 hours) at 103°C. For most wastes the total amount of sample in the 5 replicates was greater than 100 g. The crucibles were weighed after drying to calculate the DM content and then placed in a cold furnace which was then slowly heated to 550°C. The samples were held at 550°C until all the organic matter had been combusted. The crucibles were then re-weighed to determine the loss on ignition.

B3.1.2 Total carbon, nitrogen and sulfur determinations

Total C, N and S were determined using a LECO CNS2000 elemental analyser (Nelson and Sommers 1996, Bremner 1996). It was assumed that the total C approximated to the Total Organic Carbon (TOC) content for the organic wastes. In addition total N was also estimated by Kjeldahl digestion modified to include nitrates (BS EN 13654-1) and the organic C by dividing the LOI by 1.81 which assumes the C content is 55.2% of the LOI (BS EN 13039).

B3.1.3 Total elemental content

Aqua regia digests for total elements (BS EN 13650) were analysed for the elements Cd, Cu, Cr, Ni, Pb and Zn by ion-coupled plasma mass spectroscopy (BS EN ISO 11885) on an Agilent 7500a ICP-MS.

B3.1.4 Biochemical composition of organic wastes

Biochemical composition was determined (van Soest et al. 1991, Effland 1977, Richards 2005) using an adaptation of the Gerhardt Ltd. fibrebag system. Dried, ground samples, with fine material that would pass through the fibrebags removed, underwent sequential treatment with petroleum ether, neutral detergent solution, acid detergent solution, cold 72% sulphuric acid and ashing at 600 °C. The fractions removed by these processes are nominally identified as fat, soluble material, hemicellulose, cellulose and lignin respectively. These designations may not be exclusively composed of the described biochemical classes but be mixtures of different materials with similar sequential extractive properties by the methodology.

B3.1.5 Biodegradability testing of organic wastes

a) Aerobic DR4 biodegradability test

Biodegradability in aerobic conditions was determined using the DR4 (Environment Agency 2005) which is a 4 - day dynamic respiration test for waste stability, adapted from ASTM D5975-96 (ASTM, 1996) with incubation temperature 35 °C and moisture contents adjusted to 50%.

b) Anaerobic BM100 biodegradability test

Biodegradability under anaerobic conditions was measured by production of biogas according to the BM100 test (Environment Agency 2005) adapted from a sewage sludge digestion test method (SCA, 1977). The waste is incubated under methanogenic conditions and the production of biogas (CH₄ + CO₂) monitored until gas production ceases.

c) Enzyme hydrolysis test (EHT)

The enzymatic (cellulase) hydrolysis of wastes has been proposed as a potential surrogate biodegradability test that may be more rapid and reliable, and a lower cost than the DR4 and BM100 biodegradability tests (Godley *et al.* 2004). The further development and evaluation of this test was carried out by Stuart Wagland, a Ph.D student at Cranfield University sponsored by this project. Full details of the method are described in the reporting of these studies (Annex H).

B3.1.6 Leachability

A toolbox of leaching behaviour tests has been developed by CEN TC 292 (waste characterisation) (Table B1). The organic wastes were subjected to single step L/S10 compliance test for granular wastes BS EN 12457. The principal five organic waste streams were also leached in duplicate using the upflow percolation test to enable kappa values to be calculated.

Table B1 Characterization toolbox (after Environment Agency, 2005a)

Test method	Purpose
Compliance tests for granular wastes	
BS EN 12457:2002 Part 2, (L/S10 at <4mm) and Part 3 (L/S2 and L/S8 (cumulative L/S10 at <4mm))	To assess leachability under mild extraction conditions at up to L/S10 without pH control. Landfill waste acceptance compliance test. The two-step test also provides limited leaching behaviour information about relative timescales for release, particularly when placed in the context of data from the upflow percolation test.
Characterization (leaching behaviour) tests for granular or crushed monolithic wastes	
Maximum availability leaching test (EA NEN 7371: 2004)	To determine the maximum availability of components by leaching under worst-case environmental conditions. Finely ground material is tested at high liquid to solid (L/S) ratios and with pH control (pH 7 and 4). Also see maximum concentration derived from pH dependence test below. Can be used for granular and monolithic wastes.
Upflow percolation test (BS DD CEN/TS 14405: 2004)	To determine the rate of leaching of various contaminants from granular wastes as a function of liquid to solid ratio (i.e. relative time). The test conditions approximate to infiltration of liquids through a granular waste material. Cumulative L/S ratios are 0.1, 0.2, 0.5, 1, 2, 5 and 10. Initial leaching data relate to the low L/S ratios prevailing in landfill and provide context for L/S2 and L/S10 data from BS EN 12457 batch tests.
pH dependence tests (DD CEN/TS 14429:2005 and DD CEN/TS 14997: 2006)	To determine the effect of falling or increasing pH conditions on leachability of granular wastes e.g. after pre-landfill chemical treatment and following landfilling, should local porewater/leachate pH conditions change. The two test methods cover operations in either continuous pH control or in batch mode and yield a full range of acid/base neutralisation capacity values.
Characterization (leaching behaviour) and compliance test for monolithic wastes	
Diffusion test (tank test for monolithic wastes) (EA NEN 7375: 2004) Dynamic monolithic leaching test (DMLT) with periodic leachant renewal (WI 292055) (prEN 15863 or prCEN/TS 15863).	To assess the leachability of solidified wastes. <i>Characterization:</i> The test is conducted on samples > 40mm in any direction using approx. 5 times volume of deionised water leachant than sample. 8 leaching steps are carried out over 64 days at natural pH. Results are generally interpreted on a surface area basis (mg m ⁻²). <i>Compliance test:</i> Cumulative 4 and 64 day values are compared with UK monolithic waste acceptance criteria. <i>Note:</i> CEN TC292 WG2 and 6 have also been developing diffusion tests similar to EA NEN 7375 based on 7 leaching steps conducted over 36 days. During testing of the cement-stabilised residues (Annex D) the EA NEN 7375 method was modified slightly by ECN so that testing was consistent with WI 292055. Following test validation, this method will be published as a European Standard (EN) or Technical Specification (TS).

B3.2 Inorganic waste samples

Compositional and leachability testing was undertaken on the inorganic samples. To avoid limiting secondary research the full toolbox of leaching behaviour tests (Table B1) was used as appropriate. Table B2 provides details of the test methods adopted by WRc contracted laboratories to determine parameters for which acceptance limit values have been set, both parameters determined in the waste and on eluates derived from the various leaching tests. These methods are expected to give similar analytical results to those specified in the Environment Agency (2005a) sampling and testing guidance.

B2 Analytical methods for inorganic waste samples

DETERMINAND	PRESCRIBED METHOD	METHOD REFERENCES	METHOD CODE
General Waste Properties			
pH (solids)		BS 1377: Part 3: 1990 Method 9 Methods for the Examination of Waters and Associated Materials (MEWAM): Determination of the pH Value of Sludge, Soil, Mud and Sediment 2 nd Edition: 1992 Department of the Environment: Problems Arising from the Redevelopment of Gas Works and Similar Sites. 2 nd Edition 1988	39
Total Organic Carbon (TOC)	BS EN 13137 – Inorganic C removed with sulphurous acid. TOC determined by combustion in oxygen	BS EN 13137:2001 - Characterisation of waste – Determination of total organic carbon (TOC) in waste, sludges and sediments	27
Total Carbon (TC)		Vario Max CNS Macro Elemental Analyser Operating Manual. January 2004	59
Loss on Ignition (LOI)	EN 12879 – Gravimetry at 550°C	BG plc Property Division 1999: Version 2.4: Method 16.4 – Loss on Ignition	337
Dry Matter Content	PrEN 14346	Analysis of Agricultural Materials. MAFF 1986 – Method 2. Moisture Content.	QP.5.4.I
Direct analysis of waste			
Aqua Regia Extractable metals: As, Cd, Cr, Cu, Pb, Ni, Zn, Fe, Al, Ba, Be, Co, Mg, Mn, Mo, V, Ag, P, Sn & Ti.	BS EN 13657 – HNO ₃ /HCL digest	MEWAM : Methods for the Determination of Metals in Soil, Sediment and Sewage Sludge by Hydrochloric-Nitric digestion 1986. HMSO: ISBN 011 751 9081 MEWAM : Inductively Coupled Plasma Spectroscopy 1996. HMSO: ISBN 011 753 2444 MEWAM : Information on Concentration and Determination Procedures in Atomic Spectroscopy 1992. HMSO: ISBN 011 752 3755	30

DETERMINAND	PRESCRIBED METHOD	METHOD REFERENCES	METHOD CODE
Ultra-Low Level metals by ICP	EN ISO 11885 ICP-OES	The application of collision/reaction cell ICP-MS to multi element analysis in Variable Sample Matrices using Helium as a Non Reactive Cell Gas – E. McCurdy/G Woods 2004, Journal of Analytical Atomic Spectrometry 19 (3) MEWAM : Inductively Coupled Plasma Spectroscopy 1996. HMSO: ISBN 011 753 2444	WAS 060 ICP-MS
As, Se, Se & Hg by Hydride	EN ISO 11969	MEWAM : Selenium and Arsenic in sludge, soil and related material. 1985 HMSO: ISBN 011 751 9332 MEWAM : Mercury in Soils, Sediment, Water and Effluent. 1985 HMSO: ISBN 011 751 9073 Standard Methods for the Examination of Waters and Wastewaters 1995. ISBN 0 87553 223 3	30C
Macro elements by ICP-OES		MEWAM : Inductively Coupled Plasma Spectroscopy 1996. HMSO: ISBN 011 753 2444	CASQ
Nitrate, nitrite, sulphate, chloride, orthophosphate, ammonia	EN 26777 and EN ISO 13395 – Colorimetric EN ISO 10304-1&2 – IC ISO 9280 – Gravimetric EN ISO 10304-1&2 – IC EN ISO 11732 – FIA and photometric determination	MEWAM : Ammonia in Waters 1981: HMSO: ISBN 011 751 6139 MEWAM : Oxidised Nitrogen in Waters 1981: HMSO: ISBN 011 751 5930 MEWAM : Chloride in Waters, Sewage and Effluent 1981: HMSO: ISBN 011 751 6260 MEWAM : Phosphorus in Waters, Sewage and Effluent 1980: HMSO: ISBN 011 751 5825 MEWAM : Sulphate in Waters, Sewage and effluents 1980: HMSO: ISBN 011 751 5825	WAS 036
Alkalinity		MEWAM : The Determination of Alkalinity and Acidity in Water. 1981. HMSO: ISBN 011 751 601 5	WAS 025
Determination of Br		Dionex Installation Instruments and Troubleshooting Guide for the Ionpac AG14 Guard Column and AS14 Analytical Column – Section 7: Example Applications.	CON 27

DETERMINAND	PRESCRIBED METHOD	METHOD REFERENCES	METHOD CODE
Determination of F	EN ISO 10304-1 – IC ISO 10359-1 – ISE	MEWAM : Fluoride by ion-selective electrode HMSO:1982 ISBN 011 751 662 7	WAS 029
Reactive Silica by colorimetry		MEWAM : Phosphorus and Silica in Waters, Effluents and Sludge 1992; HMSO ISBN 011 752 3771	WSI 044
Water Soluble Boron		MEWAM : Inductively Coupled Plasma Spectroscopy 1996. HMSO: ISBN 011 753 2444	6
Total Phenol		Environmental Assessment Guidance Document Version 2.4 1999 – Total Phenol by HPLC	322
Phenol Index	ISO 6439 - Spectrophotometric	Environmental Assessment Guidance Document Version 2.4 1999 – Total Phenol by HPLC	322
Polychlorinated Biphenyls (PCBs)		USEPA Solid Waste Method 8082 Test Methods for Evaluating Solid Waste – Polychlorinated Biphenyls	312B
Polynuclear Aromatic Hydrocarbons (PAHs)		USEPA methods 8310 and 3540C Test Methods for Evaluating Solid Waste – Poly Aromatic Hydrocarbons.	307
PCDD/DF		USEPA 1991: Method 1613	Subcontract
Analysis of Eluates 'leachables'			
With the exception of the following parameters, detection methods listed above are adopted for eluate analysis on these parameters			
Determination of pH and Electrical Conductivity	ISO 10523	MEWAM : The measurement of EC and the laboratory determination of pH value of natural, treated and wastewaters. HMSO:1978 ISBN 011 751 428 4	WAS 039
Total Dissolved Solids (TDS)		MEWAM : Suspended, settleable and Total Dissolved Solids in Waters and Effluents. HMSO 1980: ISBN 011 751 957X	WAS 010
Total Organic Carbon (TOC)	EN1484	MEWAM : The Instrumental determination of Total Organic Carbon and Related Determinands 1995 HMSO ISBN 011 752 9796	WAS 005
Dissolved Organic Carbon (DOC)		MEWAM : The Instrumental determination of Total Organic Carbon and Related Determinands 1995 HMSO ISBN 011 752 9796	WAS 005

DETERMINAND	PRESCRIBED METHOD	METHOD REFERENCES	METHOD CODE
Dissolved Phenol		Methods for the Examination of Waters and Wastewaters 14 th Edition – Methods 510 to 510C - 1975	WAS 019

Equivalent Standing Committee of Analysts (SCA) Methods for the Examination of Waters and Associated Materials. HMSO Publication Year and ISBN Number or other methods e.g. ISO, BSi as indicated

MEWAM : SCA Methods for the Examination of Waters and Associated Materials. HMSO Publication

IC: Ion Chromatography,
ISE : Ion Selective Electrode

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BS EN 13039 (2000). Soil improvers and growing media. Determination of organic matter content and ash. ISBN 0 580 34253 0.

BS EN 13654-1 (2001). Soil improvers and growing media. Determination of Nitrogen. Modified Kjeldahl method. ISBN 0 580 38268 0.

BS EN 13650 (2001). Soil improvers and growing media. Extraction of aqua regia soluble elements. ISBN 580 38269 9.

BS EN ISO 11885 (1998). Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy. ISBN 0 580 29041 7.

BS EN 14899:2005 Characterization of waste – Sampling of waste materials – Framework for the preparation of a Sampling Plan. British Standards Institute, London.

BS EN 12457-2:2004 Characterization of waste - leaching - Compliance test for leaching of granular waste materials and sludges - Part2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction). British Standards Institute, London.

BS EN 12457-3:2002 Characterisation of waste. Leaching. Compliance test for leaching of granular waste materials and sludges. Two stage batch test at a liquid to solid ratio of 2 l/kg and 8 l/kg for materials with a high solid content and with a particle size below 4 mm (with or without size reduction). British Standards Institute, London.

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