

A proposal for a test method for assessment of hazard property HP 12 ("Release of an acute toxic gas") in hazardous waste classification - experience from 49 waste

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1. ABSTRACT

A stepwise method for assessment of the HP 12 is proposed and tested with 49 waste samples. The hazard property HP 12 is defined as *"Release of an acute toxic gas": waste which releases acute toxic gases (Acute Tox. 1, 2 or 3) in contact with water or an acid. When a waste contains a substance assigned to one of the following supplemental hazards EUH029, EUH031 and EUH032, it shall be classified as hazardous by HP 12 according to test methods or guidelines (EC 2014a, b).* When the substances with the cited hazard statement codes react with water or an acid, they can release HCl, Cl₂, HF, HCN, PH₃, H₂S, SO₂ (and two other gases very unlikely to be emitted, hydrazoic acid HN₃ and selenium oxide SeO₂ – a solid with low vapor pressure). Hence, a method is proposed:

- 1 Measurement of the volume of gases emitted into contact with water or an acid (solid/liquid ratio of 10 L water or acid / kg raw waste, acid 2.5 M HNO₃);
- 2 If gas is emitted at a rate higher than 0.1 L of gas/kg waste in 5 minutes (limit of quantification of the automated calcimètre used here), checking if one of the cited gases is emitted with electrochemical detection probes or simple qualitative colorimetric methods;
- 3 If one of these gases is detected, speciation of the emitting substance(s) (calculation by the "worst case" method from elements concentrations, or by specific analytic methods) and checking whether they have a hazard statement code EUH029, EUH031 or EUH032 (a list is provided).

For a set of 49 waste, water addition did not produce gas. Nearly all the solid waste produced a gas in contact with hydrochloric acid in 5 minutes in an automated calcimeter with a volume > 0.1 liter of gas per kg of waste. Since a plateau of pressure is reached only for half of the samples in 5 minutes, 6 hours trial with calorimetric bombs or glass flasks were done and confirmed the results. Identification of the gases by portable probes showed that most of the tested samples emit mainly

CO₂. Toxic gases are emitted by four waste: metallic dust from the aluminum industry (CO), two air pollution control residue of industrial waste incinerator (H₂S) and a halogenated solvent (organic volatile(s) compound(s)). HF has not been measured in these trials started before the present definition of HP 12. According to the definition of HP 12, only the H₂S emission of substances with hazard statement EUH031 is accounted for. In view of the calcium content of the two air pollution control residue, the presence of calcium sulfide (EUH031) can be assumed. These two waste are therefore classified potentially hazardous for HP 12, from a total of 49 waste. They are also classified as hazardous for other properties (HP 7, 10 and 14 for one of them, and HP 10 and 14 for the other one respectively) . Given these results, it can be assumed that few common household and industrial waste will be classified hazardous only by HP 12.

2. INTRODUCTION

The Waste Framework Directive (EC 2008) defines ‘hazardous waste’ as ‘waste which displays one or more of the (15) hazardous properties listed in Annex III’. The property H 12 ‘*Waste which releases toxic or very toxic gases in contact with water, air or an acid*’ was not further defined since that time. A Commission Regulation of 2014 redefined HP 12 (former H 12) as (“*Release of an acute toxic gas*”: *waste which releases acute toxic gases (Acute Tox. 1, 2 or 3) in contact with water or an acid. When a waste contains a substance assigned to one of the following supplemental hazards EUH029, EUH031 and EUH032, it shall be classified as hazardous by HP 12 according to test methods or guidelines* (EC 2014a, b). There is still no standardized test for measure of gases emission from waste. The UN N.5 method characterizes substances which in contact with water produce flammable gases (UN 2003). It is mentioned in the Dangerous Goods Transport recommendations of the UN and in the CLP regulation. The volume of gas is measured manually by displacement of water in graduated flasks. It is poorly repeatable (according to INERIS experience with powders and chemicals) since the degree or type of wetting, a major parameter, is not defined (Janes 2010, 2011). The Austrian experimental standard Önorm S 2120 also addresses only the flammable gas (contact with water and contact with a flame). The DG ENV has recently sent a mandate to Technical Committee TC 292 (Characterization of waste) of CEN to develop and validate a method for HP12.

Definition of HP 12

EU Member States have revised the definition of the hazard properties (EC 2014a, b). The HP 12 property is: “**HP 12**“*Release of an acute toxic gas:*”*waste which releases acute toxic gases (Acute Tox. 1, 2 or 3) in contact with water or an acid. When a waste contains a substance assigned to one of the following supplemental hazards EUH029, EUH031 and EUH032, it shall be classified as hazardous by HP 12 according to test methods or guidelines.*’. The waste must contain a substance or substances with the hazard statements (HSC) code EUH029, EUH031 and EUH032. There is no standardized test to date for measuring the gases emitted by the waste. These hazard statement codes are the following (CLP 2008):

“EUH029 — ‘Contact with water liberates toxic gas’ For substances and mixtures which in contact with water or damp air, evolve gases classified for acute toxicity in category 1, 2 or 3 in potentially dangerous amounts, such as aluminium phosphide, phosphorus pentasulphide.

EUH031 — ‘Contact with acids liberates toxic gas’ For substances and mixtures which react with acids to evolve gases classified for acute toxicity in category 3 in dangerous amounts, such as sodium hypochlorite, barium polysulphide.

EUH032 — ‘Contact with acids liberates very toxic gas’ For substances and mixtures which react with acids to evolve gases classified for acute toxicity in category 1 or 2 in dangerous amounts, such as salts of hydrogen cyanide, sodium azide.”

The substances with these HSC have been extracted from the CLP tables (CLP 2008) (Table 1). The gas they can emit and their molecular formula have been added. Many substances are very reactive (specially EUH029 substances that react with water) and not likely to be found in waste because the chemical industry would destroy or neutralize them before release as waste. An exception is probably thionyl chloride present in the lithium-ion batteries (EUH029). These EUH029 substances emit in contact with water HCl and SO₂, and for some H₂S and PH₃. Substances with hazard statement EUH031 include more common products (sulphides, polysulphides, hypochlorite, and carbamate derivatives of isocyanuric acid). They emit in contact with an acid mainly H₂S and Cl₂. Substances with hazard statement EUH032 mainly include cyanides (other than complex cyanides such as ferrocyanides, ferricyanides and mercuric oxycyanide), thiocyanate, and sodium fluoride. They emit in contact with an acid HCN and HF, and for some products PH₃ and HN₃.

In practice, the substances that can be present in waste in the 'normal' waste management circuits are thionyl chloride, and some hypochlorites, fluorides, cyanides, sulfides and sulfites. As mentioned, the Li-ion batteries contain thionyl chloride. Sediment and organic media can accumulate sulphides in the absence of oxygen. Some contaminants can be insolubilized as sulfides when treating effluents or chemical waste. The cyanide and fluoride are present in chemicals. Hypochlorite is present in oxidants and disinfectants. But only some salts of these anions are targeted by the CLP.

There are no routine methods of analysis in waste laboratories to identify and measure substances with HSC EUH029, EUH031 and EUH032. For example, EN 15875 determines the sulphide content in waste from the extractive industries by difference between the total sulphur and sulphate, and assumes that the sulphide is pyrite (FeS₂). It is more easy and cost-effective to start by gas detection: if a specific gas is not emitted, substances that can emit that gas are not present in the waste. The objective is to detect qualitatively if any EUH029, EUH031 or EUH032 substances are present in the waste, by their gas emission.

The waste materials potentially of concern (containing critical substances in waste for HP12) are chemical waste reacting with an acid and containing hypochlorite (disinfectant, swimming pool chemicals), sulphide (mining residues with pyrite, precipitated elements from cleaning of aqueous liquid waste by treatment with Na₂S), cyanide (salts from metal surface treatment), sodium fluoride. It is expected that the waste that react with water and produce a toxic gas is pretreated *in situ* in the chemical industry and neutralized before joining the waste flux.

The objective of the paper is a starting point which is tested for some materials, and needs for improvements and further studies to become a full “ready” test. MATERIAL AND METHODS

3.1 Protocol

From Table 1, it can be seen that two gases a priori very unlikely to be met (hydrazoic acid HN_3 and selenium oxide SeO_2 – a solid with low vapor pressure). The gases to search (sorted by main element) are HCl , Cl_2 , HF , HCN , PH_3 , H_2S and SO_2 .

The principle of the method proposed in this article is the following:

- 1 Measurement of the volume of gases emitted into contact with water or an acid (solid/liquid ratio of 10 L water or acid / kg raw waste, acid 2.5 M HNO_3);
- 2 If gas is emitted at a rate higher than the limit of quantification (in our case 0.1 L of gas at normal temperature and pressure/kg waste in 5 minutes), checking if HCl , Cl_2 , HF , HCN , PH_3 , H_2S and SO_2 is emitted with electrochemical detection probes or simple qualitative colorimetric methods;
- 3 If one of these gases is detected, speciation of the emitting substance(s) (either by direct method if they are in high concentration or by calculation by the "worst case" method if they are in low concentrations, or by specific analytic methods) and checking whether they have a hazard statement code EUH029, EUH031 or EUH032, or alternatively checking if the waste is likely to contain substances with these HSC (with information of the acid/base and redox status of the waste, and the origin or the process that has produced the waste).

Nitric acid is proposed because it is not emitted by the substances with hazard statement codes EUH029, EUH031 or EUH032. The proposed amount of acid is in excess even if the waste is composed of 100% of carbonate. Note that the assessment of the property HP 3 "Flammable" requires testing on emission of flammable gas on contact with water (UN Test N.5). If this test has already been done and showed no release of gas upon contact with water, this information can be used for the assessment of HP 12.

In this study, started before the 2014 decision, and using a preliminary and different definition of HP 12, the gases HCl , Cl_2 and HF have not been looked for. The acid used in the present study was HCl , because that acid was compatible with the (preliminary) definition of HP 12 at that time. The results are still valid for the present definition of HP 12 for the following reason. The substances with hazard statement code EUH029 may emit HCl in contact with water (Table 1), and the substances with HSC EUH031 and EUH032 don't emit HCl in contact with an acid. Since no gas emission has been observed with contact with water (see Results), HCl has not been emitted. The substances that can emit Cl_2 in contact with water or an acid are disinfectants and biocides acting by oxidation, and their presence should result in a very high redox potential (not observed, Hennebert et al. 2014). HF has not been monitored in the present study. In the protocol, we recommend the use of HNO_3 (despite its oxidative properties), rather than H_2SO_4 (also oxidant, but possibly emitting SO_2).

Table 1

3.2 Contact with water or with an acid, measurement of gas volume and gas identification

A method of gas volume measurement that could be relevant was estimated to be the volumetric measure of CO₂ produced by carbonates in soil in contact with hydrochloric acid (ISO 10693). Some biological methods measure also gas volume but during days (i. e. ISO 11734). In this study, gas volume was first measured by an automated agricultural calcimeter (Dream électronique, France) derived from ISO 10693. Weighted samples are put into flasks of 70 ml. The apparatus delivers a volume of water or acid, closes the flask and records the pressure for 5 minutes.

Different parameters (mass, granularity, liquid/solid ratio, water and acid addition, acid normality) were preliminary tested and fixed. A good wetting and a more homogeneous temperature in case of reactive waste is obtained with L/S = 10 L (water or acid plus water) / kg (waste). Lower L/S ratios are not always providing a complete wetting of the waste, since there is no agitation. Emission of gas from waste in contact with water was always very low (< 1 mbar pressure change) (results not shown). The subsequent tests were done only with an acid.

The apparatus can inject a volume up to 7.8 ml. The test sample was fixed to 1.6 g (the largest possible with that apparatus), and 7.8 ml of water were manually added. The apparatus added 7.8 ml of 5.1 N hydrochloric acid, giving a final L/S ratio of 10 L HCl 2.5 N/kg raw waste. Three replicates were done. Trials were done in an air-conditioned lab, and temperature was kept within 20°C ± 2°C.

For measurement of gas volume for a longer time, samples were put into 0.25 l glass flask. The stopper of the flask is connected to a U-shape tube filled with water. The water or acid is poured into a small test tube and the cap closed. The test tube is inverted. The difference of water level is recorded at periodic time, and converted to a volume of released gas at atmospheric pressure, taking into account the volume of the flask, the tube and the added water or acid. Stainless steel calorimetric bombs were also used but the security membrane (that burst in case of pressure > 160 bar) was corroded in some weeks by the acid vapors.

The results are expressed per kg of dry mass for solids, and per kg of raw mass for liquids.

Gas identification by electrochemical methods was done with 3 Dräger portable apparatus (A-am 5000, X-am 5600 and X-am 7000). The three detectors were connected successively to a flask where a sample was in contact with an acid. The last detector is equipped with a pump and air is allowed to flow in the flask and through the system. The concentrations are not absolute concentration values but rather indication of the nature of the gas that is/are emitted.

Figure 1

3.3 Waste samples

A series of 49 waste (industrial, municipal, mine residue, sediments) has been tested. These waste have been assessed for other hazard properties in a previous paper (Hennebert et al. 2014). Ten waste were so-called ‘mirror entries’ in the European list of waste (can be hazardous or non-hazardous depending on the contaminant content). No information about gas emission were known, and HP 12 was not assessed in France before the present study. The frequency of occurrence of

hazard by HP 12 was not known. Solid waste with volatile substances were used without pretreatment: a portion was taken in the flask. Samples without significant volatile content were pretreated according to EN 15002 (drying, crushing at 4 mm). Liquid waste were thoroughly mixed before sampling.

3. RESULTS

For blanks with water, the temperature was monitored and an increase of 2°C has been observed, due to heat of dilution of the acid. In the condition of the apparatus, it produces a mean pressure increase corresponding to an apparent gas emission of 0.06 liter of gas/kg sample (Lg/kg). The detection limit of the test was then set to 0.1 Lg/kg. For a test sample of 1.6 g of liquid or dry mass (MS) of solid, and an internal volume of 287 ml, an emission of 1 L of gas per kg of waste corresponds to a variation of pressure of 6 mbar above atmospheric pressure. It has been estimated that a plateau of pressure is reached if the relative difference in absolute pressure at 2 and 5 minutes time is lower than 5%.

Emission of gas by decreasing value and classified with or without a plateau in 5 minutes time in contact with hydrochloric acid is presented at Table 2. The group that does not reach a plateau in 5 minutes (24 samples) is composed only of solid waste and have all (but one) an emission rate > 1 Lg/kg. With the small test sample of 1.6 g, the relative standard deviation can be high for low values (Table 2), and the test should be repeated several times if the results is close to or lower than 2 Lg/kg. The relative standard deviations are quite high and further developments of the method could be done with larger aliquots. A longer duration test should be used for gas emission assessment for those waste. The group that does reach a plateau in 5 minutes (25 samples) is composed of all the liquid waste plus the sediments, one sample of air pollution control residue (APC) of municipal solid waste incinerator and the sample of scrapped tires. The sediment and the APC residue contain carbonates (information from other studies). Nine of the 25 have a gas emission rate > 1 Lg/kg.

Because a longer duration test needs to be implemented in order to better assess the gas emission and also the gas identification for some waste, emission of gas for 6 hours time of contact has been measured for some waste. Calorimetric bombs and glass flasks have been used, with a mass of 1.6 g, and $L/S = 10 \text{ L (water or acid plus water) / kg (waste)}$. The emission by decreasing value and classified with or without a plateau in contact with hydrochloric acid is presented at Table 3. The emitted volumes are higher than in 5 minutes, and for most of the waste (the relative pressure difference between 6 h and 1 h is greater than 5%), a plateau is still not reached. Since the definition of HP 12 is qualitative, the fact that the equilibrium is not reached (probably due to absence of pretreatment) is not invalidating the result.

Table 2

Table 3

Table 4

The gas identification results are presented at Table 4. Most waste emits CO₂ and one waste (a municipal waste fraction) emits methane.

Waste that emit gas toxic (for humans) are:

- Metallic dust from the aluminum industry (CO). This waste emit also H₂ in contact with an acid;
- Two air pollution control of industrial incinerators residue (H₂S);
- Halogenated solvents (volatile alcane).

Only the emission of H₂S is relevant for HP 12. The substances that can emit H₂S in contact with an acid, and having the HSC EUH031 (Table 1), are sulfide (of Ba, Ca, K), polysulfide (Ba, Ca, K, Na, NH₄), dithionite (Na), metabisulfite (Na), others (tosylchloramide sodium, di(benzothiazol-2-yl) disulfide). For the two industrial APC residues, the Ca content is between 15 and 30%, the Na content is between 1 and 2.5%, and the content of K and Ba is lower. It can be supposed that sulfide is in the form of CaS, as Ca is dominant. Those two waste are probably hazardous by HP 12. The APC residue of industrial waste #1 is classified for HP 7, HP 10 and HP 14, and the APC #2 is classified for HP 10 and HP 14 (Hennebert et al. 2014).

4. CONCLUSION

The proposed stepwise method seems quite satisfactory. Further development could be done with larger aliquots. The test is suitable for solid and liquid waste. Most of the tested samples emit gas in contact with concentrated hydrochloric acid, but it is mainly CO₂. Human toxic gases are potentially emitted by three waste: metallic dust from the aluminum industry (CO), two air pollution control residue from industrial waste (H₂S) and a halogenated solvent (gas with a response to alcane detector). The two waste that emit H₂S are potentially classified for HP 12 if the solid sulfide they content is classified EUH031, like by example calcium sulfide. The two waste are nevertheless already classified hazardous for other hazard properties. Given these results obtained from a large panel of inert, municipal and industrial waste (Table 2), it can be assumed that few common household and industrial waste will be classified hazardous only by HP 12.

5. ACKNOWLEDGEMENTS

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FIGURES

A proposal for a test method for assessment of hazard property HP 12 ("Release of an acute toxic gas") in hazardous waste classification - experience from 49 waste

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Figure 1: Automatic calcimeter, and example of emission of gas in contact with an acid

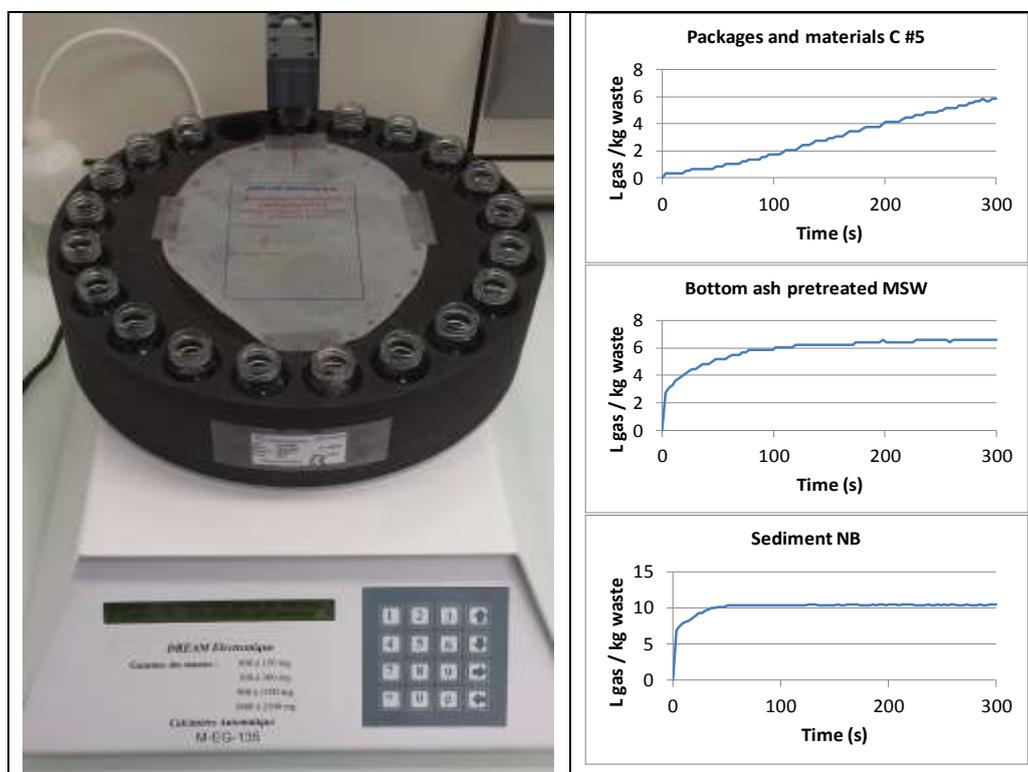


Figure 1: Automatic calcimeter, and example of emission of gas in contact with an acid

TABLES

A proposal for a test method for assessment of hazard property HP 12 ("Release of an acute toxic gas") in hazardous waste classification - experience from 49 waste

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Table 1: Substances with hazard statement codes EUH029, EUH031 and EUH032 with molecular formula and gas emission, sorted by gas (from Table 3.2 of Annex VI of CLP).

Table 2: Emission of gas by waste in 5 minutes, sorted for the presence of a plateau and decreasing emission

Table 3: Emission of gas by waste in 6 hours, sorted for the presence of a plateau and decreasing emission

Table 4: Identification of gases emitted by waste (neither NH₃ nor HCN were detected)

Table 1: Substances with hazard statement codes EUH029, EUH031 and EUH032 with molecular formula and gas emission, sorted by gas (from Table 3.2 of Annex VI of CLP).

International Chemical Identification	Index N°	EC No	CAS No	Classification	Hazard Statement Code	Molecular formula	Gas emission
EUH029 Contact with water							
thionyl dichloride; thionyl chloride	016-015-00-0	231-748-8	7719-09-7	Acute Tox. 4 Acute Tox. 4 Skin Corr. 1A	EUH014 H332 H302 H314	SOCl ₂	HCl SO ₂
phosphorus trichloride	015-007-00-4	231-749-3	7719-12-2	Acute Tox. 2 Acute Tox. 2 STOT RE 2 Skin Corr. 1A	EUH014 H330 H300 H373 H314	PCl ₃	HCl
phosphorus pentachloride	015-008-00-X	233-060-3	10026-13-8	Acute Tox. 2 Acute Tox. 4 STOT RE 2 Skin Corr. 1B	EUH014 H330 H302 H373 H314	PCl ₅	HCl
phosphoryl trichloride	015-009-00-5	233-046-7	10025-87-3	Acute Tox. 2 STOT RE 1 Acute Tox. 4 Skin Corr. 1A	EUH014 H330 H372 H302 H314	POCl ₃	HCl
disulphur dichloride; sulfur monochloride	016-012-00-4	233-036-2	10025-67-9	Acute Tox. 3 Acute Tox. 4 Skin Corr. 1A Aquatic Acute 1	EUH014 H301 H332 H314 H400	S ₂ Cl ₂	HCl SO ₂
trichlorosilane HCl ₃ Si	014-001-00-9	233-042-5	10025-78-2	Flam. Liq. 1 Pyr. Liq. 1 Acute Tox. 4 Acute Tox. 4 Skin Corr. 1A	EUH014 H224 H250 H332 H302 H314	HCl ₃ Si	HCl
chloroacetyl chloride	607-080-00-1	201-171-6	79-04-9	Acute Tox. 3 Acute Tox. 3 Acute Tox. 3 STOT RE 1 Skin Corr. 1A Aquatic Acute 1	EUH014 H331 H311 H301 H372 H314 H400	Cl-CH ₂ -COCl ; C ₂ H ₂ Cl ₂ O	HCl
3-(4-fluorophenyl)-2-methylpropionylchloride	602-099-00-1	426-370-7	-	Skin Corr. 1A Acute Tox. 4 Aquatic Chronic 3	EUH014 H314 H302 H412	C ₁₀ H ₉ ClF O	HCl (hyp.)
3,5-dichloro-2,4-difluorobenzoyl fluoride	607-181-00-0	401-800-6	101513-70-6	Acute Tox. 3 Skin Corr. 1B Acute Tox. 4 Skin Sens. 1 Aquatic Chronic 3	H331 H314 H302 H317 H412	C ₇ HCl ₂ F ₃ O	HF (hyp.)
calcium phosphide; tricalcium diphosphide	015-003-00-2	215-142-0	1305-99-3	Water-react. 1 Acute Tox. 2 Aquatic Acute 1	H260 H300 H400	C ₃ P ₂	PH ₃
magnesium phosphide; trimagnesium diphosphide	015-005-00-3	235-023-7	12057-74-8	Water-react. 1 Acute Tox. 2 Aquatic Acute 1	H260 H300 H400	Mg ₃ P ₂	PH ₃
aluminium phosphide	015-004-00-8	244-088-0	20859-73-8	Water-react. 1 Acute Tox. 2 Aquatic Acute 1	EUH032 H260 H300 H400	AlP	PH ₃

trizinc diphosphide; zinc phosphide	015-006-00-9	215-244-5	1314-84-7	Water-react. 1 Acute Tox. 2 Aquatic Acute 1 Aquatic Chronic 1	EUH032 H260 H300 H400 H410	Zn ₃ P ₂	PH ₃
diphosphorus pentasulphide; phosphorus pentasulphide	015-104-00-1	215-242-4	1314-80-3	Flam. Sol. 1 Water-react. 1 Acute Tox. 4 Acute Tox. 4 Aquatic Acute 1	H228 H260 H332 H302 H400	P ₄ S ₁₀	H ₂ S
EUH031 Contact with an acid							
sodium hypochlorite, solution ... % Cl active	017-011-00-1	231-668-3	7681-52-9	Skin Corr. 1B Aquatic Acute 1	H314 H400	NaClO	Cl ₂
tosylchloramide sodium	616-010-00-9	204-854-7	127-65-1	Acute Tox. 4 Skin Corr. 1B Resp. Sens. 1	H302 H314 H334	C ₇ H ₇ ClN O ₂ S·Na (3H ₂ O) (chloramine-T)	Cl ₂
calcium hypochlorite Ca(ClO) ₂	017-012-00-7	231-908-7	7778-54-3	Ox. Sol. 2 Acute Tox. 4 Skin Corr. 1B Aquatic Acute 1	H272 H302 H314 H400	Ca(ClO) ₂	Cl ₂
troclosene sodium, dihydrate	613-030-01-7	220-767-7	51580-86-0	Acute Tox. 4 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H302 H319 H335 H400 H410	C ₃ Cl ₂ N ₃ N aO ₃ = sodium dichloroi socyanur ate	Cl ₂
dichloro-1,3,5-triazinetriene; dichloroisocyanuric acid	613-029-00-4	220-487-5	2782-57-2	Ox. Sol. 2 Acute Tox. 4 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H272 H302 H319 H335 H400 H410	C ₃ HCl ₂ N ₃ O ₃	Cl ₂
troclosene potassium; [1] troclosene sodium [2]	613-030-00-X	218-828-8 [1] 220-767-7 [2]	2244-21-5 [1] 2893-78-9 [2]	Ox. Sol. 2 Acute Tox. 4 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H272 H302 H319 H335 H400 H410	C ₃ Cl ₂ N ₃ N aO ₃	Cl ₂
symclosene; trichloroisocyanuric acid; trichloro-1,3,5-triazinetriion	613-031-00-5	201-782-8	87-90-1	Ox. Sol. 2 Acute Tox. 4 Eye Irrit. 2 STOT SE 3 Aquatic Acute 1 Aquatic Chronic 1	H272 H302 H319 H335 H400 H410	C ₃ Cl ₃ N ₃ O 3	Cl ₂
dipotassium sulphide; potassium sulphide	016-006-00-1	215-197-0	1312-73-8	Skin Corr. 1B Aquatic Acute 1	H314 H400	K ₂ S	H ₂ S
potassium polysulphides	016-007-00-7	253-390-1	37199-66-9	Skin Corr. 1B Aquatic Acute 1	H314 H400	K ₂ S _x	H ₂ S
ammonium polysulphides	016-008-00-2	232-989-1	9080-17-5	Skin Corr. 1B Aquatic Acute 1	H314 H400	(NH ₄) ₂ S _x	H ₂ S
sodium dithionite; sodium hydrosulphite	016-028-00-1	231-890-0	7775-14-6	Self-heat. 1 Acute Tox. 4	H251 H302	Na ₂ S ₂ O ₄	H ₂ S
barium sulphide	016-002-00-X	244-214-4	21109-95-5	Acute Tox. 4 Acute Tox. 4 Aquatic Acute 1	H332 H302 H400	BaS	H ₂ S
sodium polysulphides	016-010-00-3	215-686-9	1344-08-7	Acute Tox. 3 Skin Corr. 1B Aquatic Acute 1	H301 H314 H400	Na ₂ S _x	H ₂ S
di(benzothiazol-2-yl) disulphide	613-135-00-0	204-424-9	120-78-5	Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H317 H400 H410		H ₂ S
barium polysulphides	016-003-00-5	256-814-3	50864-67-0	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Aquatic Acute 1	H319 H335 H315 H400	Ba ₂ S _x	H ₂ S
calcium sulphide	016-004-00-0	243-873-5	20548-54-3	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Aquatic Acute 1	H319 H335 H315 H400	CaS	H ₂ S

calcium polysulphides	016-005-00-6	215-709-2	1344-81-6	Eye Irrit. 2 STOT SE 3 Skin Irrit. 2 Aquatic Acute 1	H319 H335 H315 H400	Ca ₂ S _x	H ₂ S
metam-sodium (ISO); sodium methylthiocarbamate	006-013-00-8	205-293-0	137-42-8	Acute Tox. 4 Skin Corr. 1B Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H302 H314 H317 H400 H410	CH ₃ – NH – CS – SNa ; C ₂ H ₄ NNa S ₂	HCN (hyp.)
sodium selenite	034-003-00-3	233-267-9	10102-18-8	Acute Tox. 2 Acute Tox. 3 Skin Sens. 1 Aquatic Chronic 2	H300 H331 H317 H411	Na ₂ SeO ₃	SeO ₂
sodium hydrogensulphite ... %; sodium bisulphite ... %	016-064-00-8	231-548-0	7631-90-5	Acute Tox. 4	H302	NaHSO ₃	SO ₂
sodium metabisulphite	016-063-00-2	231-673-0	7681-57-4	Acute Tox. 4 Eye Dam. 1	H302 H318	Na ₂ S ₂ O ₅	SO ₂
EUH032 Contact with an acid							
calcium cyanide	020-002-00-5	209-740-0	592-01-8	Acute Tox. 2 Aquatic Acute 1 Aquatic Chronic 1	H300 H400 H410	CaCN ₂	HCN
thiocyanic acid	615-003-00-8	207-337-4	463-56-9	Acute Tox. 4 Acute Tox. 4 Acute Tox. 4 Aquatic Chronic 3	H332 H312 H302 H412	HSCN	HCN
salts of thiocyanic acid, with the exception of those specified elsewhere in this Annex	615-004-00-3	-	-	Acute Tox. 4 Acute Tox. 4 Acute Tox. 4 Aquatic Chronic 3	H332 H312 H302 H412	NaSCN	HCN
salts of hydrogen cyanide with the exception of complex cyanides such as ferrocyanides, ferricyanides and mercuric oxycyanide and those specified elsewhere in this Annex	006-007-00-5	-	-	Acute Tox. 2 Acute Tox. 1 Acute Tox. 2 Aquatic Acute 1 Aquatic Chronic 1	H330 H310 H300 H400 H410	NaCN	HCN
nickel dicyanide	028-034-00-1	209-160-8	557-19-7	Carc. 1A STOT RE 1 Resp. Sens. 1 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350i H372 H334 H317 H400 H410	Ni(CN) ₂	HCN
cadmium cyanide	048-004-00-1	208-829-1	542-83-6	Acute Tox. 2 Acute Tox. 1 Acute Tox. 2 Carc. 2 STOT RE 2 Aquatic Acute 1 Aquatic Chronic 1	H330 H310 H300 H351 H373 H400 H410	Cd(CN) ₂	HCN
nickel dithiocyanate	028-046-00-7	237-205-1	13689-92-4	Carc. 1A Muta. 2 Repr. 1B STOT RE 1 Resp. Sens. 1 Skin Sens. 1 Aquatic Acute 1 Aquatic Chronic 1	H350i H341 H360 H372 H334 H317 H400 H410	Ni(SCN) ₂	HCN
sodium fluoride	009-004-00-7	231-667-8	7681-49-4	Acute Tox. 3 Eye Irrit. 2 Skin Irrit. 2	H301 H319 H315	NaF	HF
sodium azide	011-004-00-7	247-852-1	26628-22-8	Acute Tox. 2 Aquatic Acute 1 Aquatic Chronic 1	H300 H400 H410	NaN ₃	HN ₃ (hydrazoic acid)
aluminium phosphide	015-004-00-8	244-088-0	20859-73-8	Water-react. 1 Acute Tox. 2 Aquatic Acute 1	EUH029 H260 H300 H400	AlP	PH ₃
trizinc diphosphide; zinc phosphide	015-006-00-9	215-244-5	1314-84-7	Water-react. 1 Acute Tox. 2 Aquatic Acute 1 Aquatic Chronic 1	EUH029 H260 H300 H400 H410	Zn ₃ P ₂	PH ₃

Hyp. = hypothesis

Table 2: Emission of gas by waste in 5 minutes, sorted for the presence of a plateau and decreasing emission

Sample	Plateau in 5 minutes ?	Emission (Lg/kg) in 5 minutes	SD (Lg/kg)	RSD
Sludges from landfill leachate, after evapo-concentration	no	27.1	7.7	0.28
APC residue from municipal waste after solid fuel, metals and organic matter separation	no	13.3	7.5	0.56
Sludges from treatment of urban waste water	no	10.6	7.5	0.71
Compost from organic fraction separately collected	no	8.1	0.9	0.12
Bottom ash and slag from municipal waste after solid fuel, metals and organic matter separation - matured and pretreated	no	7.3	0.5	0.06
Pasty waste #1	no	6.6	0.9	0.13
Packages and materials C #5	no	6.6	0.7	0.11
Pasty waste #3 Mix of storage tank	no	6.3	3.4	0.53
Surface treatment - sludges and filter cakes	no	4.6	0.1	0.02
APC residue industrial waste #2	no	4.6	1.4	0.30
MSWI APC residue, lime process	no	4.1	1.3	0.32
MSWI fly ash	no	4.1	1.7	0.41
Compost from mixed municipal waste, fraction < 30 mm after crushing	no	3.3	1.0	0.29
Wastes from transport tank cleaning, mixed sludge of food and chemical transport	no	3.2	1.9	0.58
Metallic dust from aluminum industry	no	3.2	0.2	0.05
Pasty waste #2	no	2.8	2.4	0.83
APC residue industrial waste #1	no	2.8	1.4	0.51
Packages and materials #3	no	2.4	0.3	0.14
Mixed municipal waste, fraction > 30 mm after crushing	no	2.2	0.5	0.23
Bauxite residue	no	2.2	0.3	0.15
Industrial waste bottom ash	no	2.1	0.7	0.31
Municipal waste - Organic fraction separately collected	no	1.7	0.7	0.40
Packages and materials B #5	no	1.1	0.6	0.55
Solid recovered fuel	no	0.4	0.1	0.25
Sediment Marseille (harbor, Mediterranean sea, FR)	yes	18.1	0.3	0.01
Sediment Dunkerque (harbor, North sea, FR)	yes	12.1	0.2	0.01
MSWI Air pollution control (APC) residue, bicarbonate process	yes	11.9	2.9	0.24
Sediment Nimy-Blaton (canal, BE)	yes	10.7	0.4	0.04
Sediment Lens (canal, FR)	yes	4.4	0.1	0.03
Halogenated solvent #3	yes	2.4	0.2	0.09
Sediment Evry (highway storm basin, FR)	yes	1.5	0.4	0.27
Waste water #2, mixture of 13 wastes	yes	1.1	1.7	1.59
Waste water #1	yes	1.0	1.5	1.57
Halogenated solvent #1	yes	0.4	0.1	0.24
Scrapped tires 4 mm	yes	0.3	0.4	1.28
Hydrocarbon #2	yes	0.2	0.2	0.99
Active landfill leachate containing hazardous substances or landfill leachate other than those mentioned in 19 07 02	yes	0.2	0.3	1.73
Hydrocarbon #3 Mixture of wastes of oils and liquid fuels without motor and lubricating oil and hydraulic oil	yes	0.2	0.2	0.99
Closed landfill leachate containing hazardous substances or landfill leachate other than those mentioned in 19 07 02	yes	0.1	0.2	1.73
Non-halogenated solvent #1	yes	0.1	0.1	0.87
Waste water #3	yes	0.1	0.2	1.73
Hydraulic oil	yes	0.1	0.1	0.87

Halogenated solvent #2	yes	0.1	0.1	0.87
Engine oil	yes	0.1	0.1	0.87
Waste water #5	yes	<0.1	-	-
Waste water #4	yes	<0.1	-	-
Waste water #6	yes	<0.1	-	-
Liquid recovered fuel	yes	<0.1	-	-
Hydrocarbon #1	yes	<0.1	-	-

Table 3: Emission of gas by waste in 6 hours, sorted for the presence of a plateau and decreasing emission

Sample	Plateau between 1 h and 6 h ?	Emission (Lg/kg) in 6 h
Sludges from landfill leachate, after evapo-concentration	no	95.8
Sludges from treatment of urban waste water	no	79.3
Sediment Marseille (harbor, Mediterranean sea)	no	56.6
Compost from organic fraction separately collected	no	46.4
Packages and materials C #5	no	36.6
MSWI Air pollution control (APC) residue, bicarbonate process	no	33.6
Pasty waste #1	no	31.2
Pasty waste #3 Mix of storage tank	no	28.6
Wastes from transport tank cleaning, mixed sludge of food and chemical transport	no	27.6
Mixed municipal waste, fraction > 30 mm after crushing	no	22.6
APC residue industrial waste #2	no	20.7
MSWI fly ash	no	16.0
Surface treatment - sludges and filter cakes	no	14.0
Industrial waste bottom ash	no	9.6
Scrapped tires 4 mm	no	8.9
Municipal waste - Organic fraction separately collected	no	8.2
Bauxite residue	no	6.6
Packages and materials B #5	no	6.1
Active landfill leachate containing hazardous substances or landfill leachate other than those mentioned in 19 07 02	no	4.2
Halogenated solvent #1	no	3.9
Waste water #2, mixture of 13 wastes	no	3.8
Waste water #1	no	2.9
Sediment Lens (canal, FR)	yes	64.5
Packages and materials #3	yes	44.7
Sediment Evry (highway storm basin, FR)	yes	5.8
Halogenated solvent #2	yes	<0.1

Table 4: Identification of gases emitted by waste (neither NH₃ nor HCN were detected) (LQ 0.1% or 0.1 ppm)

Sample	H ₂ ppm	CO ₂ % Vol.	CO ppm	CH ₄ % Vol. l.	Eq isobutene ppm	Amines ppm	H ₂ S ppm	SO ₂ ppm
APC residue from municipal waste after solid fuel, metals and organic matter separation		0.16						
APC residue industrial waste #1		2.52			2		157	
APC residue industrial waste #2		0.52				4	28	0.2
Bauxite residue		0.15						
Bottom ash and slag from municipal waste after solid fuel, metals and organic matter separation - maturated and pretreated		0.36			5			
Compost from mixed municipal waste, fraction < 30 mm after crushing		0.08						
Compost from organic fraction separately collected		0.18						
Halogenated solvent #3		0.50			610	7		
Industrial waste bottom ash		0.12			3			
Metallic dust from aluminum industry	410	0.24	22.8		3			
Mixed municipal waste, fraction > 30 mm after crushing				2.5				
MSWI Air pollution control (APC) residue, bicarbonate process		0.61		0.8	2			
MSWI APC residue, lime process		0.10						
MSWI fly ash		0.14						
Municipal waste - Organic fraction separately collected								
Packages and materials B #5								
Packages and materials C #5		0.50						
Pasty waste #1		0.15			2			
Pasty waste #2					3			
Pasty waste #3 Mix of storage tank		0.45			5			
Sediment Dunkerque (harbor, North sea, FR)		0.45			5			
Sediment Evry (highway storm basin, FR)								
Sediment Lens (canal, FR)		0.53						
Sediment Marseille (harbor, Mediterranean sea, FR)					3			
Sediment Nimy-Blaton (canal, BE)		0.45						
Sludges from treatment of urban waste water		0.46						
Surface treatment - sludges and filter cakes		0.33						
Waste water #1		0.06						
Waste water #2, mixture of 13 wastes								
Wastes from transport tank cleaning, mixed sludge of food and chemical transport		1.42						