An analytical protocol for the knowledge of waste by substances

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Pierre HENNEBERT[1], Arnaud PAPIN[2]

[1] INERIS – Institut National de l'Environnement Industriel et des Risques, Domaine du Petit Arbois BP33, F-13545 Aix-en-Provence, France. Phone: +33(0) 3 44 61 83 06. pierre.hennebert@ineris.fr
[2]INERIS, Parc Technologique ALATA, BP n°2, 60550 Verneuil en Halatte, France.

Abstract

The hazardousness of waste could be soon assessed in Europe by the hazard properties of its constituents. A quasi exhaustive knowledge of its constituents will therefore be necessary. A conceptual scheme of waste composition is proposed for analysis purpose, including unresolved pools of probably higher molecular weight organic substances supposed to be less bioactive and less hazardous ("non extractible organic compounds", "unidentified volatile compounds" and "unidentified semi-volatile compounds"). Screening ICP methods are used for major elements, and screening GC MS methods are used for volatile and semi-volatile organics. 32 laboratory samples of different industrial wastes have been tested following (with differences) this protocol by two (routine) service laboratories, with about 7 000 parameter results. A satisfactory analytical balance of 90 % is reached for 20 samples (63 % of the samples) during this first run, with identified reasons for most of the unsatisfying results. A first exploratory classification of the wastes for their hazardousness according to the Seveso legislation was performed based on data from the (chemical) CLP regulation. Using the CLP data, out of 32 samples, 27 (84 % of the samples) were classified identically by the two laboratories (23 not hazardous and 4 hazardous). Using additional EC_{50} data, out of 32 samples, 27 (84 % of the samples) were classified identically by the two laboratories (13 not hazardous and 14 hazardous).

Keywords: Hazardousness ; Substances ; Mass balance ; Waste classification

1 Introduction

The hazard of the wastes must be assessed for regulatory compliance. The on-going work of the European member states for the update of the Waste Directive defines 14 or 15 hazard criteria, mainly based on the properties of substances and the classification, labeling and packaging of substances and mixtures regulation (CLP, EC 1272/2008). Wastes will be considered as mixtures of substances, and their properties assessed by calculation from the properties of the substances, or from tests. Since tests are not available for all criteria, wastes should be known by total substances content. A protocol is proposed for this. It has been applied to 15 solid and 17 liquid wastes.
Fully detailed protocol and results (40 p) will be submitted to a scientific journal for publication.

2 Materials

The professional associations of hazardous waste handling (SYVED, SYPRED) proposed, in consultation with the French Ministry of Ecology (MEDDTL), a list of wastes to be studied. They sent laboratory samples to INERIS. The professional association of hydraulic binders (ATILH) added two samples of alternative fuels in cement kiln. These samples were supposed to be representative of the 'pool' of waste collected (constitution of primary samples, mixing - homogenization, quartering, and so on, to produce a laboratory sample of about 5 kg or 5 liters). Among these samples, three shredded packaging and contaminated materials have been received, however, in 200 liter drums. A large panel

of 15 solid and 17 liquid wastes covering most types of industrial wastes (listed in Table 1) has been studied.

Table 1. Waste samples

Solid/Name	Waste	European List of Waste code, origin of waste
S1	Air pollution control (APC) residue, bicarbonate process	19 01 07* (Wastes from incineration or pyrolysis of waste, Solid waste from gas treatment)
S2	APC residue, lime process	19 01 07* (see above)
S3	MSWI fly ash	19 01 05* (Filter cake from gas treatment)
S4	APC residue industrial waste #1	19 01 07* (see above)
S5	APC residue industrial waste #2	19 01 07* (see above)
S6	Industrial waste bottom ash	19 01 11* (Bottom ash and slag containing dangerous substances)
S7	Metallic dust from aluminum industry	10 03 19 * (Flue-gas dust containing dangerous substances)
S8-DON	Packages and materials #1	No information
S8-GEO	Packages and materials #2	19 12 11* (Other wastes (including mixtures) from the mechanical treatment of wastes containing hazardous substances)
S8-SAR	Packages and materials #3	19 12 11* (see above)
S8-SCO	Packages and materials #4	15 01 10* (Packaging containing residues of hazardous or contaminated by residues).
S8-TRI	Packages and materials #5	No information
S9-GEO	Pasty waste #1	19 08 13* (Sludges containing dangerous substances from other industrial water treatment plant)
S9-SCO	Pasty waste #2	08 01 13* (Sludges from paint or varnish containing organic solvents or other dangerous substances), 08 04 11* (Adhesives and sealants sludges containing organic solvents or other hazardous substances)
S18	Solid recovered fuel	19 02 09*Solid fuel waste containing hazardous substances
Liquid/Name	Waste	European List of Waste code, origin of waste
S9-SAR	Pasty waste #3	Mix of storage tank
S10	Engine oil	13 02 08* (Other motor oils, gear and lubricating)
S11	Hydraulic oil	13 01 13* (Other hydraulic oils)
S12-SON	Hydrocarbon #1	13 07 03* (Wastes of liquid fuels, Other fuels (including mixtures))
S13-SCO	Hydrocarbon #2	13 05 07* (Water mixed with oil from oil / water separators), 13 07 03* (see above)
S13-SON	Hydrocarbon #3	Mixture of wastes of oils and liquid fuels without motor and lubricating oil and hydraulic oil
S14-PCX	Halogenated solvent #1	07 01 03* (Organic halogenated solvents, washing liquids and mother liquors)
S14-SAN	Halogenated solvent #2	No information
S14-SAR	Halogenated solvent #3	14 06 02* (Other solvents and mixtures of halogenated solvents)
S15	Non-halogenated solvent #1	Other solvents, washing liquids and mother liquors from : 07 01 04* (Wastes from the manufacture, formulation, distribution and use (MFSU) of basic organic chemicals), 07 02 04* (idem of plastics, rubber and synthetic fibers), 07 05 04* (idem of pharmaceuticals), 07 06 04* (idem of fats, soaps, detergents, disinfectants and cosmetics), 07 07 04* (idem of chemicals from the fine chemicals and chemical products not elsewhere specified)
S16-CHI	Waste water #1	16 10 01* mixture of (Aqueous liquid wastes destined for off-site treatment, Aqueous liquid wastes containing dangerous substances).
S16-DUC	Waste water #2, mixture of 13 wastes	08 04 16 (Waste from MFSU of adhesives and sealants (including waterproofing products, Aqueous liquid waste containing adhesives or sealants other than those mentioned in 08 04 15), 11 01 06* (chemical surface treatment and coating of metals), 11 01 11* (rinsing liquids), 11 01 13* (degreasing wastes), 12 01 09* (shaping

		and physical and mechanical processing of metals and plastics), 12 01 99 (other), 19 07 03 (Landfill leachate)
S16-GEO	Waste water #3	19 12 04* Waste from mechanic treatment (by example sorting, shredding, compacting, granulating) not specified elsewhere. Plastics and rubber.
S16-HOM	Waste water #4	No information
S16-SAR	Waste water #5	16 10 01* mixture of (Aqueous liquid wastes destined for off-site treatment, Aqueous liquid wastes containing dangerous substances).
S16-SCO	Waste water #6	Wash water liquids and mother liquors from : 07 01 01* (Wastes from the manufacture, formulation, distribution and use (MFSU) of basic organic chemicals), 07 02 01* (idem plastics, rubber and synthetic fibers), 07 03 01* (idem organic dyes and pigments (except 06 11)), 07 04 01* (idem organic plant protection products, of wood protection agents and other biocides), 07 05 01* (idem pharmaceuticals), 07 06 01* (idem fats, soaps, detergents, disinfectants and cosmetics), 07 07 01(idem of chemicals from the fine chemicals and chemical products not elsewhere specified)
S17	Liquid recovered fuel	19 02 08* Liquid fuel waste containing hazardous.

3 Methods

Analytical protocol

The protocole should fulfill the following constraints: (i) the sum of measured concentrations (including indices and groups) should reach 90 et 110 % w/w ; (ii) the fractions, indices and groups should be minimized ; (iii) the measurements of metals and anions should allow, with other information sources, to build a possible mineralogical composition ; (iv) the analytical effort must be adapted to the final output, frequently binary (hazardous/not hazardous) ; (v) the results must allow the classification of the waste according to different regulations (Waste directive, Seveso directive, …). A protocole (4 pages) mainly using CEN standardized methods is proposed (Hennebert, 2011a). In brief, the water content, the sum of total major elements and metals content, the ash content less sum of metals, the sum of the volatile and semi-volatile compounds and the unidentified organic compounds (see below) are added and should be close to 100% (Figure 1). Anions (total halogens, free and bound cyanides, chromium VI) are measured to compute possible mineralogical phases of the elements. New analytical parameters are proposed: for solid wastes, “non extractible organic compounds” is the mass lost by calcination of the dried solid residue remaining after the extraction of semi-volatile substances. The aim is to globally quantify cellulose, lignin and polymers and organic compounds with high molecular weight, which are assumed not being hazardous. For liquid wastes, the parameters “unidentified volatile compounds” and “unidentified semi-volatile compounds” are calculated from the unresolved chromatographic areas of the corresponding chromatograms.

During the analytical campaign of 32 wastes, some amendments were brought to the protocol. They were not always applied by the laboratories, in particular the quantitative methods for individual chlorinated compounds and the use of 3 response factors for chromatographic calibration. One amendment was added after the campaign.

As the protocol is intended to be used routinely, the analyses were intentionally performed by two commercial service laboratories. Some methods are left open in the protocol, and some methods of the protocol were not followed. Others were more precisely defined during the analysis campaign. There were some deviations to the protocol , in particular the parameters "unidentified volatile compounds" and "unidentified semi-volatile compounds" were replaced by Lab1 by “volatile total petroleum hydrocarbon C5-C9” and “total petroleum hydrocarbon C10-C40”, and the "non-extractable organic substances" was biased for Lab1 since the aliquot for the extraction of semi-volatile substances has suffered water extraction prior to extraction, drying of residual solvent and water, and calcination (at 500 °C rather than 550 °C), resulting in a loss of mass and hence an over-estimation of the “non extractable organic substances”.

Laboratory Sample 100%				
Loss on ignition 550 °C (including carbonates and cyanides)	C O 2	C N	Ash content 550 °C (including mineral O N S Cl F)	Water

Non-extractible organic compounds 550 °C	Unidentified Semi-volatile	Unidentified volatile	Volatile	Semi-volatile

Metals S P As Hg	Ash content - Metals	Water

Figure 1. Conceptual scheme of waste composition

4 Results and discussion

4.1 Elements and metals

Detailed results are available at (Hennebert, 2011b).The measure of major and minor elements by ICP is semi-quantitative in the applied protocol (except the 12 "heavy metals" and Si). The output of the analyses is then a given range of concentration, different for the two laboratories. The center of the range is taken as result for the parameter. The concentrations are summed per sample in Figure 2. The correlation between laboratories is obvious but should for some samples and elements be improved.

Limits of quantification from 0.1 to 10 mg kg^{-1} (depending on samples) for mercury and 0.1 and 5 mg kg^{-1} for cadmium have been reported, and therefore used. Given the potential impact of the concentration of cadmium and mercury on the classification of waste hazardousness, it is recommended to reach a limit of quantification of 1 mg kg^{-1} for Hg and Cd.

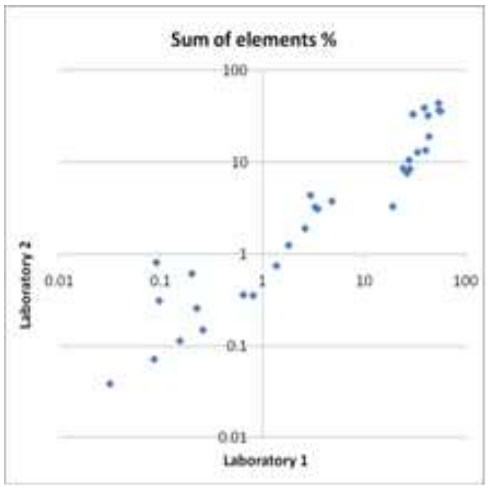

Figure 2 . Sum of ICP-measured element content (Lab 2 vs Lab1)

4.2 Non-extractible organic compounds (solid samples)

The analysis proposed in the protocol is the mass loss at 550 °C (± 25 °C) of the dry mass of the sample after extraction of semi-volatile compounds. Lab 1 performed a water extraction prior to semi-volatile extraction and conducted calcinations at 500 °C instead of 550 °C. The results are presented in

Figure 3 and in Tables 2 and 3. Some results of Lab1 are over-estimated (S1 to S5) or underestimated (S8-TRI).

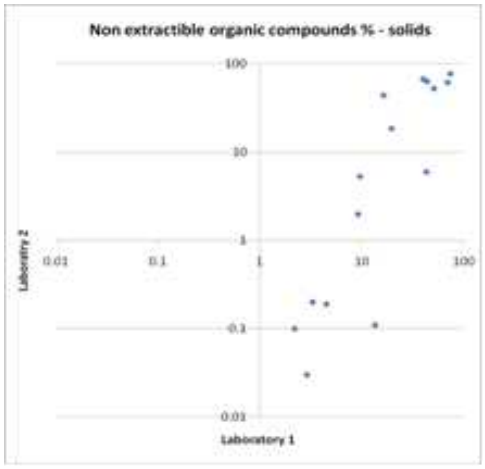

Figure 3 . Non-extractible organic compounds (Lab2 vs Lab1)

4.3 Volatile and semi-volatile organic compounds

These two families were gathered because the same compounds were sometimes assigned by laboratories in different families. Lab1 conducted further analysis "Total hydrocarbons C10-C40" on the liquid samples, but not the "unidentified semi-volatile organic compounds". The Lab2 used the bottle "fresh" or "raw" for the analysis of semi-volatile, instead of using the bottle pretreated and computed the "unidentified semi-volatile organic compounds" of liquid samples as "integration> C10". Therefore, direct comparison of "unidentified semi-volatile organic compounds" is not possible between laboratories. The results for volatile organic compounds and semi-volatile compounds are presented in Figure 4 and in Tables 2 and 3. The list of molecules is not consistent between laboratories. For molecules found by the two laboratories, the concentrations are not consistent between laboratories at concentrations below 0.1 %. An improvement could be to use three standards to quantify the substances, in place of one standard.

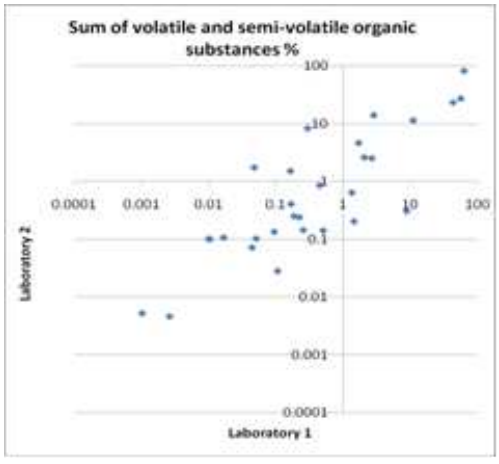

Figure 4 . Sum of organic volatile and semi-volatile substance (Lab 2 vs Lab 1)

The concordance between laboratories should be improved. The chromatographic conditions used should maybe be closer to the identification parameters of the molecules from the database. It should be noted that a therapeutic substance was detected by the two laboratories at low concentrations in a solvent from a pharmaceutical industry, showing that a fine detection of specific compounds is still possible.

If a petroleum mixture is identified, it could be quantified with the corresponding standard, and the corresponding surface subtracted from the response surface of the unidentified compounds.

Further analyses of substances important in the regulation were performed for some samples, by routine quantitative methods of the laboratories (methanol, dioxins and furans concentrations, isocyanates, organic lead derivatives (tetra methyl, tetra ethyl), PCBs.

4.4 Analytical mass balance

The analytical mass balances of the solid sample results are presented in Table 2. Values between 90% and 110% are highlighted in yellow.

For Lab1, in three out of four cases where the mass balance is less than 90%, the "ash content minus the sum of metal" is negative, while there are no cases for Lab2. These 3 cases are samples of shredded packaging with contaminated materials. This indicates, for each sample, an insufficient homogeneity of the laboratory sub-sample. This can be related to the visual high heterogeneity of the samples. It is the recommended to start from a laboratory sample of at least 30 kg of these materials, and to measure the calcinated residue with a test portion of about 30 g of ground (< 1 mm) material.

The mass balance lies between 90% and 110% in 10 cases of 15 for Lab1 and Lab2 (67% of the samples). This seems satisfactory for a first run of the protocol by routine service laboratory with deviations from the recommended methods. For comparison, a campaign analysis of solid and liquid recovered fuels (Hennebert, P., 2011b) showed that the median of the sum of known substances (the analytical mass balance) for 64 samples was 46% by weight.

The analytical mass balances of the liquid samples are presented in Table 3. Values between 90% and 110% are highlighted in yellow. The calculated parameter "ash content - sum of metals" is negative 8 and 6 times for Lab1 and Lab 2 respectively. Lab1 handled the volatile hydrocarbons C5-C10 (volatile Total Petroleum Hydrocarbons) and the standard C10-C40 (TPH) as a result for the "unidentified volatile compounds" and "unidentified semi-volatile compounds" respectively. The mass balances are therefore not strictly comparable. The mass balance relies between 90% and 110 % in 10 cases of 17 for Lab1 and 9 cases of 17 for Lab2 (respectively 59 % and 53 % of the samples). This encouraging result could be improved. When the water content is> 90%, the sum of known compounds exceeds half of the dry matter in 3 cases of 5 to Lab1 and 1 case of 6 for Lab2.

Table 2. Analytical mass balance of solid samples

Concentration (%)	Lab1	Lab2
Sample	Total	Total
S1	126.00	99.96
S2	98.70	99.83
S3	99.40	99.59
S4	91.21	99.81
S5	92.31	99.80
S6	97.26	95.83
S7	95.05	101.35
S8-DON	64.91	80.04
S8-GEO	75.60	89.60
S8-SAR	104.59	91.34
S8-SCO	84.52	100.50
S8-TRI	40.88	67.45
S9-GEO	100.03	85.24
S9-SCO	100.80	79.41
S18	98.61	94.39

Table 3. Analytical mass balance of liquids

Concentration (%)	Lab1	Lab2
Sample	Total	Total
S9-SAR	104.76	96.16
S10	87.80	84.72
S11	87.36	82.83
S12-SON	23.01	70.39
S13-SCO	95.79	112.74
S13-SON	97.27	97.25
S14-PCX	62.17	27.25
S14-SAN	96.58	83.63
S14-SAR	71.97	89.16
S15	66.45	57.88
S16-CHI	101.47	95.92
S16-DUC	99.18	96.83
S16-GEO	100.11	97.20
S16-HOM	99.41	101.40
S16-SAR	88.42	97.60
S16-SCO	97.70	90.69
S17	47.00	66.18

For hydrocarbons containing vegetable oil (sample S17), the method must be developed. Oily waste likely to contain vegetable oil should be saponified before injection so that the fatty acid products are detected in the group of semi-volatile. Otherwise, this oil will not be detected. Information on the potential presence of vegetable oil should be provided in advance by the holder of the waste.

So, it is possible with the new pooled parameters to complete the mass balance. Despite discrepancies for some parameters, a satisfactory analytical balance of 90 % is reached for 20 samples of 32 (63 % of the samples) during this first run. Technical improvements of the majority of unsatisfying results are identified.

4.5 Classification of hazardousness of waste according to the Seveso Directive

For hazard assessment according to the Seveso Directive (using concentration limits of the Dangerous Preparation Directive – DPD 1999), the total metal content must first be converted into mineral species content, since hazard properties are defined for species and not for element. A first conservative estimation was performed by arithmetically converting the total content of each element in the most hazardous form of each element, taking into account the stoechiometry of the elements in the waste sample (Rebischung 2011). For that, the hazard properties of the elements for human or environmental toxicity listed in the CLP regulation were used (CLP Annex, 2011). Exclusion of some minerals based on basic consideration of pH, pe and knowledge of waste was also integrated in this computation.

The content of organic and mineral compounds were then summed by hazard properties, and compared with the limit values (taking into account eventual additivity of properties) of the CLP regulation. This exercise was done with generic limit values given by the CLP and also, in a second run, with additional minimal aquatic ecotoxicity values EC_{50} from the literature (no evaluation of those EC_{50} was performed). The resulting classification of the waste (hazardous/non hazardous for human toxicity T+ and T and aquatic environment N R51 and N R50) is the following:
Using the CLP data, 23 out of 32 samples are not classified as hazardous from the two sets of data (one set per laboratory), 4 are classified as hazardous by the two sets of data (but largely due to different substances), 1 is classified as hazardous by the two sets of data (but for different hazard), and 4 are classified as hazardous by only one set of data ;
Using additional EC_{50} data, 13 out of 32 samples are not classified as hazardous for the two sets of data, 14 were classified as hazardous by the two sets of data, and the other 5 were classified as

hazardous by only set of data (largely because different substances are found by the two laboratories, and secondly because the concentrations found are different).
So using the CLP data and using additional ecotoxicity values, 27 samples out of 32 (84 % of the samples) are classified identically by the two laboratory data sets.

5 Conclusion

A set of 32 samples was analyzed by 2 service laboratories, giving a total of 7 000 data, from which mass balances were calculated. Despite deviations to the protocol, the mass balance lies between 90 and 110% for 20 samples of 32 (63% of the samples). Most deviations are explained and the protocol has been amended during the campaign to improve this encouraging result. A first exploratory classification of 32 wastes was performed with the protocol results. 27 samples out of 32 (84% of the samples) are classified identically by the two laboratory data set.

A first version of the protocol is included in a French application guideline of the SEVESO II Directive (MEDDTL 2011). The eco-industries started at autumn 2011 a wider analysis campaign, which will probably give insight to additional improvements to cover a wider variety of wastes (i.e. waste from electric and electronic equipment - WEEE).

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