Analysis of 32 industrial wastes by substances and classification for hazardous properties HP13 (Sensitising) and approximated classification for HP6 (Harmful/Toxic) and HP14 (Ecotoxic) based on CLP calculation

Workshop “Practical implications of the application of CLP concentration limits on the hazardous properties of waste”, Vienna, 25/10/2011

Pierre HENNEBERT, Aix-en-Provence, pierre.hennebert@ineris.fr
Flore REBISCHUNG, Verneuil-en-Halatte, flore.rebischung@ineris.fr
Institut National pour l’Environnement Industriel et les Risques, F

INERIS
maîtriser le risque pour un développement durable

Caracterisation and classification of wastes : 4 modules

1. **Analytical protocol for the knowledge of wastes by substances** ; briefly presented here

2. **From Elements to Substances** : speciation for determination of the mineralogy – various methods ; not discussed here

   In absence of experimental/observed mineralogical data, the mineralogy is calculated from the elemental composition by stoechiometry. The « worst case » (most dangerous substance) is used, and depends on the Hazardous Property that is classified.

3. **Database of properties of substances** : CLP

4. **Classification for each hazardous property (HP)** :

- HP 13 Sensitising : according to proposed method
- Toxic and Ecotoxic : according to Seveso II rules : N/N^+ and T/T^+

(lack of time for HP6 and HP14 but quite similar)

INERIS

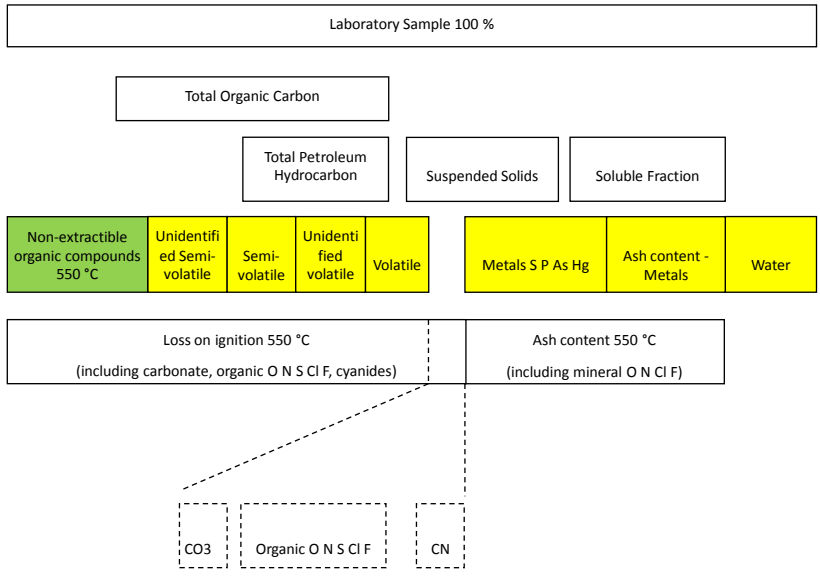
Module1 : An analytical protocol for the knowledge of wastes by substances

An analytical protocol to achieve sufficient knowledge of organic and mineral substances in the waste to enable the determination of their properties for regulatory or recycling objectives is proposed and tested. It uses a combination of quantitative methods, screening methods and measure of pools of unresolved composition, to reach an analytical mass balance of at least 90 %. As a result, the waste samples are known as far as possible by substances.

The protocol includes 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. For elements (heavy metals) and compounds particularly hazardous and subject to regulation (chromium(VI), cyanides, organo-halogens, PCB …), classical quantitative analysis are used.

INERIS maîtriser le risque pour un développement durable

Conceptual scheme of waste composition



INERIS maîtriser le risque pour un développement durable

Module1 : An analytical protocol for the knowledge of wastes by substances

The protocol is build to 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, …).

The protocol (4 pages, in French) is available (http://www.ineris.fr/centredoc/ineris-protocole-analyse-d%C3%A9chets.pdf)

It uses mainly using CEN standardized methods, is discussed at AFNOR and could be presented to CEN TC292 in june 2012.

INERIS maîtriser le risque pour un développement durable

Protocol testing : 32 samples from eco- and cement-industries (SYVED, SYPRED, ATILH (F)) by 2 service laboratories (Eurofins and SGS (F)).

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

Funding : Ministry for Ecology, F

INERIS maîtriser le risque pour un développement durable

Solid/Name	Waste	European List of Waste code, origin of waste
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 12 10 (Fuel waste (fuel from waste))

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)

Liquid/Name	Waste	European List of Waste code, origin of waste
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* (Waste from MFSU of plastics, rubber and synthetic fibers), 07 05 04* (Waste from MFSU pharmaceuticals), 07 06 04* (Waste from MFSU of fats, soaps, detergents, disinfectants and cosmetics), 07 07 04* (Waste from MFSU 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* (Wastes from chemical surface treatment and coating of metals, Acids not elsewhere specified), 11 01 11* (11 01, Aqueous rinsing liquids containing dangerous substances), 11 01 13* (11 01, Degreasing wastes containing dangerous substances) , 11 01 98* (11 01, Other wastes containing dangerous substances – note : mirror code of 99 code used in France for hazardous waste), 12 01 09* (Wastes from shaping and physical and mechanical processing of metals and plastics, Machining emulsions and solutions free of halogens), 12 01 99 (12 01, Wastes not otherwise specified), 19 07 03 (Landfill leachate other than those mentioned in 19 07 02)

Liquid/Name	Waste	European List of Waste code, origin of waste
S16-GEO	Waste water #3	19 12 04* Waste from mecanic 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* (Waste from MFSU of plastics, rubber and synthetic fibers), 07 03 01* (Wastes from the MFSU of organic dyes and pigments (except 06 11)), 07 04 01* (Wastes from the MFSU of organic plant protection products (except 02 01 08, 02 01 09), of wood protection agents (except 03 02) and other biocides), 07 05 01* (Waste from MFSU pharmaceuticals), 07 06 01* (Waste from MFSU of fats, soaps, detergents, disinfectants and cosmetics), 07 07 01(Waste from MFSU chemicals from the fine chemicals and chemical products not elsewhere specified)
S17	Liquid recovered fuel	19 12 10 (Fuel waste (fuel from waste))

Results : exemple of mass balance

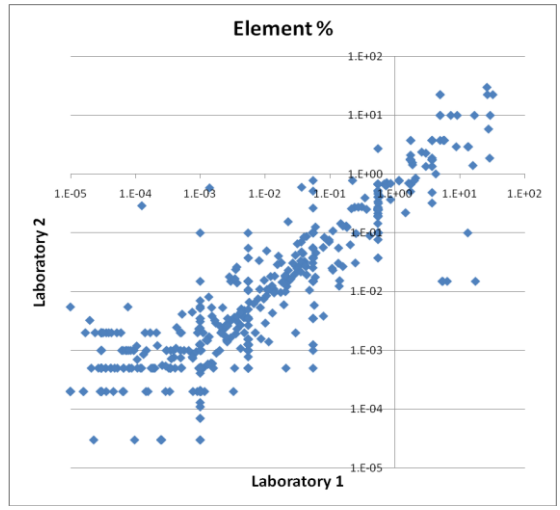
± 7 000 results and groups for the 32 samples and the two laboratories

Substances/group (% m)	Lab1	Lab2
S6 : Industrial waste bottom ash	97.26	95.83
Non-extractible organic compounds (pool)	9.60	5.30
Volatile organic compounds (sum of -)	0.11	0.03
Volatile organic compounds (sum of -)	0.00	0.00
Total Petroluem Hydrocarbons (TPH)	0.56	
Ash content – Metals (sum of -)	44.64	58.98
Metals (sum of -)	42.36	31.52

Important differences between laboratories…

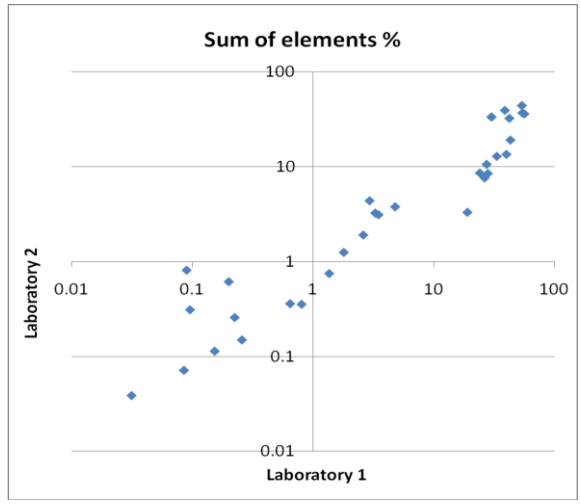
INERIS

Comparison of results between labs

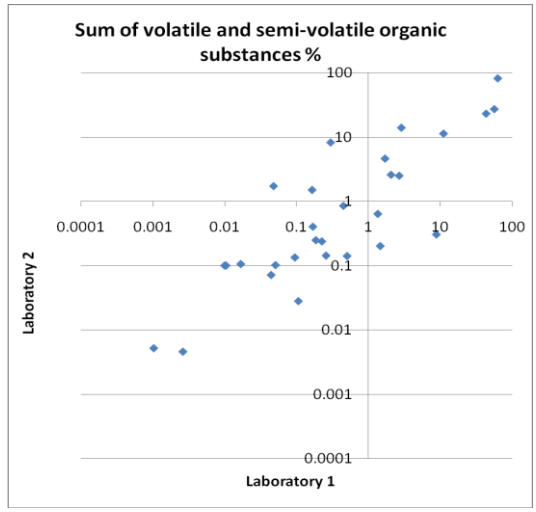


INERIS

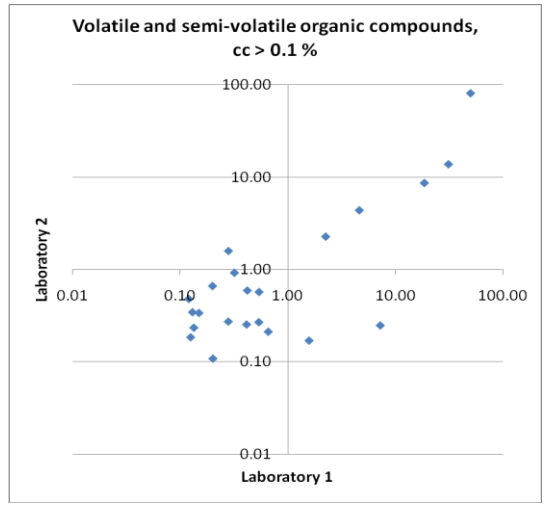
Comparison of results between labs



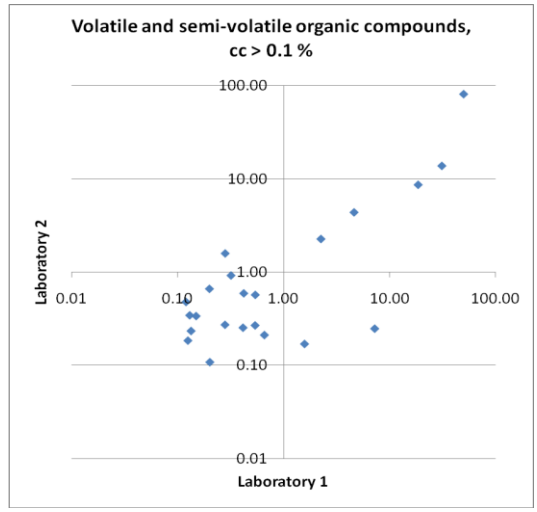
Comparison of results between labs



Comparison of results between labs



Comparison of results between labs



Results : mass balance for solid samples

Teneur en substance pour bilan de masse (% m)	Lab1	Lab2
S1 : APC Bicarbonate	126.00	99.96
S2 : APC Lime	98.70	99.83
S3 : MSWI fly ash	99.40	99.59
S4 : APC residue industrial waste #1	91.21	99.81
S5 : APC residue industrial waste #2	92.31	99.80
S6 : Industrial waste bottom ash	97.26	95.83
S7 : Metallic dust from aluminum industry	95.05	101.35
S8-DON : Packages and materials	64.91	80.04
S8-GEO : Packages and materials	75.60	89.60
S8-SAR : Packages and materials	104.59	91.34
S8-SCO : Packages and materials	84.52	100.50
S8-TRI : Packages and materials	40.88	67.45
S9-GEO : Pasty waste	100.03	85.24
S9-SCO : Pasty waste	100.80	79.41
S18 : Solid recovered fuel	98.61	94.39

Results : mass balance for liquid samples

Teneur en substance pour bilan de masse (% m)	Lab1	Lab2
S9-SAR : Pasty waste	104.76	96.06
S10 : Engine oil	90.28	84.67
S11 : Hydraulic oil	87.36	82.83
S12-SON : Hydrocarbon	23.01	70.39
S13-SCO : Hydrocarbon	95.79	112.73
S13-SON : Hydrocarbon	97.27	97.24
S14-PCX : Halogenated solvent	62.17	27.25
S14-SAN : Halogenated solvent	96.58	83.63
S14-SAR : Halogenated solvent	71.97	89.06
S15 : Non-halogenated solvent	66.45	57.88
S16-CHI : Waste water	101.47	95.92
S16-DUC : Waste water	99.18	96.83
S16-GEO : Waste water	100.11	97.20
S16-HOM : Waste water	99.41	101.40
S16-SAR : Waste water	88.42	97.39
S16-SCO : Waste water	97.70	90.69
S17 : Liquid recovered fuel	47.00	66.18

Conclusion over protocol

Despite discrepancies for some parameters, a quite satisfactory analytical balance of 90 % is reached for 20 samples (63 % of the samples) during this first run, with for most of the unsatisfying results identified reasons.

A report is available :

Caractérisation des déchets industriels en vue de la détermination de leur potentiel de danger dans un objectif de classement SEVESO : résultats de la campagne d'analyses. Rapport d'étude 07/04/2011 N° INERIS DRC-11-118161-04055A (http://www.ineris.fr/centredoc/ineris-campagne-analyse-d%C3%A9chets.pdf)

INERIS

Module 2 : from elements to substances

A stoechimetric approach is proposed.

The « worst case » substances are screened from the CLP annex for each HP.

The amount of each elements is distributed in one or more substances.

A report and an Excel® sheet are available (in French) (mail to flore.rebischung@ineris.fr) :

Reconstitution d'une spéciation des éléments totaux en minéraux dans les déchets en vue de la détermination d'un potentiel de danger dans un objectif de classement SEVESO. Principes et mode d'emploi de l'outil de calcul . Rapport d'étude 10/08/2011 N° INERIS-DRC-11-118157-06170A (http://www.ineris.fr/centredoc/ineris-sp%C3%A9ciation-d%C3%A9chets-seveso.pdf)

INERIS

Temptative classification of wastes : HP 13 Sensitising

HP 13 Sensitising	Waste which contains one or more substances known to cause sensitising effects to the skin or the respiratory organs (new proposal! Not yet discussed)	Skin Sens. 1 Skin Sens. 1A Skin Sens. 1B Resp. Sens. 1 Resp. Sens. 1A Resp. Sens. 1B	H 317 H 334	Concentration limit Proposals: **1%, 10%** CLP (solid liquid): Skin/Resp. Sens. 1 + 1B: **1%** Skin/Resp. Sens. 1A: **0.1%** Stricter values for information issues, up to **0.01%**	Cut off limits : n.a.	Not additive

Source : Ökopol synthesis file of Oct 2011

HP 13 Sensitising / mineral substances : 7 or 1Sens/32

Sample Lab2	Skin Sens H317	Resp Sens H334
Solid		
S4	Ni 0.0216%	
S5	Ni 0.0209%	
S6	Ni 0.2526%	
S8-DON	Ni 0.0484%	
S8-SAR	Ni 0.2463%	
S9-SCO	Ni 0.1110%	
Liquid		
S16-HOM	Cr(VI) 0.2739%	Cr(VI) 0.2739%

- Ni calculated by default as most sensitizing Ni mineral NiF2, specific concentration limit : 0.01% for H317
- Cr(VI) measured, specific concentration limit : 0.2 % for Skin H317 and Resp H334

HP 13 Sensitising / organic substances : 0 Sens/32

HP 13 Sensitising substances	Highest obs. concentration (%)	Occurrence /32
2-Propenoic acid, 2-ethylhexyl ester	0.0372	2
2-Propenoic acid, (1-methyl-1,2-ethanediyl)bis[oxy(methyl-2,1-ethanediyl)] ester	0.0240	1
benzo(a)pyrene	0.0120	5
Metalaxyl	0.0023	1
2-Propenoic acid, 2-methyl-, methyl ester	0.0013	2
octhilinone (ISO); 2-octyl-2H-isothiazol-3-one	0.0001263	1
Penoxaline	0.0000806	1
Trifluralin	0.0000632	1
Bisphenol A	0.0000295	1
Prosulfocarb	0.0000036	1

H317 substances specifically measured in 4 liquid samples and not found : 2-4 Toluene diisocyanate (2-4 TDI), 2-6 Toluene diisocyanate (2-6 TDI), Methylène diphényl isocyanate (MDI) : < 0.0001%

INERIS

HP13 Sensitising results : summary

1. One waste water H16-HOM is skin and respiratory sensitising (> 0.2 % Cr(VI))

2. True speciation of Ni forms should be performed instead of worst case calculation.

   Proposed method : solubility at different pH and reverse geochemical modelling (from solution to solid phase)

3. No organic sensitising substances found in 32 wastes at concentration > 0.1 % or > specific concentration limit

INERIS

Toxicity T/T+ and ecotoxicity N/N+ according to Seveso II

Lack of time to perform a classification according to HP6 and HP14 proposals (every mineralogical composition must be recalculated…).

The classification according to the Directive Preparations (1999/45/CE) based on R risk phrase of the CLP (1272/2008) is available for :

- human toxicity T+ and T and
- aquatic environment N R50 and N R51.

Specific concentration limits and M factors are used. Cut-off limits are not applied. Weighted addition of concentrations of substances (« additivity ») is used.

It is expected that the classification with H hazard statement will be close from this classification with R risk phrase.

Results

Risk Phrase	Classified HAZARDOUS by both labs	Classified HAZARDOUS by one lab and not by the other	Classified NOT HAZARDOUS by both labs
T+	0/32	0/32	32/32
T	0/32	1/32	31/32
N R50/53	6/32	2/32	24/32
N R51/53	8/32 N R51/53 (and 6 NR50)	4/32	14/32
All	16/32 (14 identical classes and 2 different classes)	3/32	13/32

-Most wastes are not toxic (only 1 sample : Halogenated solvent)
-Most wastes are ecotoxic
-Most wastes are classified identically by the two lab results sets : 14 + 13/32 = 84 % of the samples

Substances/Elements potentially triggering the classification as hazardous N and N+:

APC, fly ash : Cd, Pb, Zn, Co ;

Industrial bottom ash : Cd, Pb, Hg, Zn ;

Metallic dust from aluminum industry : PAH, Cd, Pb, Hg ;

Packages and materials : Cd, Pb, Hg, Zn, Cu, chromium(VI), pesticides (chorpyrifos) ;

Pasty waste (considered solid after pretreatment) : Cd, Cu, Pb, Hg, chromium(VI), Zn ;

Solid recovered fuel : Cd, Cu, Pb, Hg, chromium(VI), Zn ;

Pasty waste (liquid) : Cd, Pb ;

Hydrocarbons : PAH, Hg, Cd ;

Halogenated solvents : volatile halogenated compounds, Pb, Hg, Cd ;

Waste water : chromium(VI), Cd.

INERIS
maîtriser le risque pour un développement durable

Conclusion

A protocol for the knowledge of waste by substances is considered as validated. It is currently applied in France. It is submitted to normalisation process (F and then EU).

An Excel® sheet for the computation of substances from mineral elements (worst case) is available.

Classification for hazardous properties shows :

- 1 waste/32 classified HP13 sensitising (used water, chromium(VI), further studies on forms of Ni needed for 6 wastes)
- 1 waste/32 classified toxic T (halogenated solvent)
- 19 waste/32 classified ecotoxic N R50 or N R51 (mainly heavy metals and PAH)

INERIS
maîtriser le risque pour un développement durable

Acknowledgements

This work was supported by the Ministry for Ecology, France (www.ecologie.gouv.fr). The continuous support of Mr Eric Gaucher and Ms Pauline Langeron was much appreciated.

The wastes samples have been provided by professional associations SYVED (SYndicat pour la Valorisation et l'Elimination des Déchets http://www.fnade.org/sites/fnade/la_fnade/partenaires_detail.php/id/23214), SYPRED (Syndicat Professionnel du Recyclage et de l'Elimination des Déchets Dangereux, www.sypred.fr) and ATILH (Association Technique de l'Industrie des Liants Hydrauliques - cement industry, www.atilh.fr).

The protocol uses partly methods of analysis of (identified) organic compounds practiced by Holcim (cement) and Micropolluants Technologie (laboratory) companies. The contributions of Mr François David (Research and Development Manager, SGS Multilab) and Christophe Allamelle (Development Engineer, Eurofins laboratory) were essential to this work. The work of Mrs Pauline Molina (treatment of samples) was greatly appreciated.

INERIS
maîtriser le risque pour un développement durable