Annex 1

PCB in sludge, waste, soil and sediment.

This paper has been written for the ad-hoc group of TC292 and TC308 on analysis of PCB in solid material meeting on March 27, 2003 in Oslo

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This paper is based on the following documents:
CEN/TC19: EN12766-1- PCB in oils (GC/ECD)
CEN/TC 292 WI028, PCB in soil sludge and solid waste (version 2003-2) (GC/ECD/MS)
ISO/TC190: ISO/FDIS 10382, PCB in soil (GC/ECD)
DIN: DIN38414-20, PCB in sludge (GC/ECD)
CEN/TC292 and 308: Consensus document ad-hoc group TC 292 and TC 308 (N0002)
ISO/TC147: NWI dioxin-like PCB's (N0633) (GC/MS)

ISO/TC 190: ISO/DIS 22892 GC-MS Identification

ISO/TC 190: ISO/FDIS 14507, Pre-treatment of soil (organic contaminants)
ISO/TC 190: ISO/CD 11464 , Pre-treatment of soil (physico-chemical analysis)
CEN/TC292: WG5 N0296, Waste: preparation of test portions
ISO/TC 147: ISO/FDIS 5667 part 3 and 15, Water Quality, Sampling

1 Introduction

PCBs are measured in several matrices. For environmental purposes it is necessary that the methods applied in these matrices are comparable and making use of the same principles and instrumentation. The project HORIZONTAL has been started to develop horizontal and harmonised European standards in the field of sludge, soil, contaminated soil and treated biowaste. As shown above several standards and/or draft standards are available for measurement of PCBs in different environmental matrices. Reading these documents it becomes clear that depending on the properties of the matrix different or slightly different steps in the method can be necessary. In a standard the choices to be made must be clear and hence, a decision structure is described in this discussion paper. Later on, all the steps necessary to analyse the different matrices can be described in more detail using the technical content of the documents mentioned before.
The analysis of PCBs can be described with the following steps:

- Pre-treatment of the sample and preparing of the test portion
- Extraction
- Clean-up
- Measurement by GC in combination with ECD or MS
- Requirements for identification and calculations

In the following the steps and decisions to be made are described.

2 Pre-treatment of the sample and preparing of the test portion

For the analysis of PCBs, the following relevant sample types are distinguished

- **Sludge**
  - ☐ Sewage sludge
  - ☐ Industrial sludge
  - ☐ Sediment/dredged sludge
- **Waste**
  - ☐ Soil-like waste
  - ☐ Building materials containing sealings, insulation's, wood, surface treated materials
  - ☐ Shredder, plastic, bitumen[1]
  - ☐ Mixed waste (containing different phases)
- Soil improvers
  - ☐ Compost (stabilized)
  - ☐ Biowaste (not stabilized) containing organic matter of natural origin
- **Soil**
  - ☐ Sandy
  - ☐ Clay
  - ☐ Organic rich

Excluded from further consideration are organic liquids waste and aqueous wastes. There are existing standards for these matrices (CEN/TC19, ISO/TC147 and CEN/TC 235). If possible, components of these standards will be used in the horizontal standard for PCB's.

For the extraction of the sample it is necessary that the starting material is comparable. This is true for waste and soil. Pre-treatment methods exist to deliver a dry or relatively dry test portion. Work has to be done for sludges. A freeze dry method is available, but may be more simple approaches (centrifugation, filtration) can also be used to remove the main part of the water. For the extraction of PCBs from solid materials (see further) it is necessary that the test portion contains less than 25% of water.

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[1] More important for PAHs

3 Extraction

For choosing a proper extraction technique and solvent it is important to realise the different properties of the materials to be extracted. PCBs can be present in plastic or surface-treated materials. This requires an extraction solvent in which PCBs are well soluble in combination with an exhaustive extraction technique. Petroleumether (PE)[2] in combination with Soxhlet or ASE is a good combination in this case. The sample has to be dry.

In soil and sludges PCBs are adsorbed on or in soil aggregates. Especially in aged materials it is important to to get access to the PCB adsorbed inside the aggregates. Acetone, in combination with some mechanical forces, will disintegrate the aggregates, improving the extraction. For these materials acetone in combination with PE is appropriate. The amount of water (ml) in the test portion should be less than 10 % of the amount of acetone used (ml). Methods that can be used are shaking or sonification. If disintregation of the aggregates is not important, like in sandy soils and organic rich materials with a low clay content Soxhlet can also be used.

These considerations are valid for non-polar organic compounds log $K_{ow} > 3.5$. Comparable arguments can therefor be used for PAHs and nonylphenol. PAHs will not be present in plastic, but in bitumen.

Having in mind the above considerations the following decision table can be made for the extraction of the test sample. ++ is used if the method is applicable, + means may be applicable.
+ may become ++ after applying the following general rules:
Shaking and sonification, not applicable for:
materials like plastic and bitumen
Soxhlet and ASE, not applicable for:
Materials that need mechanical disintegration like clay

Other applicability's have to be proven. For instance plastic material can be extracted using sonification, provided that during pre-treatment, grinding occurs to a size smaller than 500 µm. Results are given in annex 1.

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[2] In this paper petroleumether is used. Hexane could also be used, but because of the neuro-toxic properties of hexane we did not describe this solvent. Because it is to be expected that the use of dichloromethane will be limited in the near future this solvent is not taken into account

Table 1 Charactristics of the sample and possible extractions

		Shaking/ ultrasonic	ASE	Soxhlet
Sludge				
Sewage sludge	dry	++	x	+
	wet	++	+	+
Industrial sludge	dry	++	+	+
	wet	++	+	+
Sediment/dredged sludge	dry	++		
	wet	++		
Waste				
Soil like waste	dry	++		
	wet	++		
Building materials,	dry		++	++
Shredder, plastic, bitumen	dry		++	++
Mixed waste	dry	+	+	+
	wet	+	+	+
Soil improvers				
Compost	dry	++	x	x
	wet	++		
Biowaste	dry	+	++	++
	wet	+		
Soil				
Sandy	dry	++	+	+
	wet	++		
Clay	dry	++		
	wet	++		
Organic rich	dry	++	++	++
	wet	++		

++ = well applicable
+ = may be applicable

After the extraction it is necessary to remove the acetone, because this disturbs in the GC. Shaking with water can do this. The results is a PE-extract. Removal of acetone is also the first clean-up step (see further).

This will lead to the following generalised procedures. In a following document procedures from relevant papers will be used

Soxhlet/ASE Extraction of a dry test sample with PE. Addition of internal standards to the extract.

Shaking/sonification Extraction of X g sample (moisture < 25%) with at least 2X ml acetone (5 min) followed by X ml PE.(30 min). Phase separation (settling, centrifugation) and storage of the organic layer. Repeated extraction with X ml PE (30 minutes) and storage of the organic layer. Addition of internal standards. Washing the organic layer with 2 times 20X ml of water.

4 Clean-up

Clean-up has to be used if compounds are present that can interfere with the PCB congeners of interest in the gas chromatogram disturbs in the GC-procedure. If no or negligible interfering substances are present, no clean-up is necessary and a clean-up procedure has to be optional. De pending on the substances to be removed the following decision table has to be used. Before application of the clean-up to real samples the laboratory has to ensure that recoveries after use of the clean-up are at least 80% for all relevant congeners (including internal standards). If polar compounds have to be removed take special care on the recoveries of the low chlorinated PCB's.

Table 2. Possible clean-up methods

Clean-up	Removal of	Special for	Also applicable for	Described in	Remarks
Washing with water	Most polar compounds		PAH	O28, ISO 10382	
Aluminium oxide	polar		PAH	O28, ISO 10382, N0633	Difficult to adjust water content and keep it constant
Silica	polar		PAH	O28, ISO 10382, N0633	Attention; some charges of silica can contain low concentrations of PCBs
Florisil	polar			028, N0633	
H_2SO_4/Silica NaOH	Polar. PAH, lipides			O28	
Benzenesulfonic acid/sulfuric acid	Polar, (poly)aromatics, bases, hetero compounds			EN 12766	
gelpermeation	High molecular	MS	PAH	N0633	
H_2SO_4 (conc)	lipids			O28, EN 12766	
TBA	sulphur	ECD		O28, EN 12766, ISO 10382	
Cu	sulphur	ECD		O28, EN 12766, ISO 10382	
$AgNO_3$/Silica	Sulphur + polar	ECD		DIN 38414, N0633	
DMSO/hexane	Alipahatic hydrocarbons	MS		O28	
Thermal shock	Chlorinated waxes			O28, EN 12766	

5 Chromatographic separation

5.1 Choice of detector

ECD and MS detectors are allowed, but in special cases only one will give the proper results. For instance in the presence of mineral oil, ECD is the best choice. ECD is also an important detector for recognition of the pattern of the PCBs. In the presence of ECD-sensitive interfering components MS is the best choice. The necessary sensitivity of the detector will be described.

5.2 Choice of the column

No specification of the column will be described. Specifications for critical pairs will be given (i.e. 28/30 and 118/149). This will be illustrated with an example in the annex including a chromatogram.

5.3 Use of internal standards

Internal standards have to be used. If MS-detection is used, isotopes have to be used; at least one for every level of chlorination. For ECD-detection PCB30 (only for calculation of relative retention times) and PCB209[3] (for quantification and calculation of relative retention times are advised. The internal standards are added[4] to the sample together or after addition of the PE. The internal standards are also used for calculation of the relative retention time.

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[3] ISO10382 uses 138 and 155

[4] No fixed amount will be described.. This depends on the expected concentration. C13-PCBs contain also a small amount of C12-PCBs

6 Identification and quantification

6.1 Identification

Identification is based on relative retention times. ECD uses PCB-30 and PCB-209 and MS uses the added isotopes (use peaks of isotopes before and after the relevant peak). The principle of identification points will be followed (EU 2002[5] and ISO/DIS 22892. 3 identification points are necessary. For MS this means 3 masses and for ECD a second column including pattern recognition. Additional evidence is allowed. Absence of the peak in the chromatogram means a value > detection limit. It is possible to combine both detectors to obtain enough identification points[6]. If identification is difficult another clean-up may be necessary

6.2 Calibration

Linear calibration and second order are both allowed. For checking the validity of an established second order calibration curve at least 4 points (+ blank) are necessary. If less calibration points are used, calibration has to be limited to the linear part of the curve. Minimum requirements will be described.
For MS calculations of the results are based on isotope dilution and for ECD on the internal standard PCB209. For MS PCBs 30 and 209 do not have to be added, if done it is only used for calculation of RRT

6.3 Interferences

The following substance groups should be taken into consideration as possible interferences:

- Polychlorinated naphthalenes
- Ugilec (Dichlorophenyl-dichlorotoluyl-methane isomers, $C_{14}H_{10}Cl_4$, other synonyms are tetarchlorobenzyltoluen and monomethyl-tetrachlorodiphenylmethane
- Polychlorinated Terphenyls
- Toxaphenes
- Chlorinated Paraffins
- Brominated diphenyl ethers (BDE-47 can interfere with CB-180 under some circumstances)
- PCDD/PCDF
- Mineral oil

There is no separation for 101/90 under certain circumstances for 138/163

For the time being these problems are only mentioned. Later on we have to give proposals how to solve the problems, perhaps once again preparing a decision table

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[5] EU, 2002. Commission Decission 12 August 2002. Implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Docnr: C(2002) 3044

[6] MS after ECD will mosten ofter occur, but in presence mineral oil ECD may be used. If MS is used for these materials, you have to take care of interferring masses. A step by step clean up is necessary

Annex 1

Comparison of extraction methods from plastics using a non-polar solvent

extraction	ASE	Soxhlet	sonification	shaking			
solvent	hexane	80 ml hexane	Cyclo-hexane	hexane			
sample amount	3,5 g	9 g	20 g	20 g			
ISTD (before extraction)	PCB 209	PCB 209	PCB 209	PCB 209	MW	SD	RSD
particle size	0,5 - 1 mm	0,5 - 1 mm	0,5 - 1 mm	0,5 - 1 mm			
PCB content	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
28	0,183	0,181	0,179	0,227	0,193	0,023	11,98
52	0,785	0,624	0,569	0,737	0,679	0,100	14,67
101	4,030	4,875	4,782	4,538	4,556	0,379	8,31
153	6,880	6,882	7,118	6,611	6,873	0,207	3,01
138	5,010	4,947	5,129	4,725	4,953	0,170	3,42
180	4,380	4,144	3,232	3,980	3,934	0,496	12,61

Influence of particle size by ASE

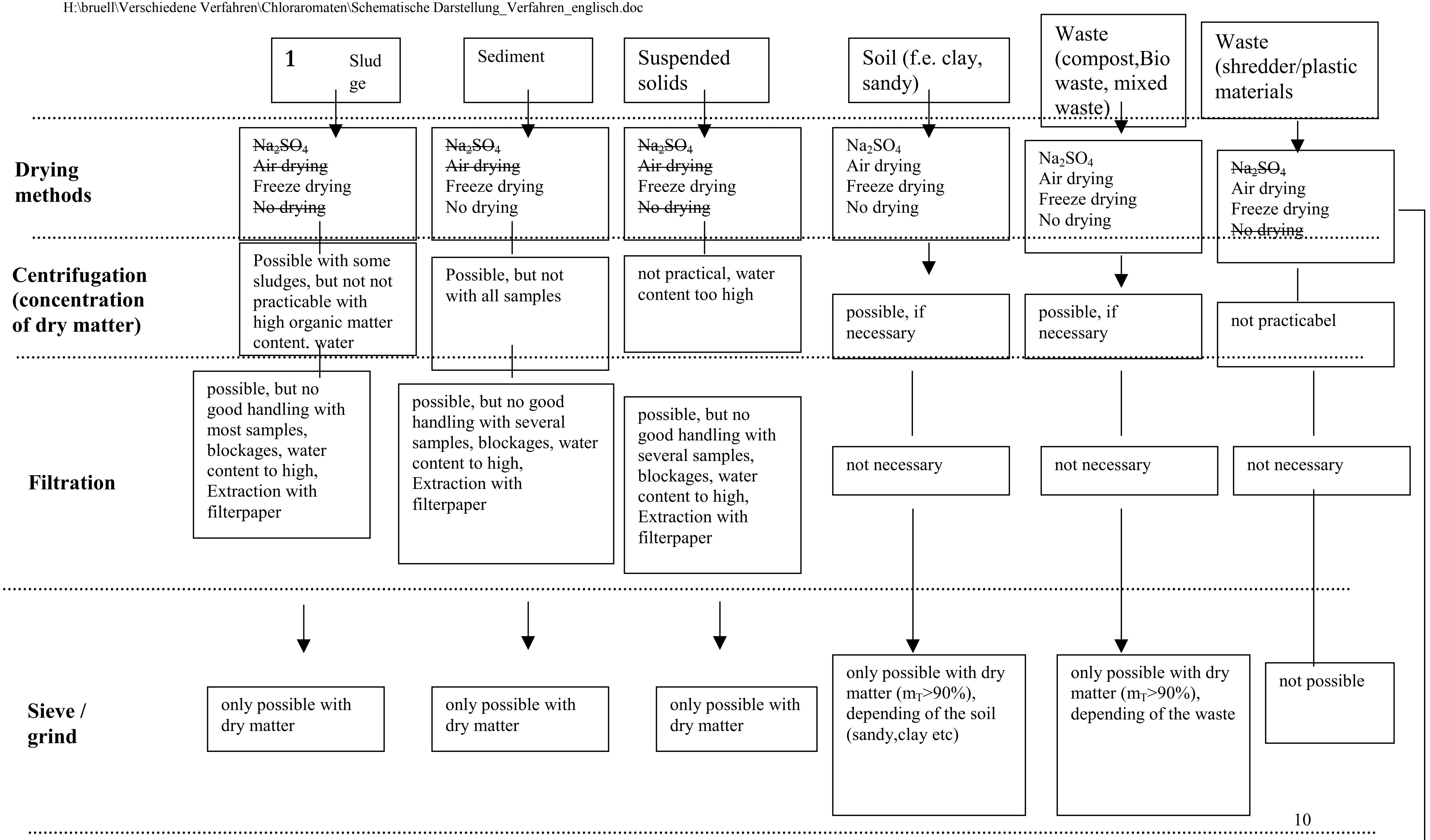
extraction	ASE	ASE	ASE			
solvent	hexane	hexane	hexane			
sample amount	3,5 g	3,5 g	3,5 g			
ISTD (before extraction)	PCB 209	PCB 209	PCB 209	MW	SD	RSD
particle size	0,5 - 1 mm	< 0,5 mm	< 0,25 mm			
PCB content	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
28	0,183	0,188	0,178	0,183	0,005	2,73
52	0,785	0,708	0,665	0,719	0,061	8,45
101	4,030	5,004	4,852	4,629	0,524	11,32
153	6,880	7,254	7,014	7,049	0,189	2,69
138	5,010	5,056	4,875	4,980	0,094	1,89
180	4,380	4,248	3,998	4,209	0,194	4,61

There are no differences between the different extraction procedures for plastic materials. The particle size has an influence of the reproducibility during ASE– see the following table.

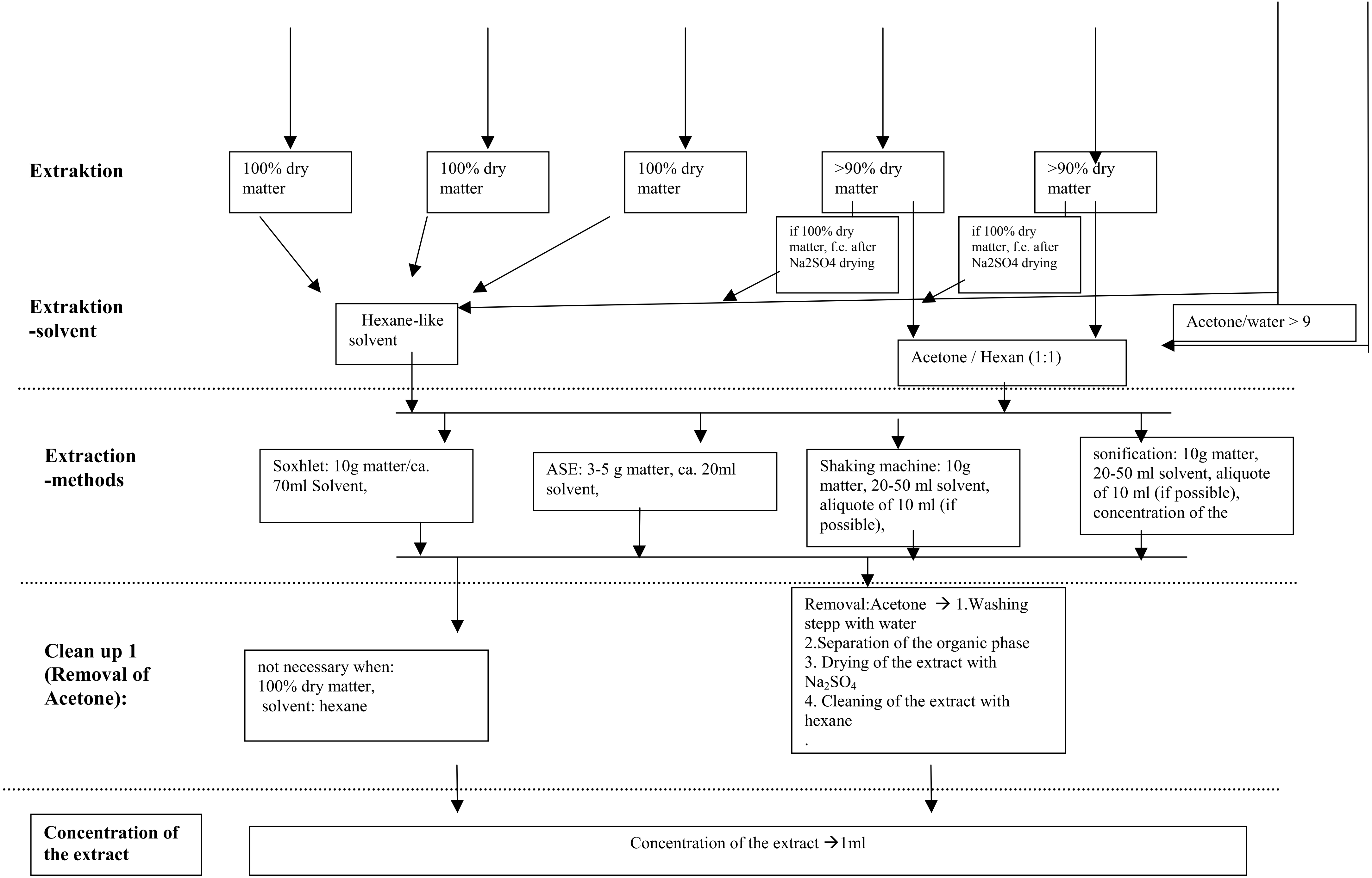
Influence of particle size by ASE
Standard deviation of 8 extractions

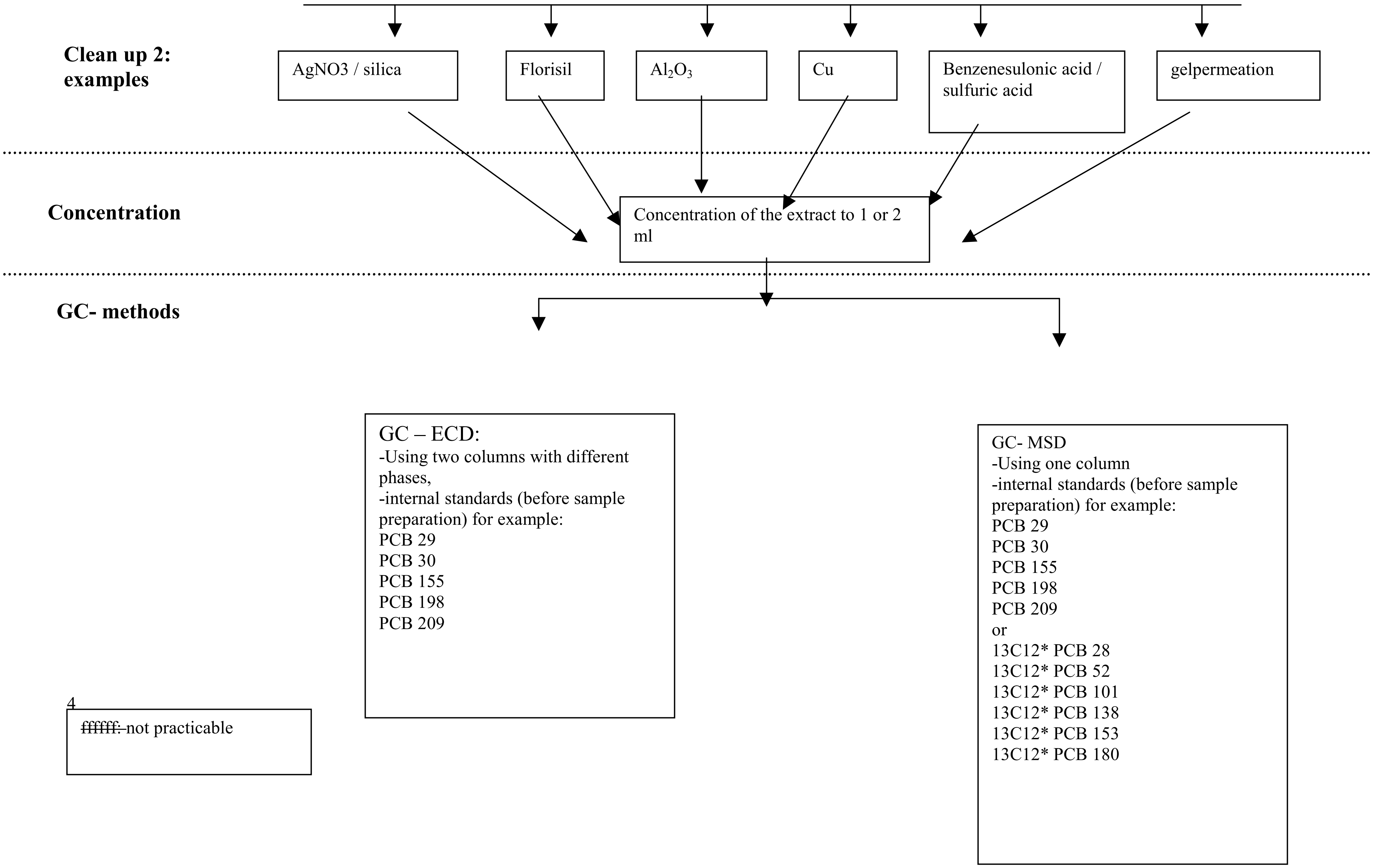
extraction	ASE	ASE	ASE
solvent	hexane	hexane	hexane
sample amount	3,5 g	3,5 g	3,5 g
ISTD (before extraction)	PCB 209	PCB 209	PCB 209
particle size	0,5 - 1 mm	< 0,5 mm	< 0,25 mm
SD	%	%	%
PCB 28	2,44	5,49	5,14
PCB 52	8,50	5,04	5,33
PCB 101	1,78	1,94	2,65
PCB 153	6,55	1,81	2,10
PCB 138	11,72	3,54	3,19
PCB 180	17,37	2,02	1,96

Annex 2: LUA NRW Brüll
H:\bruell\Verschiedene Verfahren\Chloraromaten\Schematische Darstellung_Verfahren_englisch.doc



	1 Sludge	Sediment	Suspended solids	Soil (f.e. clay, sandy)	Waste (compost,Bio waste, mixed waste)	Waste (shredder/plastic materials)
Drying methods	~~Na_2SO_4~~ ~~Air drying~~ Freeze drying ~~No drying~~	~~Na_2SO_4~~ ~~Air drying~~ Freeze drying No drying	~~Na_2SO_4~~ ~~Air drying~~ Freeze drying ~~No drying~~	Na_2SO_4 Air drying Freeze drying No drying	Na_2SO_4 Air drying Freeze drying No drying	~~Na_2SO_4~~ Air drying Freeze drying ~~No drying~~
Centrifugation (concentration of dry matter)	Possible with some sludges, but not not practicable with high organic matter content, water	Possible, but not with all samples	not practical, water content too high	possible, if necessary	possible, if necessary	not practicabel
Filtration	possible, but no good handling with most samples, blockages, water content to high, Extraction with filterpaper	possible, but no good handling with several samples, blockages, water content to high, Extraction with filterpaper	possible, but no good handling with several samples, blockages, water content to high, Extraction with filterpaper	not necessary	not necessary	not necessary
Sieve / grind	only possible with dry matter	only possible with dry matter	only possible with dry matter	only possible with dry matter (m_T>90%), depending of the soil (sandy,clay etc)	only possible with dry matter (m_T>90%), depending of the waste	not possible


Extraktion
100% dry matter
100% dry matter
100% dry matter
>90% dry matter
>90% dry matter
if 100% dry matter, f.e. after Na2SO4 drying
if 100% dry matter, f.e. after Na2SO4 drying
Extraktion -solvent
Hexane-like solvent
Acetone / Hexan (1:1)
Acetone/water > 9
Extraction -methods
Soxhlet: 10g matter/ca. 70ml Solvent,
ASE: 3-5 g matter, ca. 20ml solvent,
Shaking machine: 10g matter, 20-50 ml solvent, aliquote of 10 ml (if possible),
sonification: 10g matter, 20-50 ml solvent, aliquote of 10 ml (if possible), concentration of the
Clean up 1 (Removal of Acetone):
not necessary when: 100% dry matter, solvent: hexane
Removal:Acetone → 1.Washing stepp with water
2.Separation of the organic phase
3. Drying of the extract with Na2SO4
4. Cleaning of the extract with hexane
.
Concentration of the extract
Concentration of the extract →1ml



Clean up 2: examples

- AgNO3 / silica
- Florisil
- Al_2O_3
- Cu
- Benzenesulonic acid / sulfuric acid
- gelpermeation

Concentration

Concentration of the extract to 1 or 2 ml

GC- methods

GC – ECD:
-Using two columns with different phases,
-internal standards (before sample preparation) for example:
PCB 29
PCB 30
PCB 155
PCB 198
PCB 209

GC- MSD
-Using one column
-internal standards (before sample preparation) for example:
PCB 29
PCB 30
PCB 155
PCB 198
PCB 209
or
13C12* PCB 28
13C12* PCB 52
13C12* PCB 101
13C12* PCB 138
13C12* PCB 153
13C12* PCB 180

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~~ffffff:~~ not practicable