APPLICATION NOTE

F&F-S-003-2017/A1

Determination of PCBs in Sediment Samples with Automatic Solvent Extraction

Reference: **UNI EN 16167:2012; EPA Official Method 1668C-2010**

Tested with **VELP Scientifica SER 158/6 Solvent AutoExtractor** (Code S303A0380)

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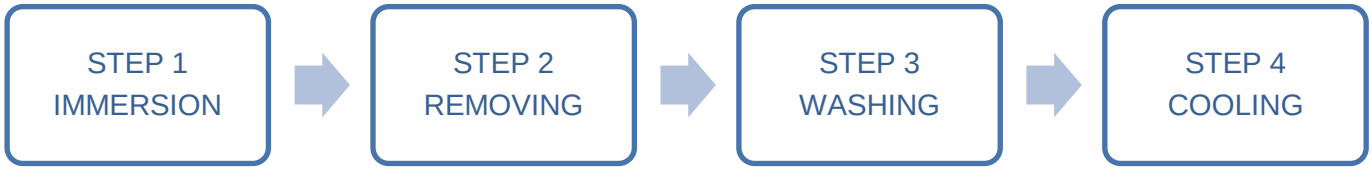
DETERMINATION OF PCBs IN SEDIMENT SAMPLES
AUTOMATIC SOLVENT EXTRACTION

Introduction

PCBs (polychlorinated biphenyls) are non-polar organochlorine substances, soluble in organic solvents, oils and fats, characterized by a high resistance to high temperatures, to acids and bases, with a high vapor pressure and with the ability to be transported at long distance. The analysis of these compounds has become a routine analysis in environmental laboratories. Despite the use it is banned in Italy since the 80's, PCBs are ubiquitous[1] contaminants considered persistent and bio-accumulative and included in the list of priority substances drawn up by the European legislation. They are actively monitored in different abiotic matrices (sludge, soil, sediment) and biotic matrices with restrictive limits on the dioxin-like congeners.

Extract Determination in Certified Reference Material

Hot solvent extraction process with SER 158 Series can be summed up in 4 steps, for a fully unattended operation:



During IMMERSION the sample is immersed in boiling solvent. Then the REMOVING step automatically lowers the level of the solvent to below the extraction thimble. During WASHING the condensed solvent flows over the sample and through the thimble to complete the extraction process. The final step is the COOLING of the extraction cups containing the extracted matter.

Sample

Certified reference material	CNS329 – “PCBs and PBDEs on Fresh Water Sediment”
Certified reference material	CRM961 – “PCB Congeners - Clay Soil”

The certified reference material were delivered lyophilized, ready for extraction.

Chemicals and Equipment Required

- Extraction glass fiber thimbles 33x80 mm (Code A00000313)
- Glass extraction cups Ø 56x120mm (Code A00000290)
- Vaflon seals (Code A00000288)
- n-hexane:aceton solvent (75:25) for pesticide residue analysis
- $^{13}C_{12}$PCB111 and $^{13}C_{12}$PCB170 recovery standards and P48-W-ES internal standards mix were supplied by Wellington Laboratories (Canada)
- Automatic Solvent Extractor VELP SER 158/6
- GC-MS with a Trace 1310 chromatograph coupled with a triple quadrupole mass TSQ 8000 EVO (Thermo Fisher Scientific, USA)
- Analytical balance, 3 decimals

Sample Preparation

Fix the Extraction thimbles with the Extraction thimbles holders (Code A00000312). Put 0.5 g of sample in the VELP extraction thimbles with a spatula.

Glass Extraction Cups Preparation

Add the internal standards into the extraction cups. Position the extraction thimbles in the extraction cups. The extraction cups containing the extraction thimble can now be placed on the ultra-fast heating plate of SER 158.

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Extraction Procedure with SER 158

Select “Analysis” on the ControlPad and method n°25 “Organic micro-pollutants for GC-MS analysis”. It shows the following parameters:.

- Immersion Time: 60 minutes
- Removing Time: 10 minutes
- Washing Time: 60 minutes
- Recovery Time: 0 minutes
- Cooling Time: 4 minutes
- Extraction cups: standard Ø 56x120mm
- Glass fiber Thimble: 33x80 mm
- Solvent: n-hexane: acetone (75:25 *v/v*), 100 ml

Close the safety guard and add the solvent using the automatic solvent dispensing system SolventXpress™ to minimize exposure to the solvent ensuring operator safety.
Press START to begin the extraction process

Clean up

Concentrate the extracts to 1-2 ml by an evaporation system at 40°C and at a pressure of 300 – 400 mBar, then the extracts go under purification.
In order to avoid the congeners interferences in Gas chromatography analysis, separates the coplanar PCBs not ortho substituted (PCB-126, -77, -81, -169) by passing through activated carbon. Purify the extract through a multilayer glass column (ø 1, .5 cm, H 15 cm) filled from the bottom with 2 g of the acidified silica, 2 g basic silica and 2 g activated Florisil®, prepared as indicated in the UNI EN 16167: 2012[3] (7.3.4 and following).
Place the column in series on a second column SUPELCLEAN ENVI-Carb™ (Supelco) containing the activated carbon. Condition both the columns with 25 mL of n-hexane (for residual Pesticide analysis, Riedel-de Haen), then load and elute the extract by collecting another 25 mL of n-hexane. The collected fraction (F1) contains the mono-ortho substituted PCB (PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, PCB-189 and "indicators PCB" -28, -52, -44, -101, -138, -153, -180).

Reduce this fraction to a volume of 200 µL with a gentle nitrogen stream at a temperature of 50°C, after the addition of 0.5 mL of toluene (Pesticide for residual analysis, Riedel-de Haën) and added with 2 ng of the recovery standard (Wellington Labs RS-P48, containing the $^{13}C_{12}$PCB-70 congeners, -111 and -170), in order to evaluate the recoveries of internal standards. Finally transfer the extract to an autosampler vial for GC-MS analysis. Subsequently, remove the multi-layer column and elute the activated carbon with 15 mL of toluene. The eluate (F2) contains the coplanar PCB (PCB-77, PCB-81, PCB-126, PCB-169). Finally reduce this fraction to a volume of 50-100 µL with a nitrogen stream at a temperature of 50°C, and transferred into autosampler vials, after the addition of 2 ng of the recovery standard P48-RS.

Gas Chromatography analysis

Analyzed the extracts by GC-MS with a Trace 1310 gas chromatograph coupled with a triple quadrupole mass spectrometer TSQ 8000 EVO (Thermo Fisher, USA) acquiring in SRM mode (Selected Reaction Monitoring) as indicated in the tables below:

GAS CHROMATOGRAPH	
Injector	PTV
Injection type	Splitless
Time (min)	2
Volume	1 µL
Injection Temperature (°C)	60
Time (min)	0.1
Transfer Ramp (°C sec^{-1})	8
Final Temperature (°C)	270
Cleaning Temperature (°C)	300
Column:	Supelco SLB-5ms 60m X 0.25mm X 0.25µm
Carrier gas	Elio 6.0
Flow (mL min^{-1})	1.3 ml min^{-1}
Isotherm 1 (°C)	60
Time 1 (min)	1.5
Ramp 1 (°C min^{-1})	30
Isotherm 2 (°C)	210
Time 2 (min)	0.1
Ramp 2 (°C min^{-1})	10
Isotherm 3 (°C)	15

MASS SPECTROMETER	
Acquisition	SRM
Temperature Source (°C)	300
Temperature Transfer Line (°C)	300
Time (min)	0.1
Transfer Ramp (°C sec^{-1})	8
Final Temperature (°C)	270
Cleaning Temperature (°C)	300
Polarity	+
Ionization	EI, 70 eV
Collision Gas	Argon 6.0
Emission current	50 µA

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Results on Certified Reference Material

Using the six extraction position in SER 158, four extractions with certified material CNS329 – "PCBs and PBDEs on Fresh Water Sediment and two blanks were performed. For each congeners were calculated the recovery for the Internal Standards, the parameter concentrations and the relative standard deviations. In the blanks no congeners were found above the detection limit; the certified material recovery were included in the range 84-107%. All the obtained values fall in the confidence range declared for the certified material.

CNS329 "*PCB and PBDE on Fresh Water Sediment*"

	Extraction System SER 158/6		**Certified values**		**Confidence range**
PCB congeners	Mean (ng/g)	SD (SD, *n=4*) ±	Mean (ng/g)	SD (SD, *n=4*) ±	
PCB 52	257.2	11.3	230	29.6	195-265
PCB 180	112.9	6.3	104	34.5	68.8-138
PCB 153	148.7	4.3	133	26.1	110-155
PCB 138	233.4	14.9	226	4.99	220-231
PCB 118	192.3	13.4	175	26.1	149-201
PCB 101	414.5	28.2	390	99.6	291-489

CRM961 "*Clay Soil*"

	Extraction System SER 158/6		**Certified values**		**Confidence range**
PCB congeners	Mean (ng/g)	SD (SD, *n=4*) ±	Mean (ng/g)	SD (SD, *n=4*) ±	
PCB 52	100.3	1.5	85.9	18.2	67.8-104
PCB 180	127.9	6.4	116.0	11.6	105-128
PCB 153	143.7	3.0	137.0	18.5	120-154
PCB 138	146.8	3.7	130.0	22.8	108-153
PCB 118	184.7	9.9	173.0	19.9	154-191
PCB 101	115.9	0.9	106.0	11.0	95.2-116
PCB 81	175.5	24.7	205	35.8	171-238
PCB 77	197.1	44.4	23	31.5	197-249
PCB 126	201.3	32.3	213	26.6	188-238
PCB 189	245.5	43.5	247	60.2	184-309
PCB 167	206.8	36.0	236	43.7	194-279
PCB 123	158.3	28.4	170	24	147-194
PCB 114	159.6	33.3	183	28.9	153-213
PCB 105	137.2	28.1	147	18.5	130-164

Conclusion

The average recoveries of the INSTDs were within the range of acceptability of the reference material (70-110%) as indicated by the norm UNI EN 16167, while the concentrations found in the analyzed materials were within an acceptable error (± 30%, average error 12%) for the type of analytical method used, thus concluding that the extraction of the compounds from the considered matrices is complete.

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Benefits of hot solvent extraction (Randall) by using 158 Automatic Solvent Extractor:
- up to 5 times faster than Soxhlet (hot solvent vs. cold solvent)
- no exposure to solvent
- refer to European official method
- full traceability with automatic result calculation and on-board archive

Acknowledgments

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2. *DIRECTIVE 2013/39/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.*

3. UNI EN 16167:2012 Sludge, Treated Biowaste And Soil - Determination Of Polychlorinated Biphenyls (P*CB*) By Gas Chromatography With Mass Selective Detection (G*C*-M*S*) And Gas Chromatography With Electron-Capture Detection (G*C-ECD*)

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