Is the SRM for PCDD/F appropriate for PCB measurements ?

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IS THE SRM FOR PCDD/F APPROPRIATE FOR PCB MEASUREMENTS

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Abstract

A previous work carried out between 2000 and 2002 has shown that the use of an XAD 2 sorbent in the case of PCB sampling tends to under-estimate PCB concentrations, specially when PCB concentrations are low (< 100 µg/m3).
The objective of this new study was to compare PCBs sampling efficiencies for several methods, at lower concentrations. First, this study consisted in the comparison of 3 sampling methods: washing bottles filled with heptane, adsorption on XAD 2 (such as used for PCDD/F samplings according to EN 1948) and adsorption on polyurethane foam (PUF). Results have shown that washing bottles filled with heptane are far more efficient than XAD 2 or PUF adsorbtion.
In addition, the second objective of the study was to optimize the washing bottles method by comparing several solvents (isooctane, hexane and heptane) and by working at two different temperatures (0°C and -20°C).

Introduction

The toxicity of PCB compounds tends to be assimilated as the PCDD/F ones: the World Health Organization has proposed toxicity equivalence factors (TEF) for coplanar PCBs (or dioxin-like PCBs), with regard to the 2-3-7-8 TCDD reference. In addition, the European 2002/69/CE directive concerning PCB sampling in food sets a TEF value for 12 PCBs. These TEFs are in the range 0.0001-0.1 and some current official studies show clearly that the ratio of PCB in the TEQ value measured in food or feed tends to increase. Thus, the need for measuring PCB concentrations emitted from industrial sources may be a matter of concern soon.

However, there are not any EU standard related to PCB measurements and EN 1948 (dioxins) standard is commonly used to measure PCB concentrations.

Still, a former work carried out by INERIS with an ADEME grant between 2000 and 2002 has shown that the use of an XAD 2 sorbent in the case of PCB sampling tends to under-estimate PCB concentrations, specially when PCB concentrations are low (< 100 µg/m3). [FERRIERES, 2002].

These unexpected preliminary results has led to a new study aiming at :

- For lower concentrations (between 100 ng/m3 and 40 µg/m3), comparing efficiencies between several sampling methods : XAD 2, PUF and washing bottles.
- Enhancing the washing bottle method efficiency by studying several solvents and several temperatures

Experiments were achieved at the INERIS test bench which features:

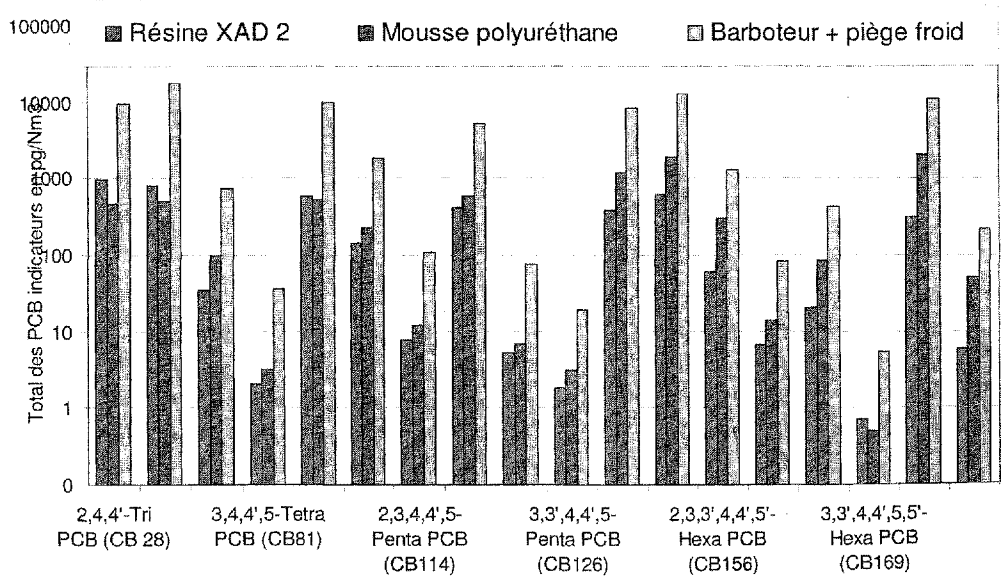
- Waste gas from a fuel boiler (50 kW), heated at 150°C
- PCB introduced in the gas by spraying (pyralene oil diluted in heptane)
- Simultaneous sampling with the three sampling lines

The 18 following PCBs have been studied and analyzed: 77-81-126-169, 105-114-118-123-156-157-167-189, 28-52-101-138-153, 180.

Comparison between several sampling methods

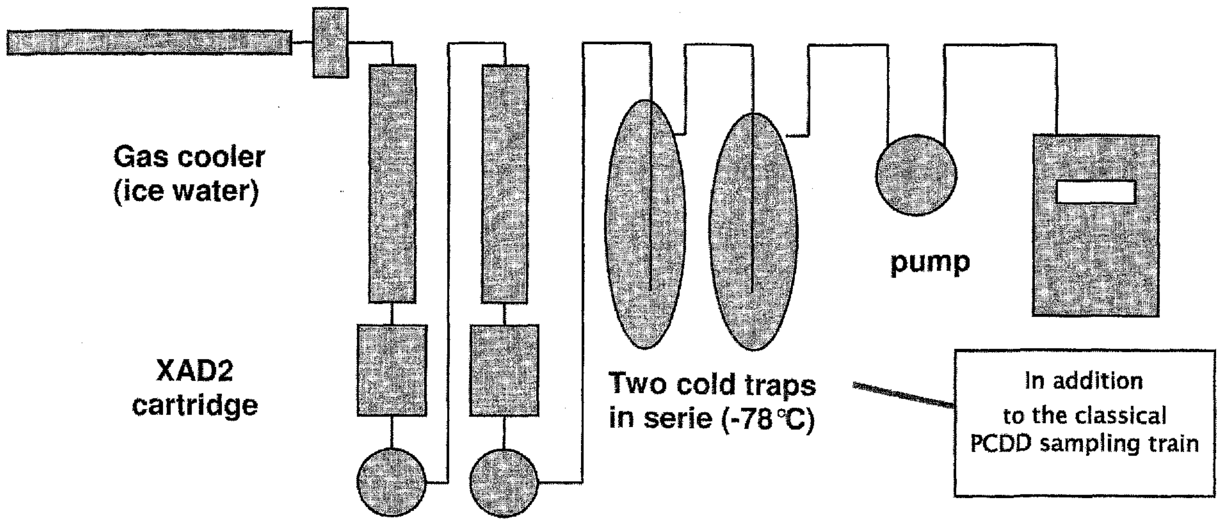
The XAD 2 and PUF adsorbents are used as described in the EN 1948-1 method.
The heptane washing bottle method consists in two 500 ml washing bottles containing 250 ml of heptane. The solvent evaporation is limited by a cooling device. A cold trap is then added (-70°C).

Results are shown on the following figure.

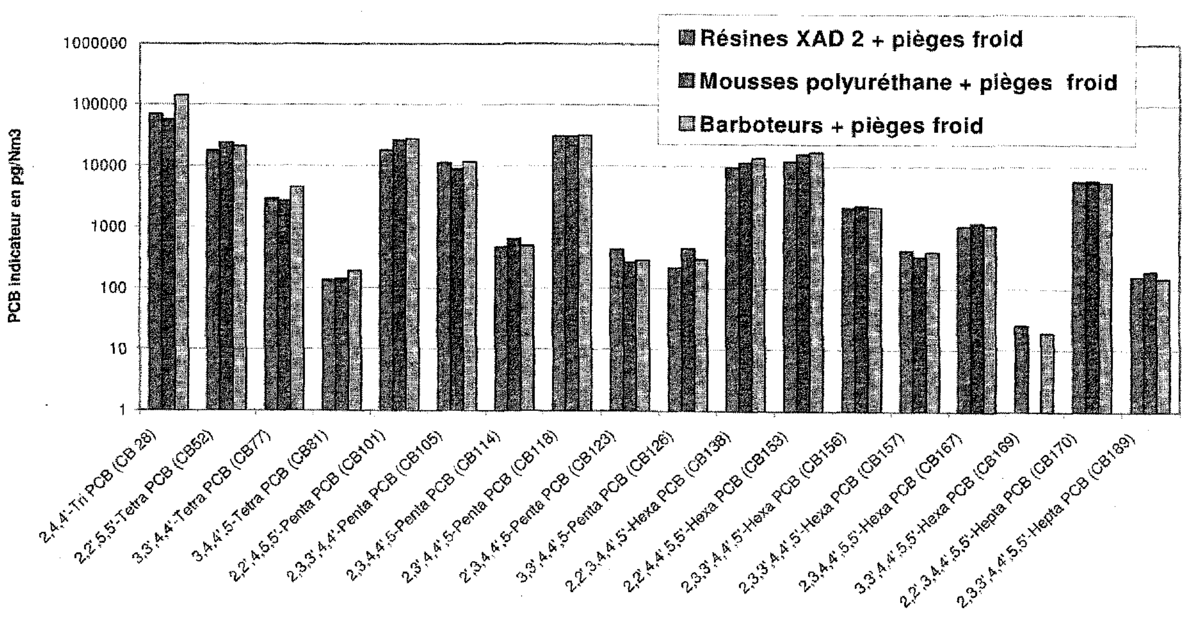


From this figure, it is clear that the washing bottles are far more efficient than the two solid adsorbents, even for light PCBs. The efficiency of washing bottles with hexane is 10 times higher than the PUF one and 20 times higher than the XAD 2 one.

Another set of experiments was carried out by using, for each of the 3 methods, two sampling devices with two cold traps. In the case of the XAD 2 method for instance, the experiment device is described in the following figure.



The results then obtained are summarized in the next figure.



By using two sampling devices and two cold traps together, results are very similar for each of the 3 methods and for each of the 18 PCBs. The only exception being the lighter tri PCB where the concentration obtained by the washing bottle method is twice the values obtained by the 2 other methods.

As shown in next table, the analysis of each part of the whole sampling device shows strong differences between lighter (tri and tetra) and heavier (hexa and hepta) PCBs. A very poor efficiency is observed in the case of light PCB with solid adsorbents (PUF and XAD2) and more than 70% is collected in the cold traps. Moreover, the XAD2 efficiency is very low for a large majority of PCBs (up to the hexa category).

	Washing bottles	PUF	XAD 2
Tri PCB	40%	17%	7%
Tetra PCB	44%	30%	19%
Penta PCB	51%	48%	21%
Hexa PCB	54%	40%	29%
Hepta PCB	67%	47%	58%

Optimization of the washing bottles method

Three different solvents were studied, each one having a different solubility towards PCBs: heptane, hexane and iso-octane. Experiments were carried out at two different temperatures: 0°C and -20°C. The sampling line was composed by a condensate flask, then 2 washing bottles, then 2 cold traps (-70°C).

Results showed that sampling efficiencies for the 3 solvents at -20°C were very poor, for each PCB: the mean value for iso-octane and hexane efficiencies was only 45% in the condensate and bottles part.

At 0°C, efficiencies are quite similar for every solvent. Iso-octane is more efficient than hexane and heptane is clearly less efficient (see table below). Efficiencies were slightly lower for light PCBs.

Solvent	**PCB sampling efficiency (%) at 0°C Condensate and bottles part**		
	Mean value	Min	Max
Iso-octane	71	68	74
Hexane	65	63	68
Heptane	55	48	64

Thus, between 29% and 45% were collected in the cold traps. However, it was not easy to validate the quantitative efficiency of these as the quantity of PCB contained in the second cold trap was usually higher than the one in the first one.

Conclusion

The results of this work confirm those obtained in the 2000-02 preliminary study, namely that the EN 1948 standard is not suitable for heavy and light PCB measurements. In particular, using XAD 2 sorbents leads to a strong under-estimation of PCB concentrations.

Best results were obtained by using washing bottles containing iso-octane or hexane at 0°C and a cold trap (-70°C).

However this method is quite difficult to implant in real operating conditions on an industrial plant and, for cold traps, the quantitative efficiency needs to be proven more deeply.

Hence, some further work seems necessary in order to increase the efficiency of cold traps, to study other solvents or to investigate some new solid adsorbents.

References

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FERRIERES Claude, INERIS, Evaluation of the efficiency of several available sampling methods for PCB measurements, june 2005, ADEME grant n°0374030