

The Fate of Sampling Standard Solution on the Filter: Critical Issues and Remedies

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1 Introduction

Among POPs, polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/Fs) need to be quantified in the atmosphere due to several toxic effects they may exert on humans and the wildlife [1],[2]. As semi-volatile organic compounds (SVOCs), they are present in the atmospheric environment in both the gaseous and particulate phases. According to several standard reference methods [3],[4][5],[6], the sampling step requires a quartz fiber filter (QFF) to collect particle-bound contaminants, followed by a cartridge filled with a solid sorbent, usually, polyurethane foam (PUF) or styrene-divinylbenzene polymer (i.e., XAD-2 resin) to collect the vapor phase and compound stripped from the particulate present on QFF. A sampling standard solution (SS) is required to be spiked on the filter before sampling, and the recovery rate of each congener has to fall in a stated range to validate the sampling itself. Standard solutions containing ¹³C-labeled compounds – that behave most likely the native analytes - are used when working in the isotopic dilution method and are added in three different phases of the analysis. It is an apparently simple operation that helps in avoiding errors during the analytical workflow, but very often its importance is underestimated, even though standard reference methods underline it. The recovery rates of sampling standards allow the assessment of efficiency, accuracy, and overall capabilities of the sampling device and analytical method[3],[6].

The step of adding the standard is a critical point throughout the analysis, and the one related to the sampling standard solution is maybe the most critical. The addition is performed on the QFF directly on the sampling site. This procedure reduces possible losses of the standard due to its degradation or volatilization during transportation, but on the other hand, it is prone to some potential drawbacks. The stability of the standard during the sampling campaign, the reproducibility of the operator, the subjective execution of the spiking between one operator and another, and the atmospheric and environmental conditions in which the procedure is carried out must not be underestimated. In addition, spiking on site should be a time-consuming and risky (carcinogenic labeled compounds) operation in a tight scheduled sampling campaign contest. The function of sampling standards is to evaluate the possible losses of analyte during the sampling step. Low recoveries may be due to the breakthrough of the filter/adsorbent system, reactions with substances present in the sampled matrix, and possible evaporative or degradative processes occurring during the time between sampling and subsequent chemical analysis. Using a combined QFF/PUF adsorption system introduces a greater possibility of errors in the analysis due to contamination and sample losses related to the analyst and the sample processing steps. A pre-labeled filter that is practical, long-lasting, and prepared to be utilized throughout an experimental measurement campaign would be excellent since it would reduce setup costs and timeframes. Active carbon fiber-based (ACF) sorbents are used in adsorption and filtering applications; recently, Cerasa et al. (2021) demonstrated that an efficient extraction of SVOCs from ACFs is possible and that they can also be used for analytical purposes, such as air sampling [7]. In this paper, the most common critical issues related to the SS spiking step will be addressed, and the effect of temperature storage and the stability of the sampling standards added on ACF over three months will be evaluated. The work aims to demonstrate that a pre-labeled ACF can advantageously replace QFF and the need to spike it on the field.

2 Materials and Methods

2.1 Standards and Reagents

Three ¹³C-labelled solution mixtures at a concentration of 10 pg/μl have been prepared, identified according to the order of use in the analysis: Sampling Standard solution (SS) containing EN-1948SS and P48SS, Extraction Solution (ES), containing EN-1948ES and WP-LCS and Injection solution (IS), containing EN-1948IS and WP-ISS. All the standards were purchased from Wellington Laboratories. Acetone, toluene, dichloromethane, and hexane were used during the cleanup.

2.2. Active Carbon-based Material

The physical-chemical characterization of the active carbon-based material used in this work was described in previous studies [7],[8]. The ACF filters were cut into 102 mm diameter disks, the same dimensions as quartz fiber filter (QFF) used on a high-volume sampling head. The filters were pre-cleansed in Soxhlet with toluene for 24h and left to dry overnight at 150 °C under N₂ flow.

2.3 Experimental setup

The sampling standard was added at the same amount used on the field in all the following experiments, according to the ISO and EPA methods. All tests were carried out in triplicate, and all the filters were analyzed as described in the following subsection.

1) *QFF vs. ACF – stress temperature*

Three pairs of ACFs and QFF filters were spiked and stored in aluminum foil at three different temperatures for 24h: room temperature (20 °C), refrigerated at 4 °C and exposed to a stress temperature of 35°C.

2) *ACF – stress temperature and time*

Two sets of ACFs filters were spiked and stored in aluminum foil at room temperature (ACF_20) and refrigerated at 4°C (ACF_4). They were analyzed at different times: 7 days, 1 month, and 3 months.

3) *ACF – losses of material*

Three pairs of ACFs were spiked with SS; for each couple, only one was enclosed in an inert housing (as a "sandwich") while the other two were left untouched ("free fibers") and stored in aluminum foil. All were analyzed after 24h at room temperature.

2.4 Extraction & Clean-up

Each filter was spiked with 100µl of the ES solution and extracted in 250 mL Soxhlet for 36 hours with toluene. The extract was first concentrated with a rotary evaporator (40 ± 2 °C and 49 mbar) up to 10 ml and then with a gentle flow of N₂ in a water bath (40 ± 2 °C) up to 1 ml. The cleanup involved a multilayer silica column (eluted with hexane) and an alumina microcolumn separating PCDD/Fs from dl-PCBs, as described in Mosca et al. [9]. The two fractions were concentrated, and the corresponding IS solutions were added. Instrumental analyses were performed using a triple quadrupole GC/MS, and chromatographic separation was achieved using a DB-XLB column (60 m 0.25 mm, 0,25 mm ID) [10].

2.5 QA/QC

The requirements of reference methods ISO 16000 [3,4] and EPA TO [5,6] for determining PCDD/Fs and PCBs in indoor air and ambient air were considered. The recovery rates of the SS solution have been compared to the ones indicated by those official methods. The recovery rates of the single congeners of the SS must fall in the range 75%-125%; values below 50% or above 150% invalidate the sampling.

3 Results

3.1 QFF VS ACF – stress temperature

Table 1 shows the average recovery rates of the sampling standard solution (%R) added on QFF and ACFs exposed at 4, 20, and 35 °C for 24h. The uncertainty of the results, expressed as a standard deviation, was within the range of 5-10%, with the highest values corresponding to congeners with lower chlorination degrees.

Table 1: Average recovery rates of the sampling standard solution (%R) on QFF and ACF

	QFF_4	QFF_20	QFF_35	ACF_4	ACF_20	ACF_35
60L	79	32	8	99	96	77
127L	86	25	9	93	109	85
159L	91	85	25	113	92	83
¹³ C-12378-PeCDF	77	12	11	93	76	79
¹³ C-123789-HxCDF	84	20	33	104	85	86
¹³ C-1234789-HpCDF	92	32	40	109	92	92

3.2 ACF – stress temperature and storage time

The temperatures of 4 and 20 °C have been selected for some long-time recovery assessments. These experiments aimed to test the stability of the SS standard added to the ACF filter over time. The uncertainty of the results was within the range of 1-12%, with the highest values corresponding to PCDD/Fs congeners. Table 2 shows the average recovery rates of SS solution added on ACF stored at 4 and 20 °C and analyzed after 7, 30, and 90 days.

Table 2: Average recovery rates of SS solution added on ACF stored at 4 and 20 °C and analyzed after 7, 30, and 90 days.

Storage Temperature	4 °C			20 °C		
	7	30	90	7	30	90
60L	91	87	89	78	92	95
127L	76	84	98	98	90	106
159L	93	90	75	80	78	95
¹³ C-12378-PeCDF	99	106	96	101	114	115
¹³ C-123789-HxCDF	101	99	91	103	107	117
¹³ C-1234789-HpCDF	103	115	100	96	115	103

3.3 ACF – losses of material

Figure 1 shows average recovery rates of SS standard added on "free" ACF and encapsulated one ("sandwich"), stored at ambient air temperature in an aluminum foil for 24h.

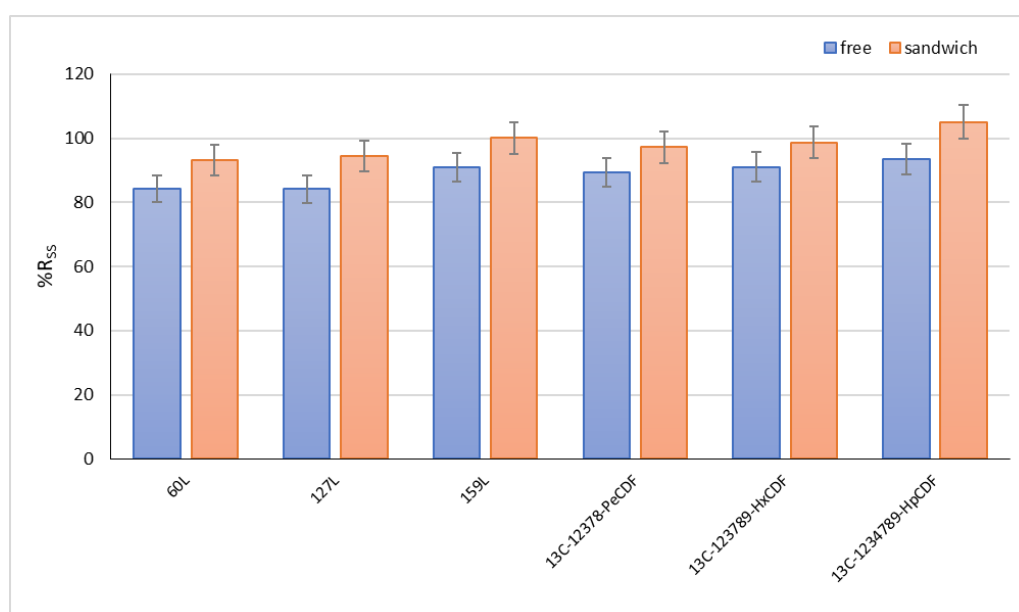


Figure 1: Average recovery rates of SS standard added on "free" ACF and encapsulated one ("sandwich")

4 Discussion

4.1 QFF vs. ACF – stress temperature

The storage temperature is one of the parameters that act on the volatilization process of the SS standard from the adsorbent medium. From the analysis of the results of the tab. 1, it is evident that the QFF's ability to retain the SS solution is strongly influenced by temperature, even though QFF is the most used means for sampling PCDD/Fs and PCBs as indicated by the ISO and EPA methods. For example, it is possible to spike a quartz fiber filter in the laboratory and transport it to the field, but you must keep it refrigerated at 4 °C. Otherwise, the minimum requirements of the reference method would not be satisfied. ACF filter, meanwhile, guarantees the stability of the SS standard up to extreme temperatures (35 °C) that can be reached during a summer measurement campaign or during field transportation, with recoveries that meet the requirements of the reference methods (table 1). Comparing only the results of the filters kept refrigerated, the recovery rates of the SS on QFF (77-92%) show a percentage difference of about 20% compared to the SS on ACF (93-113%).

4.2 ACF – stress temperature and storage time

At the basis of this type of test, there is the question: "How far in advance is it possible to spike the filter without loss?". The data in Table 2 do not show any significant differences in recovery rates of SS standards even after three months, and the rates are all within the requirements of EPA and ISO reference methods. The recovery rates of the SS on ACF at 4 °C show an overall standard deviation of 7.6 and 5.7 % for PCBs and PCDD/F, respectively. The standard deviation values are higher when ACF is kept at room temperature: 9.8% and 7.4% for PCBs and PCDD/Fs,

respectively. Despite the variability of the results between the different storage times and temperatures, it can be said that it is possible to use a pre-spiked ACF filter even after three months.

4.3 ACF – losses of material

When the filter is spiked before a sampling campaign, it could happen a partial loss of the standard due to the degradation of the sorbent medium through phenomena like exfoliation, abrasion, contact with the storage container, operator errors, and needle or tweezers piercing. The ACF is a material with a very high specific surface thanks to its fiber structure, but those fibers can get lost quite easily when handling the material itself. Figure 1 illustrates how crucial it could be to store the pre-labeled adsorbent in an inert wrapper. On average, recovery rates of sampling standards on the "free" ACF are about 10% lower for either PCBs and PCDD/Fs. This is because the inert envelope allows retaining inside the possible release of prelabeled fibers during the sampling and extraction phases.

The advantage of the wrapping is even more evident when considering the recovery rates of the ES Solution, which are not shown in this paper: about 20% for PCDD/Fs and even about 30% for PCBs. That can be explained by considering the adsorption of the fibers released into the solvent during the extraction phase in Soxhlet. Even a 5 mL toluene wash failed to release the target analytes due to the ability of these loose fibers to retain the compounds extracted from the filter.

5 Conclusions

The importance of correctly applying the SS solution is fundamental for sampling PCDD/Fs and PCBs in air, and too often, it is underestimated. This paper aimed to demonstrate how commonly used practices of adding SS to filters are prone to errors. It is therefore natural to ask: "are you really sampling correctly from an analytical point of view?". The use of an ACF filter in place of the usual quartz fiber filter is the solution suggested in this paper. By analyzing the recovery rates of the sample standard solution, it has been demonstrated that ACF may preserve the titer of the previously added solution with slight variation owing to temperature storage. In addition, it has been shown that the ACF filter can be pre-labeled in the laboratory and stored for up to 3 months with good repeatability, as defined by the moderated standard deviation values. The use of the filter in ACF compared to QFF ensures better accuracy and repeatability of the spiking operation with SS since the adsorbent material allows it to be easily pre-spiked in the laboratory without any significant loss of the standard during the storage. This means that the time needed to set up the onsite sampling decreases, that the operator is not subject to adverse weather conditions (wind, rain, snow) or temperatures, and that sampling can be quickly started even with poor visibility (night). In addition, the operator is less exposed to risks in the field, chemical (presence of solvents) and physical (possible accidents in the management of micro-syringes). ISO and EPA reference methods require using a combined sampling system: QFF for the particulate phase and polyurethane foam (PUF) cartridge to collect the gaseous phase. EPA TO-9A suggests spiking SS solution on the PUF. According to other studies carried out by our research group, ACF can collect both the particulate and gaseous phases. That means ACF could replace the double system QFF/PUF with significant advantages in terms of costs, waste, time, and solvents reduction.

6 Patents

Filing of an international patent application n. PCT/IB2021/056894 of 29 July 2021, with the claim of the priority of the Italian application n. 10202000019936 filed on 11 August 2020

7 References

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