**Chromatographic and Mass Spectral Characterization of Candidate mono-flourinated PCBs for Analytical Internal Standards and Recovery Surrogates**

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**Abstract**
This study looked at the use of fluorinated-polycyclic hydrocarbons (F-PCB) as internal standards in environmental and other matrices. These compounds have been introduced as internal standards because of their lower cost than istopically (i.e. C13 or deuterated) PCBs and because there is no chance they found in environmental matrices like "non-Aroclor" PCB standards could be. The study's main goal was to use characterize these compounds chromatographically and obtain mass spectral data.. This study found that there is potential for these fluorinated compounds to be used as internal standards or recovery surrogates on both GC-ECD and GC-MS. It was also found that, because of the ability to isolate specific ions using GC-MS, this analysis is the best method to use with F-PCBs due to possible coelutions in GC-ECD.

**Introduction**
Recovery surrogates (surrogates) and Internal standards (IS) are used to provide information on efficacy of extraction, solution preparation and injection precision for GC analysis. The ideal surrogate and IS will have similar physical and chemical properties to the compounds of interest but can be differentiated in the analysis step, usually by a different retention time and/or mass spectrum. Flourinated PAHs and PBDEs have been previously characterized for use with these compounds [1-9]For PCB analyses of environmental samples many procedures exist which specify the use of "non-Aroclor" PCB such as PCB-14, 65, 166 for surrogates and 30 and 204 for IS. Inherent in their use is that assumption that they will not occur in the environmental sample. The use of isotopically (C13 and/or D)-labeled PCBs for GC-MS analysis is also common practice. Deuterated PCBs have proven to be less than ideal due to the possibility of deuterium exchange. C-13 labeled standards are considered ideal for GC-MS. However, these standards are expensive and cannot be used for GC-ECD analysis. The use of mono-fluorinated-PCBs (F-PCBs) offers the possibility of a surrogate/IS which has a different mass than PCBs and might also have differing retention times (RT). The F-PCBs are less expensive than isotopically-labeled PCBs and were never used in industry so are not found in environmental samples. A description of the synthesis and initial characterization of candidate F-PCBs has been reported [10,11] Of the seventeen F-PCBs studied, several of them have previously been studied (m_28, o_30, m_30, and m_31) under different chromatographic conditions.

We have carried out chromatographic and mass spectral characterization of a series of 17? F-PCBs by GC-ECD and/or GC-MS detection (GC-MS). One of the goals of the study was the determination of whether the F-PCBs could be used for GC-ECD and GC-MS characterization or whether they would only be useful in GC-MS. This study also looked into the relationship the F-substitution pattern and their retention time relative to their parent PCB.

**Materials and Methods**
All glassware was thoroughly cleaned prior to use by muffle furnace or solvent flushing. Pesticide grade n-Hexane was obtained from Fisher Scientific. 209 PCB congeners were obtained from Accustandard (mix 1-9) and solutions were prepared for instrumental analysis as described in Schwope and Nienow[12,13]. Calibration solutions contained PCB 30 and PCB 204 at a concentration of 17.5 ng/ml as internal standards. Individual F-PCB standard solutions were provided by Chiron (Trondheim, Norway). These standards are listed in Table 1. Solutions containing F-PCBs were made from these standard solutions using PCB 30 and PCB 204 as internal standards (17.5 ng/ml).

Analyses were carried out on one or more of the following instruments using split/splitless injection 1) Agilent 6890N (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph with electron capture detection 2) Agilent 6890N/5975 GC-MS or 3) 6890 N 5973 Inert GC-MS

GC-MS detection was performed in both scan and selective ion monitoring to detect for specific mass to charge ratios (m/z) at specific retention times. The ions selected for SIM monitoring are provided in Table 1.

**Results and Discussion**

The seventeen F-PCBs solutions were analyzed initially using the GC-ECD. The retention times and responses of these F-PCBs were compared to those of the IS PCB 30 and PCB 204 to provide Relative retention times (RRT) and Relative Response Factors (RRF) to the internal standards were tabulated for each of the F-PCB. These results are shown in Tables 2. The chromatograms of the individual F-PCBs were then compared to the RTs for all 209 PCBs to determine if coelution was an issue or not. Through this process, it was determined that only two of the F-PCBs, F-PCB m_14 and F-PCB o_30 could be used as IS or surrogates in GC-ECD. Several of the F-PCBs also coeluted with each other including F-PCB m_14 and F-PCB o_30. The F-PCBs were then analyzed further using GC-MS and different stationary phases (DB-5 and DB-1) (see Table 1 and 2). The mass spectrum for each of the F-PCBs was obtained and compared with the predicted molecular ion ratio (ACD labs software). Although the F-PCBs often coeluted with each other or with one or more of the PCBs, their different mass allowed for them to be quantified in SIM mode. In some instances F-PCBs of similar chlorination level did coelute on a column (see Table 2), which meant they would not be candidates for both being used on a sample.

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**Conclusions**

Fluorinated-PCBs have the potential to be used as internal standards in environmental and other matrices (for example blood). Two of the seventeen F-PCBs have been found that do not coelute with any PCBs which might allow them to be used for both GC-ECD and GC-MS analysis. Although a couple of the F-PCBs were distinguishable on the GC-ECD, GC-MS is the ideal method of detection for F-PCBs because of the ability to isolate specific ions, thus differentiating them from PCBs with which they coelute. Nearly all of the F-PCBs tested appear to be amenable to use for IS or surrogates for GC-MS analysis.. Further studies must be done to ensure that these F-PCBs will hold up under various extraction and clean-up methods. Current work in our laboratory includes the evaluation of all 17 surrogates for the soxhlet extraction of a NIST Standard Reference Material (1939a)

**References**

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Table 1: F-PCB Information

| | F-PCB | Name | Molecular Formula | Molecular Weight | Quant Ion (m/z) | Confirmation Ion |
|---|---|---|---|---|---|---|
| 1 | **m_14** | 3'-fluoro-3,5-dichlorobiphenyl | C12H7Cl2F | 241.088 | 240 | 242 |
| 2 | **m_28** | 3'-Fluoro-2,4,4'-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 3 | **m_29** | 3'-Fluoro-2,4,5-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 4 | **m_30** | 3'-Fluoro-2,4,6-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 6 | **o_30** | 2'-Fluoro-2,4,6-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 8 | **m_31** | 3'-Fluoro-2,4',5-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 9 | **m_37** | 3'-Fluoro-3,4,4'-trichlorobiphenyl | C12H6Cl3F | 275.533 | 274 | 276 |
| 10 | **m_65** | 3'-fluro-2,3,5,6-tetrachlorobiphenyl | C12H5Cl4F | 309.979 | 310 | 308 |
| 11 | **p_67** | 4'-Fluoro-2,3',4,5-tetrachlorobiphenyl | C12H5Cl4F | 309.979 | 310 | 308 |
| 12 | **m_77** | 5-fluro-3,3',4,4'-tetrachlorobiphenyl | C12H5Cl4F | 309.979 | 310 | 308 |
| 13 | **m_81** | 3'-Fluoro-3,4,4',5-tetrachlorobiphenyl | C12H5Cl4F | 309.979 | 310 | 308 |
| 14 | **m_105** | 5'-fluro-2,3,3',4,4'-pentachlorobiphenyl | C12H3Cl5F | 344.422 | 343 | 345 |
| 15 | **m_114** | 3'-fluro-2,3,4,4',5-pentachlorobiphenyl | C12H3Cl5F | 344.422 | 343 | 345 |
| 19 | **m_118** | 5'-fluro-2,3',4,4',5-pentachlorobiphenyl | C12H3Cl5F | 344.422 | 343 | 345 |
| 16 | **m_126** | 5'-fluro-3,3',4,4',5-pentachlorobiphenyl | C12H3Cl5F | 344.422 | 343 | 345 |
| 17 | **m_156** | 5'-fluro-2,3,3',4,4',5-hexachlorobiphenyl | C12H3Cl6F | 378.867 | 378 | 380 |
| 18 | **m_166** | 3'-fluro-2,3,4,4',5-pentachlorobiphenyl | C12H3Cl5F | 344.422 | **343** | **345** |

Table 2: Chromatographic Information

| | | GC-ECD (HT8) | | | GC-MS (DB5) | | | GC-MS (DB1) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Retention Time | RRT to PCB 30 | RRT to PCB 204 | Retention Time | RRT to PCB 30 | RRT to PCB 204 | Retention Time | RRT to PCB 30 | RRT to PCB 204 |
| 4 | **m_14** | 11.183 | 0.965 | 2.367 | 8.513 | 0.953 | 0.366 | 13.917 | 0.931 | 0.384 |
| 5 | **m_29** | 13.199 | 1.139 | 2.005 | 9.697 | 1.085 | 0.406 | 16.827 | 1.126 | N/A |
| 1 | **m_28** | 14.145 | 1.220 | 1.871 | 10.193 | 1.142 | 0.427 | 17.75 | 1.186 | N/A |
| 2 | **o_30** | 11.191 | 0.965 | 2.365 | 8.721 | 0.977 | 0.365 | 14.694 | 0.983 | N/A |
| 3 | **m_30** | 11.438 | 0.987 | 2.314 | 8.794 | 0.984 | 0.367 | 14.417 | 0.964 | 0.398 |
| 6 | **m_31** | 13.935 | 1.202 | 1.899 | 10.110 | 1.131 | 0.423 | 17.65 | 1.181 | N/A |
| 15 | **m_37** | 16.817 | 0.965 | 2.367 | 11.891 | 1.330 | 0.498 | 20.817 | 1.391 | 0.574 |
| 7 | **p_67** | 17.667 | 1.526 | 1.497 | 12.845 | 1.439 | 0.538 | 22.571 | 1.510 | 0.622 |
| 8 | **m_65** | 15.232 | 1.315 | 1.736 | 11.253 | 1.260 | 0.484 | * | * | * |
| 9 | **m_77** | 20.767 | 1.793 | 1.274 | 15.536 | 1.740 | 0.667 | * | * | * |
| 10 | **m_81** | 20.779 | 1.795 | 1.273 | 15.557 | 1.742 | 0.666 | * | * | * |
| 16 | **m_105** | 23.047 | 1.139 | 2.006 | 18.135 | 2.029 | 0.759 | 29.337 | 1.962 | 0.737 |
| 11 | **m_114** | 22.799 | 1.969 | 1.160 | 17.881 | 2.003 | 0.749 | 27.871 | 1.866 | 0.769 |
| 17 | **m_118** | 21.666 | 1.202 | 1.900 | 16.707 | 1.871 | 0.699 | 14.950 | 1.946 | 0.801 |
| 12 | **m_126** | 24.778 | 2.140 | 1.067 | 19.815 | 2.217 | 0.829 | 31.426 | 2.102 | 0.866 |
| 13 | **m_156** | 26.685 | 2.305 | 0.991 | 22.160 | 2.482 | 0.927 | * | * | * |
| 14 | **m_166** | 25.041 | 2.163 | 1.056 | 20.719 | 2.320 | 0.891 | 32.525 | 2.174 | 0.897 |
| | | **Temperature Program** | | | **Temperature Program** | | | **Temperature Program** | | |
| | | 120-180 C at 35.87 C/min<br>180-260 C at 3.59 C/min<br>260-300 C at 8.79 C/min; held for 3.79 min | | | 90-200 C at 15.00 C/min; held for 5.00 min<br>200-285 C at 2.50 C/min; held for 5.00 mins | | | 75-150 C at 15.00 C/min<br>150-2.70 C at 2.50; held for five minutes | | |

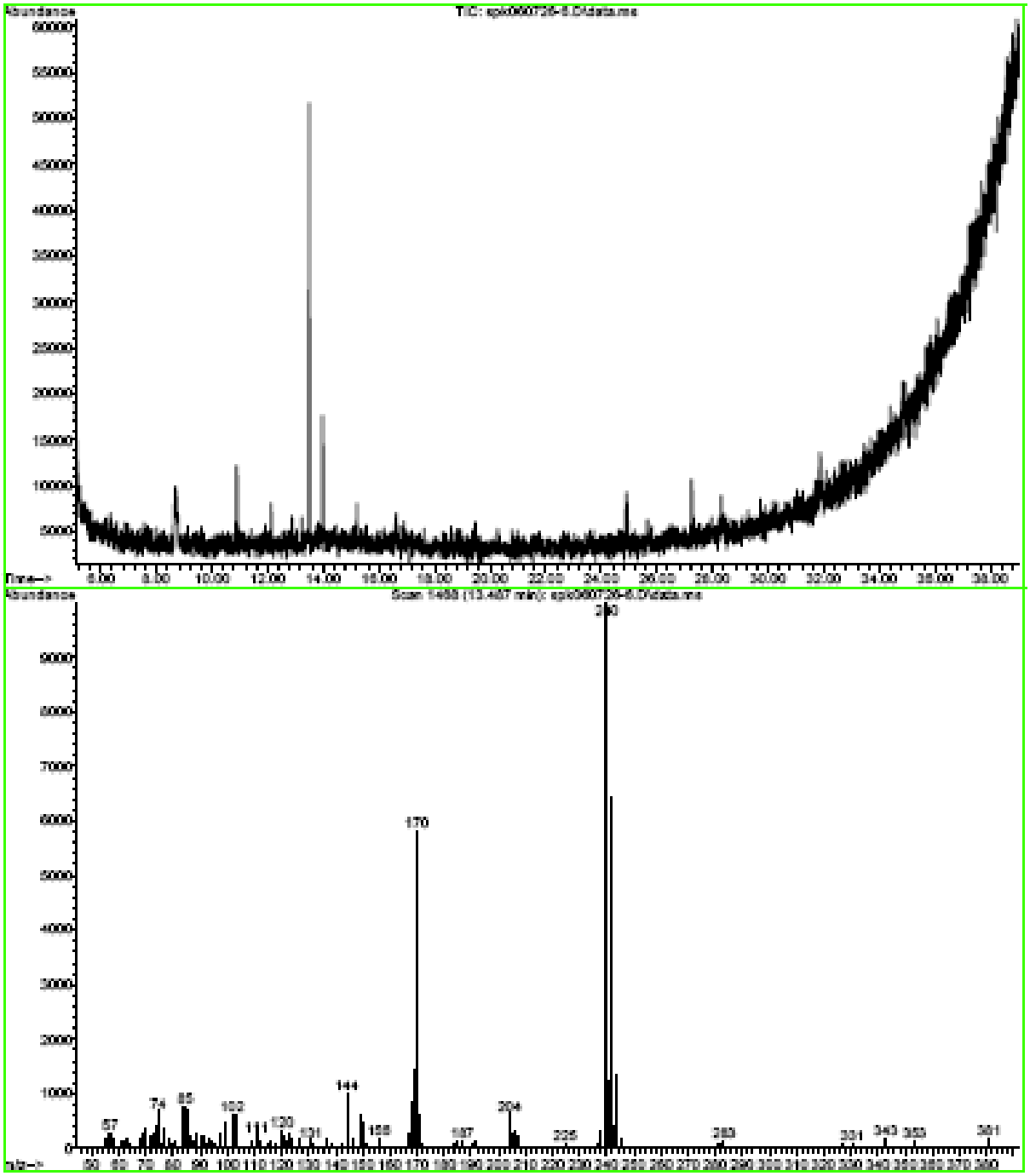


Figure 1: GC-MS chromatogram and mass spectrum for F.-PCB m_14