

# APPLICATION OF THE NEW C<sub>18</sub> SPEEDISKS™ TO THE ANALYSIS OF POLYCHLORINATED DIBENZO-*P*-DIOXINS AND DIBENZOFURANS IN WATER AND EFFLUENT SAMPLES

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## INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are present in almost all kind of environmental samples, such as soils, fly ashes, sewage sludges, water, etc. The concentration of these compounds in water is extremely low (pg/L or fg/L) due to their low solubility in this medium (from 10<sup>-4</sup> to 10<sup>-8</sup> ng/L), but they are strongly bound to the particulate matter present in the water. Such a low level in concentration of PCDD/F makes analytical methods long and difficult. Lately, the use of solid-phase extraction (SPE), with several adsorbents and devices, has increased for the extraction of lipid-soluble pollutants like PCDD/F from water in front of liquid-liquid extraction because it avoids the formation of emulsions, reduces the time of analysis and the amount of solvent needed. Several adsorbents are reported in bibliography for this extraction. When very high volumes of water are analysed (up to 1000 L, in some cases) the use of polyurethane foam (PUF) and Amberlite XAD-2 is common [1-5]. However, when the volume of samples is not so high (1–10 L) most of authors proposed the extraction with octadecyl (C<sub>18</sub>) membrane disks [6-8]. In the latter system, the plugging of the disk due to the content of particulate matter present in the sample can be a problem to solve. In these cases a complete filter bed with sand, glass wool, filter papers of several sizes, etc. in addition to the membrane disk is necessary [7].

In our work we have extracted water samples (particulate-free and with high content of suspended matter) with a new type of octadecyl disk (Speedisk) specially designed for analysis of organic pollutants in water samples with a high level of particulate material but not previously reported for PCDD/F analysis. This kind of disk allows a higher filtration flow and therefore the time of analysis is reduced. The complete analytical method has been validated and successfully applied to the analysis of water samples with very different characteristics and with an important environmental interest: a landfill leachate, an industrial effluent, rain water, seawater and the inlet and outlet water from a wastewater treatment plant.

## EXPERIMENTAL

**Reagents and materials:** 3M Empore™ octadecyl (C<sub>18</sub>) disks (47 mm i.d., 0.5 mm thick, maximum flow 10 mL/min) and high density glass bead Filter Aid 400 were supplied by Varian (Harbor City, CA, USA). Bakerbond Speedisks™ octadecyl (C<sub>18</sub>) (50 mm i.d., 1 mm thick, size of particle 10 µm irregular, maximum flow 200 mL/min) were obtained from J. T. Baker (Deventer, The Netherlands). Hexane, dichloromethane and acetone (Pestipur) were supplied by SDS (Peypin, France), toluene (glass distilled grade) by Rathburn (Walkerburn, Scotland) and ethanol and methanol (HPLC Grade) by Carlo Erba (Rodano, Italy). Sodium sulphate (GR) and silica were from Merck (Darmstadt, Germany), sulphuric acid (GR) from Scharlau (Barcelona, Spain), silver

nitrate and sodium hydroxide from Panreac (Barcelona, Spain) and Florisil from Supelco (Bellefonte, PA, USA).

**Analytical method:** Water (1-10 L), sampled in amber 2.5-litre glass flasks and acidified to pH 5-6 with 50 % sulphuric acid, were spiked with a mixture of  $^{13}\text{C}_{12}$  labelled 2,3,7,8-PCDD/F and 5 mL of methanol per litre of sample were added. The samples were left to equilibrate for 3 h before processing. The extraction with  $\text{C}_{18}$  Empore disks was adapted from that previously reported by Taylor *et al.* [7]. When these disks were used, the SPE system was composed by (from bottom to top):  $\text{C}_{18}$  disk, 1 cm of Filter Aid 400, a cellulose filter, glass wool and pre-cleaned (with hexane) sand. When the  $\text{C}_{18}$  Speedisks were used, only the disks were necessary. In both cases, the filtration-SPE system was cleaned and conditioned with 20 mL of ethanol/toluene (70/30, v/v), 25 mL of methanol and 50 mL of deionised water. Avoiding the SPE system to arrive to dryness, the whole sample was passed through the disk with the assistance of a vacuum pump. Afterwards, the disks were dried and PCDD/F were eluted with 60 mL of ethanol/toluene (70/30, v/v). The extract was concentrated under reduced pressure and cleaned up in a multilayer silica column (from bottom to top: glass wool, silver nitrate-silica, silica, sodium hydroxide-silica, silica, sulphuric acid-silica, silica, sodium sulphate) eluted with 100 mL of hexane. Afterwards, the extract was purified in a Florisil (activated to 450°C overnight) column eluted with 50 mL of hexane and 50 mL hexane/dichloromethane 95/5 v/v (PCB fraction) and with 100 mL of dichloromethane (PCDD/F fraction). Dichloromethane fraction was concentrated in a Kuderna-Danish apparatus and under nitrogen stream up to 15  $\mu\text{l}$  and the syringe standards ( $^{13}\text{C}_{12}$ -1234-TCDD and  $^{13}\text{C}_{12}$ -123789-HxCDD) were added. Finally, the samples were analysed by HRGC-HRMS in a CE 8000 gas chromatograph coupled to an AutoSpec-Ultima (Micromass, Manchester, UK) mass spectrometer, operating in EI ionisation (32 eV) at 10,000 resolving power. The samples were analysed in a DB-5 (60 m x 0.25 mm, 0.25  $\mu\text{m}$ ) capillary column and in a DB-DIOXIN (60 m x 0.25 mm, 0.25  $\mu\text{m}$ ) capillary column, both from J&W Scientific (Folsom, CA, USA). The latter was used in order to separate those 2,3,7,8-congeners that were not resolved in DB-5 column. Monitored masses were those proposed by EPA 1613 method [9].

With each series of samples a complete procedure blank was performed. The blank consisted of the same volume of deionised water as the sample, spiked with the mixture of  $^{13}\text{C}_{12}$  labelled 2,3,7,8-congeners and analysed exactly as the samples.

**Validation of the method:** The whole analytical procedure, using  $\text{C}_{18}$  Speedisks in the extraction step, was validated with deionised water spiked with a mixture of  $^{12}\text{C}_{12}$ -2,3,7,8-congeners. Accuracy, expressed as recovery (in %), precision (reproducibility in % RSD), obtained from three repetitions of the analysis in different series of samples, and limit of detection (LOD) of the method, calculated for each congener as the average of limits of detection (S/N=3) in the three analysis of reproducibility, were studied.

**Samples analysed:** The developed method using the new device of extraction (Speedisk) was applied to water samples from very different origins and characteristics: an industrial effluent; the leachate from a urban waste landfill; the inlet and chlorinated and non-chlorinated outlet water from the wastewater treatment plant in Vila Seca (Tarragona, Spain); rain water collected with a humid deposition sampler in the city of Barcelona (Spain) from May to July 1998; two samples of seawater from the harbour and the beach of Barcelona (Spain).

**RESULTS AND DISCUSSION**

SPE C<sub>18</sub> Empore disks plug readily when suspended material is present in the sample and therefore a filter bed with sand, glass wool, filter papers, etc. or the use of disks with bigger diameter is required. Focused on this problem, the C<sub>18</sub> Speedisks are specially designed for the analysis of pollutants in waters with high content of particulate matter. Since both types of disk are coated with octadecyl phase, the extraction procedure used for Speedisks has been the same as that previously used in our laboratory with Empore disks. First, the correct performance of the method was checked with spiked (sum of 2,3,7,8-PCDD/F: 150 pg/L) deionised water samples. The results obtained in this study with Speedisks are compared with those that we had previously obtained with Empore disks in Table 1.

**Table 1.** Results of validation study

	<b>Empore disks</b>	<b>Speedisks</b>
<b>Accuracy, %</b>	95 (96)	92 (89)
<b>Reproducibility, % RDS</b>	3.5 (3.1)	5.8 (4.3)
<b>LOD, pg/L (pg ITEQ/L)</b>	11 (1.9)	4.2 (0.6)

Since the validation of Speedisks with spiked water yielded similar results to that of Empore disks, the performance with two real samples (a landfill leachate and an industrial effluent) was compared. The landfill leachate was sampled in an urban landfill, it had a very dark colour and a lot of particulate suspended material. The industrial effluent was from a chemical industry, it was colourless and the particulate material was settled in the bottom of the flask. The two disks were applied to these samples. In spite of using the filter bed as described above, the landfill leachate made the Empore disk plug quickly, avoiding its analysis. However, the extraction with Speedisk was successful. In the case of the industrial effluent, both disks allowed the analysis but with Speedisk the extraction spent 15 min, while with Empore disk this step spent more than 1 h.

In addition of the samples mentioned above, the extraction with C<sub>18</sub> Speedisks was applied to other different samples of environmental interest: seawater, rain water and inlet and outlet water of a wastewater treatment plant. The results obtained are shown in Table 2. The recoveries of the <sup>13</sup>C<sub>12</sub> internal standards in the samples were in the same range that those obtained in the validation study.

**Table 2.** Concentration of PCDD/F in water and effluent samples

<b>Sample</b>	<b>Sum of 2,3,7,8-PCDD/F (pg/L)*</b>	<b>Sum of 2,3,7,8-PCDD/F (pg ITEQ/L)*</b>
<b>Industrial effluent</b>	77000	170
<b>Landfill leachate</b>	704	6.4
<b>Inlet WWTP</b>	344	1.2
<b>n.chl. Outlet WWTP</b>	2.32	0.006
<b>chl. Outlet WWTP</b>	5.15	0.3
<b>Rain water</b>	56.9	1.1
<b>Harbour water</b>	33.9	0.3
<b>Beach water</b>	24.7	0.9

\* These values do not include those congeners whose results are lower than LOD

In almost all the samples analysed the homologue profile is characterised by a higher content of PCDD than PCDF and an increase from tetra- to octachlorinated congeners, which is the trend reported by other authors [3, 10]. Only one of the samples, the industrial effluent, which has a clear different origin, shows a profile with a very high concentration of OCDF 135.

Seawater was sampled in the beach and harbour of Barcelona (Spain) and rainwater was collected with a humid deposition sampler in the downtown of the same city, with no direct focus of emission of dioxins in the vicinity. Therefore, the values obtained represent the background pollution of the city. The concentrations obtained for seawater are higher than those found in the Japanese coast and open-ocean (North Pacific) water by other authors [3, 4]. The measurements of PCDD/F in rainwater reported in bibliography are only a few, but our result is in the same order of concentration [10].

In the wastewater treatment plant of Vila Seca (Tarragona, Spain) the inlet water and the outlet water (this latter before and after a process of chlorination) were sampled. The inlet water was brown coloured and it had a lot of suspended material, while the two outlet water samples were colourless and with almost no particulate material. The concentration of PCDD/F obtained for the inlet water is much higher than those obtained in both outlet water samples. The dioxins removed from the inlet water are concentrated in the lipophilic by-product of the plant, the sewage sludge, which presents a value of 2360 pg/g d.m. of sum of 2,3,7,8-substituted PCDD/F.

After the analysis of these samples with different characteristics and amount of particulate matter we can conclude that the method based on the SPE with C<sub>18</sub> Speedisk is successful and allows to reduce the total time of analysis.

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