IDENTIFICATION OF KEY SURROGATES FOR REAL-TIME DIOXINS MONITORING

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Abstract

Dioxins emissions from combustion plants are stringently regulated. In Europe, the emission limit value is 0.1ng ITEQ/Nm^3 and this concentration is checked by manual sampling according to the European standard NF EN1948. Automatic continuous sampling devices were developed and installed at stack during these 10 last years. These systems allow calculating more accurately the dioxins flow released yearly. No dioxins continuous emission monitoring system is operated today. They need very specific and sensitive technologies, not easy to run on site. Therefore the use of surrogate compounds could be a good alternative to simplify the real time monitoring of dioxins. The surrogate compound can be a precursor of dioxin formation or others organic molecules in flue gas, as, for instance, a single dioxin. For a good estimation of dioxin concentrations (I-TEQ value), it is necessary to have a good correlation between surrogate concentration and I-TEQ value. This study reports potential surrogate compounds of dioxins I-TEQ. Correlations have been assessed in laboratory from flue gas samples of several EfW plants. Then analytic methods are suggested to allow their on-line monitoring, with good specificity and sensitivity.

Introduction

European regulation ensures two dioxins emission controls per year in the flue gas of EfW plants. Polychlorinateddibenzo-p-dioxins and polychlorinateddibenzofurans concentrations are measured according to the standard NF EN 1948. This sampling and analysis method has a long time delay (about 2 weeks) and is expensive. It allows to control emissions, but not to control process on real time. Dioxins continuous emission monitors (CEM) could be interesting for adjusting the flue gas treatment, but no system is available today. Automatic continuous sampling devices were developed and installed at stack during these 10 last years. These systems still provide interesting data to improve the yearly dioxins flow assessment of the plants. But it is not on-line monitoring and the analysis time delay is as long as the one related to the standard method.

CEM systems for dioxins I-TEQ value measurement should involve very specific and sensitive technologies, not easy to install and to operate on site. Therefore, the use of a surrogate compound could be a good alternative to simplify the real time monitoring of dioxins. The main aim of the study is to identify and to select surrogates presenting good correlation with dioxins I-TEQ value and then to suggest a suitable technology to measure the very low concentrated surrogate.

In literature, two kinds of molecules are mentioned to have good correlation with dioxins I-TEQ value : one of the 17 dioxins or one precursor of dioxins formation. Several studies have been realised in the past on different samples such as exhaust gas, soils, river water and flue gas. These studies confirmed the possibility to obtain a good assessment of the I-TEQ value from the measure of a single dioxin belonging to the 17 toxic congeners.

Pentachlorinated dibenzofurans, in particular the 2,3,4,7,8-PeCDF congener, are generally better correlated to theI-TEQ value than the other dioxins congeners. Indeed, the correlation coefficients calculated for 2,3,4,7,8-PeCDF reach 0.99 [1,2].

Elsewhere others studies showed that dioxin precursors can be good surrogates, with correlation coefficients above 0.9. Polychlorinated benzenes and polychlorinated phenols are mentioned in these studies [2,3,4,5].
Trials presented below focalized on the correlation between a single dioxin and I-TEQ value. Results concerning precursors are found in literature. Yet research on continuous monitoring technologies has been realized on all potential surrogates.

Materials and Methods

Tests on dioxins surrogates have been performed at a municipal solid waste incineration plant. The aim was to correlate I-TEQ values with the concentrations of each dioxin among the 17 toxic dioxins, in order to find the most suitable dioxin for on-line monitoring.

The presented results are obtained from twenty-one samples carried out during one year at the considered plant. The sampling and the analysis are realised according to the standard NF EN 1948 in our laboratory. All the results are reported to the normal conditions of temperature and pressure, and at 11% oxygen rate.

Results and Discussion

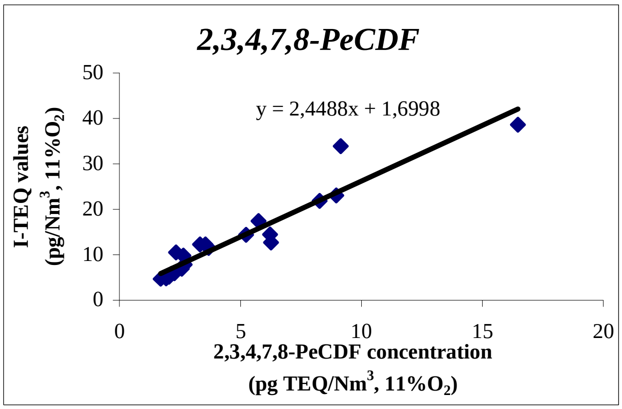
Correlation between I-TEQ value and each dioxin or dioxins group :

The table 1 indexes the correlation coefficients between I-TEQ values and each dioxin concentrations. Comparisons are also done with congeners groups including the same number of chlorine atoms and belonging to the 17 toxic congeners. The sums reported in the table 1 are calculated with congeners concentrations not corrected by the toxic equivalent factor.

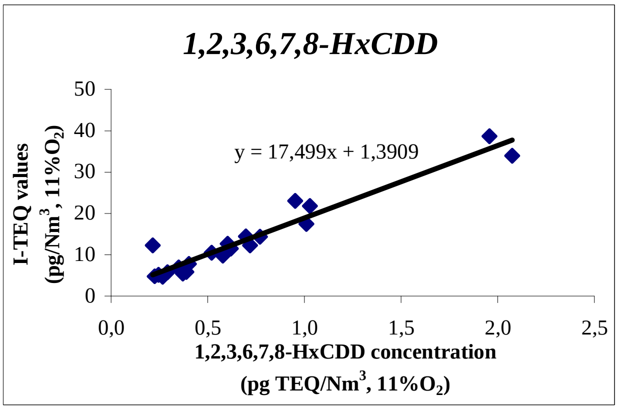
<table>
<tr><th>Molecule</th><th>Correlation coefficients</th><th>Sum of congeners</th><th>Correlation coefficients</th><th>Type of dioxin</th><th>Correlation coefficients</th></tr>
<tr><td>2,3,7,8-TeCDF</td><td>0.673</td><td colspan="2"></td><td rowspan="10">Furans</td><td rowspan="10">0.730</td></tr>
<tr><td>1,2,3,7,8-PeCDF</td><td>0.833</td><td rowspan="2">∑ PeCDF</td><td rowspan="2">0.910</td></tr>
<tr><td>2,3,4,7,8-PeCDF</td><td>0.950</td></tr>
<tr><td>1,2,3,4,7,8-HxCDF</td><td>0.958</td><td rowspan="4">∑ HxCDF</td><td rowspan="4">0.957</td></tr>
<tr><td>1,2,3,6,7,8-HxCDF</td><td>0.897</td></tr>
<tr><td>2,3,4,6,7,8-HxCDF</td><td>0.873</td></tr>
<tr><td>1,2,3,7,8,9-HxCDF</td><td>0.755</td></tr>
<tr><td>1,2,3,4,6,7,8-HpCDF</td><td>0.777</td><td rowspan="2">∑ HpCDF</td><td rowspan="2">0.749</td></tr>
<tr><td>1,2,3,4,7,8,9-HpCDF</td><td>0.525</td></tr>
<tr><td>OCDF</td><td>0.351</td><td colspan="2"></td></tr>
<tr><td>2,3,7,8-TeCDD</td><td>0.452</td><td colspan="2" rowspan="2"></td><td rowspan="7">Dioxins</td><td rowspan="7">0.617</td></tr>
<tr><td>1,2,3,7,8-PeCDD</td><td>0.878</td></tr>
<tr><td>1,2,3,4,7,8-HxCDD</td><td>0.816</td><td rowspan="3">∑ HxCDD</td><td rowspan="3">0.967</td></tr>
<tr><td>1,2,3,6,7,8-HxCDD</td><td>0.962</td></tr>
<tr><td>1,2,3,7,8,9-HxCDD</td><td>0.924</td></tr>
<tr><td>1,2,3,4,6,7,8-HpCDD</td><td>0.740</td><td colspan="2" rowspan="2"></td></tr>
<tr><td>OCDD</td><td>0.528</td></tr>
</table>

Table 1 : Correlation between dioxins (pg/Nm^3, 11%O_2) and I-TEQ value (pg/Nm^3, 11%O_2)

In this table, three dioxins seem to be well correlated with the I-TEQ value : the 2,3,4,7,8-PeCDF (graph 1), the 1,2,3,4,7,8-HxCDF, and the 1,2,3,6,7,8-HxCDD (graph 2) with respective correlation coefficients of 0.950, 0.958 and 0.962. These dioxins are then likely to be the best indicators for estimation of the I-TEQ value (all three dioxins have very close correlation coefficients and can be good indicators for dioxins I-TEQ value).



Graph 1 : Correlation between the 2,3,4,7,8-PeCDF concentrations and I-TEQ values



Graph 2 : Correlation between 1,2,3,6,7,8-HxCDD concentrations and I-TEQ values

Two other dioxins can also be considered as potential surrogates : the 1,2,3,6,7,8-HxCDF and the 1,2,3,7,8,9-HxCDD, whose correlation coefficients (respectively 0.897 and 0.924) are lower than the three molecules above but remain satisfying.

The worst correlation results are obtained with OCDF, 2,3,7,8-TCDD, 1,2,3,4,7,8,9-HpCDF and OCDD. The determination coefficients are respectively 0.351, 0.452, 0.525 and 0.528.

Although results for sum and single congeners are similar, it is easier to select only one dioxin and then to simplify the development of CEM systems.

Correlation between I-TEQ value and dioxins precursors :

The table 2 presents results from different studies realised during these last years [1,3,4]. Correlations were specifically studied for polychlorinated benzenes and polychlorinated phenols.

Type of molecule	Molecule	Concentrations range	I-TEQ values	Correlations coefficient (r)
Precursors ClBzs	ClBz	1.10^2 à 1.10^5 ng/m^3	0.1 à 100 ng-TEQ/m^3	0.83-0.91
	Cl_5Bz	500 à 100000 ng/m^3_N	0.5 à 100 ng-TEQ/m^3_N	0,91
	Cl_6Bz	100 à 5.10^6 ng/m^3	0.5 à 50 ng-TEQ/m^3	0.954
Precursors ClPhs	2,4,6- Cl_3Ph	0.5 à 1000 ng/m^3	0.1 à 0.5 ng-TEQ/m^3	0.82
	2,3,4,6- Cl_4Ph	10 à 1000 ng/m^3	0.1 à 1 ng-TEQ/m^3	0.79
	Cl_5Ph	5 à 100 ng/m^3	0.1 à 1 ng-TEQ/m^3	0.82

Table 2 : Correlation between precursors and I-TEQ values

Polychlorinated benzenes appear to be the most interesting surrogates along with correlation coefficients of Cl_5Bz and Cl_6Bz respectively equal to 0.910 and 0.954.

Continuous Emission Monitoring Devices

Continuous monitoring of dioxins surrogates need very specific and sensitive technologies enough reliable to detect these molecules in a complex matrix as flue gas. Several technologies can be suggested to measure molecules in these conditions.

The first one is the REMPI-TOFMS system, which is a Resonance Enhanced Multi-Photon Ionization coupled with a Mass Spectrometer Time of Flight [5,6]. It offers a selective ionization realised in two steps. Thanks to the REMPI ionization, an isomer selective ionization can be obtained for detecting targeted compounds. The detection limit indicated on the publications is ppt range.

Other techniques can be interesting to monitor molecules such as polychlorinated benzenes and polychlorinated phenols. The proposed devices are generally gas chromatographs with ECD detectors (Electron Captures Detector) or even on-line ion trap mass spectrometer. The detection limit is ppb range.

If the correlation is sufficient between dioxins surrogates and I-TEQ value, two main objectives can be underlined to the equipment of EfW plants with Continuous Emission Monitoring device : firstly, it could become a pertinent research tool to understand dioxins synthesis mechanisms. It also could be a mean to regulate on-line and automatically flue gas treatment by adsorbent injection.

Sensitive analysis technologies are proposed for dioxin surrogates monitoring but are not available in Europe. It can be noted that concentration measurement of these particular compounds is still complicated in regard to the implied analysis sophisticated technique and also to the sampling method at EfW stack conditions.

Acknowledgements

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