



One of the users of DX100 is the waste-to-energy plant of Lidköping Energi in Sweden. Technician William Axelsson is responsible for the daily operation of Lidköping Energi's DX100 sampler and also for the practical handling of the dioxins samples. In the picture, he is holding up a new sample container. Behind it is the sample cabinet with the container that is currently collecting a dioxins sample. To the right of the picture, OPSIS service engineer Kristoffer Martinsson gives the sampling probe a helping(?) hand. Photo: Peter Smedberg.

# Dioxins sampling yes, but then what?

Text: Bengt Löfstedt

The OPSIS dioxins sampler DX100 is designed to perform long-term sampling of dioxins, primarily in connection with waste incineration. But what happens after the sampling is done?

The requirement to measure dioxins emissions from waste-to-energy plants comes from the EU Industrial Emissions Directive and its “BATC” for waste incineration. According to this, sampling and evaluation of dioxins levels in flue gases must be carried out as specified in standard EN 1948. In some cases, long-term sampling is required, and this is where the OPSIS DX100 comes into play. Long-term sampling is not covered

by the current EN 1948, but it is described in a technical standard CEN/TS 1948-5, which is currently being incorporated as a fifth part of the EN standard, EN 1948-5.

### The Basics

“Dioxins” are a group of over 200 different substances that can be produced, for example, during waste incineration. Some of the substances can be significantly toxic also at very low levels. The complex structure of these sub-

stances combined with the need for very low detection limits makes it practically impossible to measure their levels in real time. Instead, samples are collected and sent to laboratories for analysis. In some cases, short-term sampling (six to eight hours) is sufficient, in other cases long-term sampling is required.

The rules require long-term sampling to take place every month with a sampling period of two to four weeks. During this period, a

small part of the flue gas passes through a sample container fitted with an adsorbent with a high capacity to accumulate dioxins. The total volume of gas passing the adsorber is measured. By dividing the total amount of dioxins in the sample by the volume passing the sample container, an average dioxins content in the flue gas is obtained.

### Handling of Dioxins Samples

Sampling is all well and good, but there are many other things that need to be done to determine dioxins emissions, such as practical handling of sample containers, laboratory analysis, and reporting.

Sample containers are reused, but at least two and preferably three individual containers are still needed to keep a sampler operational. One container sits in place in the DX100 and collects samples. At the same time, a second container is in transit, or is at the analytical laboratory to measure the amounts of dioxins collected. If the laboratory is running smoothly and the logistic chains are working, this second container can also be zeroed

(refilled and spiked, see below) and returned to the measurement site before it is time to make a new change of sample container. However, it may be worth the extra cost to have a third container in the rotation. It can then be on its way to or already in place at the measurement site to replace the first container regardless of the location or state of the second container.

A new, zeroed sample container is always sealed to prevent the sample material from being affected while waiting for sampling. When changing containers, the seal is transferred to the old container before it is sent to the laboratory, to prevent contamination of the sample material prior to analysis.

A container that is not in active sampling should be stored in a dark and cool place to prevent deterioration of the adsorption capacity. There is a time limit between the zeroing of a sample container and the start of sampling.

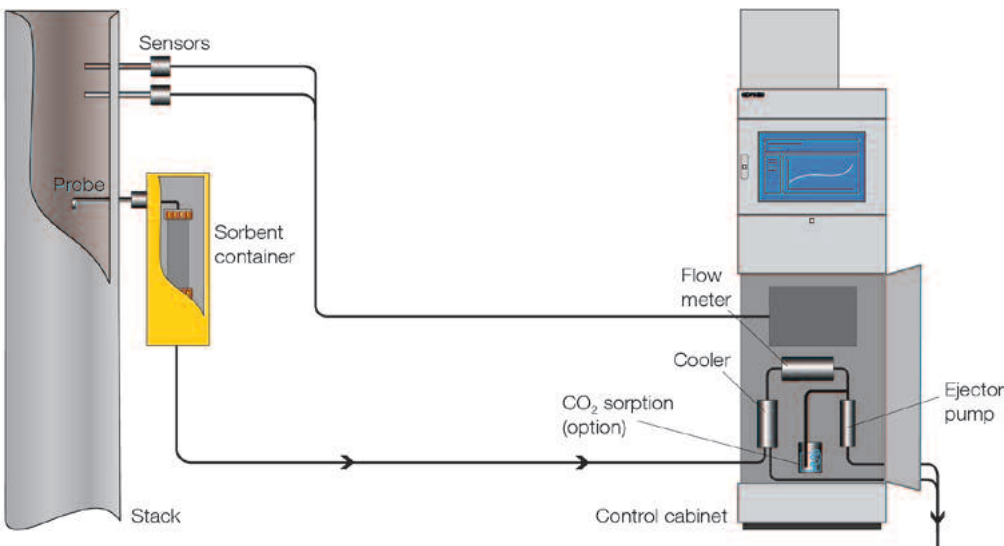
### Laboratory analysis

The material inside the sample container consists of granules, e.g. of a material designated XAD-2,

and glass fibre wool which holds the granules in place and acts as a protective filter. When a container arrives at the laboratory, the seal is broken, and the contents are removed and dissolved. The inner walls of the container are also washed, and any resulting solution is concentrated for analysis in a combined gas chromatograph and mass spectrometer (GC-MS). This instrument provides the weight of the individual dioxins types present in the extracted sample.

In both sampling and analysis, there is a risk that some of the dioxins are lost, in the former case because the adsorption is not 100 % efficient and in the latter case because of losses during sample handling in the laboratory. To compensate for such losses, a technique called spiking is used.

When a sample container is zeroed and provided with new granules and glass wool, it is also prepared with a known amount of a few specific dioxins. These come from a special manufacturing process where the carbon atoms are not ordinary carbon-12 but carbon-13. The level of car-



The OPSIS DX100 sampler, here in the version with the probe and the sample cabinet in a single unit.



bon-13 dioxins in the flue gases is much lower than in the material with which the sample is prepared (spiked). All the carbon-13 dioxins found at the laboratory during analysis therefore in practice come from the preparation. The ratio between the prepared content and the detected content of these carbon-13 dioxins will thereby also indicate the overall collection efficiency of dioxins in the flue gas, referred to as recovery rate in the current standard.

*“The analysis itself easily distinguishes between carbon-12 dioxins and artificial carbon-13 dioxins.”*

To account for losses due to sample handling at the laboratory, the incoming sample is also spiked with certain carbon-13 dioxins, but of different types than those used for the zeroed sample. This isolates the lab-specific losses incurred, e.g. during washing and concentration of the sample and due to the efficiency of the GS-MS equipment. The analysis itself easily distinguishes between carbon-12 dioxins and artificial carbon-13 dioxins. The ratio between the expected and measured amounts of carbon-13 dioxins from both sample spiking and analytical spiking is used to determine the actual amounts of carbon-12 dioxins that should have been present in the sample if the whole sample and analytical chain was 100 % efficient. This value is also the basis for the dioxins content applicable to the flue gas duct.

Reporting

There are many different substances in the dioxins family, and they can have different toxicities. In practical terms, however, the

levels of individual dioxins types are usually of no interest. Instead, the amounts of dioxins and their limits are expressed in “ng I-TEQ” (international toxic equivalent) which is the sum of the amounts of the different dioxins substances weighted by toxicity. The laboratory often reports the amount (weight) of individual dioxins, or at least the most common and most likely to be present, but they are weighted against the degree of toxicity and then summed to give a total amount of dioxins in I-TEQ units. That is what is of practical interest. The laboratory can report the value with uncertainty margins in the same way as a gas concentration measurement, for example as a total expanded uncertainty.

Once the analytical report is finalised, it remains to pair the result with all the information needed to determine the sampling volume and then compile a report. Here it must be taken into account that the concentrations given by the rules are for standardised volume at 0 °C, 101.3 kPa, dry gas, and for waste incineration 11 % oxygen.

The basis for the measurement of the volume passing through the sample container is, according to the standard, a type of volume meter called a gas meter. It may have a visual counter but, above all, it has to have a pulsed output that gives a signal for each unit of volume passed. Normally there is a condensing unit that dries the gas before the gas meter. The value reported by the gas meter is therefore the volume as dry gas, but at real temperature, pressure and oxygen content. The gas meter signal must therefore be corrected with the actual temperature, pressure and oxygen content in real time. The values are then stored and totalled over the entire sampling period.

The final calculation is then simple; the amounts of dioxins

in I-TEQ unit of the lab result is divided by the standardised sample volume. The measurement uncertainties in the amount of dioxins and the standardised volume with its auxiliary parameters can also be weighted together and reported.

It is important that both the sample containers and the individual samples are labelled so that they can be traced through the whole chain from sampling via analysis to reporting. However, this is only one of the many formal requirements that the standard imposes on the design of the final dioxins emissions report. For long-term sampling, the interested party is currently referred to the requirements of CEN/TS 1948-5, although this is not yet an EN standard and not yet mentioned in the BATC.

An example of a combined gas chromatograph and mass spectrometer (GC-MS) that could be used to analyse dioxins samples at a laboratory.



Measurement results PCDD/Fs:					
Sample:			Final extract [µl]: 60		
			Injection volume [µl]: 4		
			Acquisition date [d.m.y h:m]:		
2,3,7,8-PCDD/Fs	Result [ng/sample]	Limit of Detection [ng/sample]	Limit of Quantification [ng/sample]	1-TEFs	I-TEQ Upperbound [ng/sample]
2,3,7,8-TCDD	0.064	0.019	0.038	1	0.064
1,2,3,7,8-PeCDD	0.41	0.027	0.053	0.5	0.2
1,2,3,4,7,8-HxCDD	0.13	0.036	0.072	0.1	0.013
1,2,3,6,7,8-HxCDD	0.51	0.036	0.072	0.1	0.051
1,2,3,7,8,9-HxCDD	0.26	0.036	0.072	0.1	0.026
1,2,3,4,6,7,8-HpCDD	0.74	0.061	0.12	0.01	0.0074
OCDD	0.43	0.094	0.19	0.001	0.00043
2,3,7,8-TCDF	1.4	0.017	0.034	0.1	0.14
1,2,3,7,8-PeCDF	1.7	0.022	0.044	0.05	0.083
2,3,4,7,8-PeCDF	2.2	0.022	0.044	0.5	1.1
1,2,3,4,7,8-HxCDF	1.4	0.023	0.045	0.1	0.14
1,2,3,6,7,8-HxCDF	1.7	0.023	0.045	0.1	0.17
1,2,3,7,8,9-HxCDF	0.35	0.023	0.045	0.1	0.035
2,3,4,6,7,8-HxCDF	2.3	0.023	0.045	0.1	0.23
1,2,3,4,6,7,8-HpCDF	1.8	0.028	0.057	0.01	0.018
1,2,3,4,7,8,9-HpCDF	0.18	0.028	0.057	0.01	0.0018
OCDF	0.32	0.083	0.17	0.001	0.00032
I-TEQ from quantified 2,3,7,8-PCDD/Fs - "Lowerbound"					2.3
I-TEQ from 2,3,7,8-PCDD/Fs - "Mediumbound"					2.3
Maximum possible I-TEQ - "Upperbound"					2.3
PCDDs	Result [ng/sample]	PCDFs		Result [ng/sample]	
Tetra-CDDs	28	Tetra-CDFs		88	
Penta-CDDs	31	Penta-CDFs		51	
Hexa-CDDs	12	Hexa-CDFs		21	
Hepta-CDDs	2.5	Hepta-CDFs		3.4	
OCDD	0.43	OCDF		0.32	

Recovery:					
			Final extract [µl]: 60		
			Injection volume [µl]: 4		
			Acquisition date [d.m.y h:m]:		
Standard	Recovery [%]	Acceptable range [%]		Accept. rec. with respect to basic range extended range	
2,3,7,8-TCDD	98	50 - 130	30 - 150	YES	-
2,3,7,8-PeCDD	96	50 - 130	30 - 150	YES	-
2,3,4,7,8-HxCDD	92	50 - 130	30 - 150	YES	-
2,3,6,7,8-HxCDD	87	50 - 130	30 - 150	YES	-
2,3,4,6,7,8-HpCDD	48	40 - 130	20 - 150	YES	-
OCDD	49	40 - 130	20 - 150	YES	-
2,3,7,8-TCDF	77	50 - 130	30 - 150	YES	-
2,3,4,7,8-PeCDF	100	50 - 130	30 - 150	YES	-
2,3,4,7,8-HxCDF	81	50 - 130	30 - 150	YES	-
2,3,6,7,8-HxCDF	79	50 - 130	30 - 150	YES	-
2,3,4,6,7,8-HpCDF	75	50 - 130	30 - 150	YES	-
OCDF	78	40 - 130	20 - 150	YES	-
13C12-OCDF	50	40 - 130	20 - 150	YES	-
Sampling standard	Recovery [%]	Acceptable range [%]		Rec. in range?	
13C12-1,2,3,7,8-PeCDF	87	> 50		YES	
13C12-1,2,3,7,8,9-HxCDF	90	> 50		YES	
13C12-1,2,3,4,7,8,9-HpCDF	76	> 50		YES	

NOTE

The description of sample preparation and sample analysis is simplified. The reader is referred to the procedures in the EN 1948-series standard and the standards they refer to for the exact descriptions.

We have written several articles about the DX100 sampler in previous On the Beam issues and it is also mentioned in a number of blog texts on our website opsis.se - search for "DX100"!