

SAMPLING METHOD FOR PCDD/PCDF IN CORROSIVE OFF-GASES FORMED
DURING THE CHLORINATION STEP OF THE MAGNESIUM PROCESS

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INTRODUCTION

Norsk Hydro's magnesium plant in Norway is situated in Porsgrunn, approximately 150 km south of Oslo. The chlorination step of the production process, which is a high temperature process, leads to formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF). The production process is described by Oehme et al [1]. This reference also reports the annual waste water emission to be about 500 g TCDD-equivalents (Nordic model). At the end of 1989, cleaning equipment for this effluent was installed.

The dioxin content in off-gases from the chlorination step corresponds to an annual emission to air of 20-30 g TCDD-equivalents (Nordic model). The emission from this source will be reduced to below 1.5 g per year in 1991.

A simple, accurate and precise sampling method was needed in order to perform pilot plant tests for choosing suitable cleaning equipment for the off-gases.

The purpose of this work was to develop a sampling method with the following requirements: simple, with high precision and high collecting efficiency, especially for aerosols. Furthermore, low blank levels and no artifact formation in the sampling equipment. Earlier experiences showed that polyurethane foam (PUR) was not suitable as adsorbent due to reactions with the off-gases.

The experiment was designed to gain information about the distribution of PCDD/PCDFs between the different parts of the sampling train. Another object of the experiment was to study the validity of correction for losses in the sampler by addition of internal standards prior to sampling.

EXPERIMENTAL PART

The gas cleaning system of the magnesium plant consists of three sea water scrubbers. A typical particle size distribution of the gas from the last scrubber, shows that particles of diameter 0.4-2 μm and >15 μm dominate (on weight basis). The content of HCl, Cl₂ and SO₂ is, on average, 60, 20 and 100 mg/Nm³, respectively. With respect

to other chlororganic species the gas contains pentachlorobenzene, hexachlorobenzene, octachlorostyrene and decachlorobiphenyl. The concentration is, on average, 140, 80, 10 and 5 $\mu\text{g}/\text{Nm}^3$, respectively. The gas temperature was 10–15 °C.

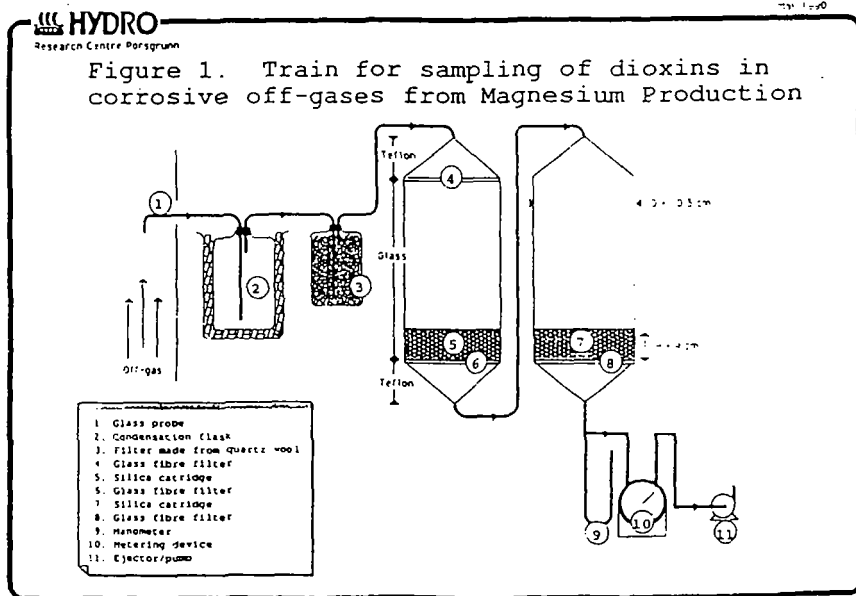
Sampling

The velocity of the gas in the duct was measured by means of a pitot tube at 16 points evenly distributed across the area. These measurements showed that the flow in the channel is of a homogenous turbulence type which is ideal for sampling.

The sampling train is shown in Figure 1. To ensure high collecting efficiency, for aerosols present in the gas and those which are produced during sampling, glass fibre filters were placed at three different points on the sampling train. Silica gel was chosen as adsorbent due to its inert properties. Before sampling, the silica gel (type Merck 7733 0.2–0.5 mm) was activated for 24 hours at 600 °C. The glass fibre filters (Gelman 61635, type A/E 142 Φ mm) were activated for 4 hours at 400 °C.

Four ^{13}C -marked 2,3,7,8-substituted congeners were added to the sampling train prior to sampling and five prior to extraction and clean-up (see Table 1). The amount of the standards added varied between 50 and 180 ng (100 μl).

Simultaneous sampling was performed at two points in the gas-stream. Due to the particle size distribution it was very important to carry out an isokinetic sampling. The sampling period was 8 hours, at a rate of 20 litres per minute. The total sample volume was in the order of 8 Nm^3 .



Extraction, clean-up and analytical procedures

Quantification of PCDD/PCDF was carried out according to the method described in /2/, except that an up-scale of the clean-up columns by a factor of 3 was employed.

Each of the samples was divided into three fractions prior to extraction and analysis; consisting of subsamples 1 to 4 (fraction 1), 5 and 6 (fraction 2), 7 and 8 (fraction 3, see Figure 1). All parts belonging to one sub-sample were rinsed with acetone followed by toluene.

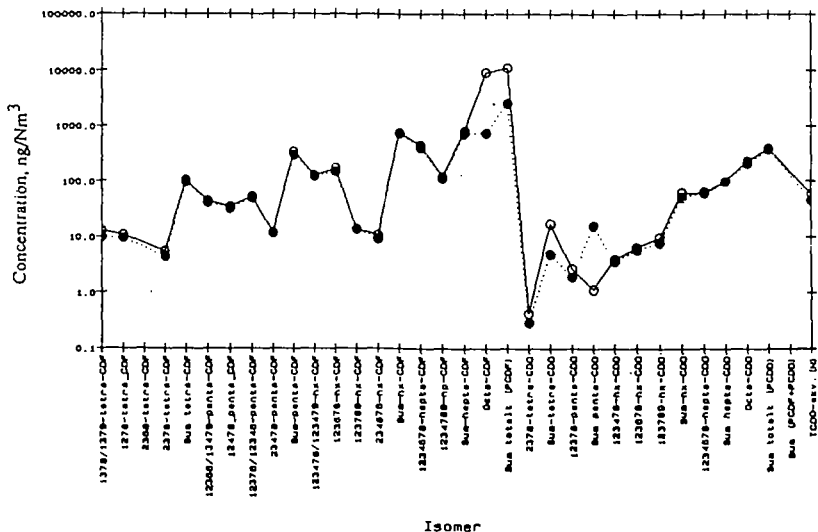
RESULTS AND DISCUSSION

The isomer profiles of the two samples taken simultaneously are compared in Figure 2.

More than 95% of the total amount of PCDD/PCDF in the sample was found in the first fraction containing most of the particulate matter. The levels in fraction 3 were equal to the detection limits for nearly all isomers (0.03 ng/Nm³ on average) indicating a complete collection of the fine particle fraction. The collection efficiency of the glass fibre filters mounted at the bottom of the silica cartridges is, in an experiment, proved to be more than 99.9% for particles >0.035 µm /3/. No significant difference was found between the two samples taken out in parallel. This confirms that the sampling was carried out under controlled isokinetic conditions.

The recovery rates for the congeners added prior to sampling and prior to extraction/clean-up were comparable (see Table 1). This means that no additional losses occurred during sampling. The relatively low recovery rates of 40%

Figure 2. Measurement of dioxins in off-gases
Comparison between two simultaneous samplings



to 50% can mainly be explained by considerable quantities of solvents which had to be used for rinsing and extraction due to large surfaces in the sampler. Therefore, a new version is now under construction which will reduce the employed solvent volume substantially.

The results for the ^{13}C -marked isomers were confirmed by comparing the concentrations of the 2,3,7,8-substituted isomers and isomer group parameters for both collected samples. The standard deviation of the logarithmically transformed isomer concentration was 13% on average (6% for the calculated 2,3,7,8-TCDD-equivalents according to the Nordic model). This measure of random scattering is used to give an estimate of the number of samples necessary for testing cleaning equipment. Assuming that the estimated cleaning efficiency is 90% and 99%, based on the average of two samples, the uncertainties corresponding to 95% confidence limits would be $\pm 1.2\%$ and $\pm 0.1\%$ respectively.

Table 1. Recovery rates of ^{13}C -marked isomers added before sampling and extraction/clean-up of the two samples taken in parallel

Recovery of ^{13}C -marked isomers, %					
Isomers added before sampling	Sample no. 1	Sample no. 2	Isomers added before extraction/clean-up	Sample no. 1	Sample no. 2
	Fraction no. 1			Fraction no. 1	
2378-tetra-CDF	23	39	23478-penta-CDF	23	38
123478/123479-hexa-CDF	33	48	1234678-hepta-CDF	39	50
12378-penta-CDD	26	44	2378-tetra-CDD	21	44
1234678-hepta-CDD	33	39	123678-hexa-CDD	31	51
			Octa-CDD	38	35
	Fraction no. 2			Fraction no. 2	
2378-tetra-CDF	< 1	< 1	23478-penta-CDF	54	39
123478/123479-hexa-CDF	< 1	< 1	1234678-hepta-CDF	59	45
12378-penta-CDD	4	3	2378-tetra-CDD	58	46
1234678-hepta-CDD	< 1	< 1	123678-hexa-CDD	62	46
			Octa-CDD	54	45
	Fraction no. 3			Fraction no. 3	
2378-tetra-CDF	< 1	< 1	23478-penta-CDF	56	42
123478/123479-hexa-CDF	< 1	< 1	1234678-hepta-CDF	59	49
12378-penta-CDD	3	2	2378-tetra-CDD	58	52
1234678-hepta-CDD	1	1	123678-hexa-CDD	59	28
			Octa-CDD	54	41

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