USE OF THE DILUTION METHOD FOR CONTINUOUS SAMPLING OF PERSISTANT ORGANIC COMPOUNDS FROM INDUSTRY EMISSIONS

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Introduction

Since publication of EN 1948[1] in 1996 the dilution method is described in this European standard to be used for the sampling of polychlorinated dioxins and furans. The sample gas is sucked through the nozzle and the probe (3). In the mixing channel (4) the waste gas is mixed turbulently with dry dilution air. The sampling filter (5) is located at the exit from the mixing channel.

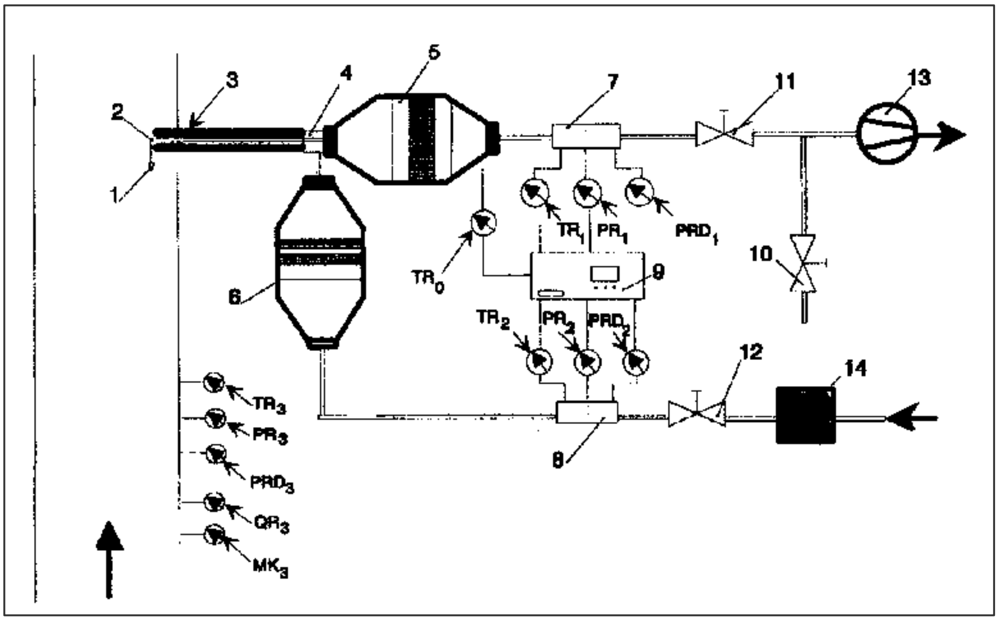


Fig. 1: scheme of the dilution method according EN1948-1

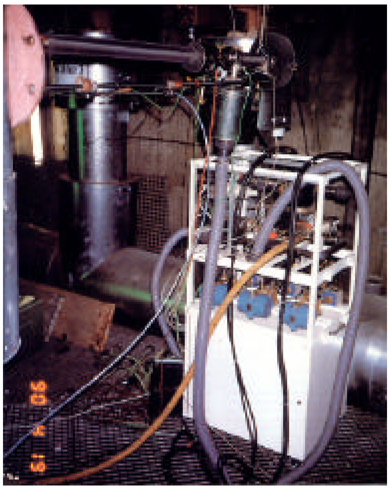
Since publication 1991 the automated variant of the dilution method was improved to a very high standard, which enables to extend the measurement time up to 30 days and can be used also for more volatile components with several advantages.

Because of isokinetic sampling and the used dilution method, the DioxinMonitoringSystem is able to sample also other organic components like CTPV (coal tar pitch volatiles) and PCB´s (polychlorinated biphenyls) according this standard also continuously.

The developed isokinetic sampling system has two principal parts, the sampling unit and the control unit. The sampling unit includes 2 tubes with one nozzle each, a mixing chamber and the filter cartridge. The control unit includes the conditioning of dilution air, the pumps for sucking, accurate volume measurement equipment and the control system with its visualisation.

An update of the EN1948 will be valid within one year. Several details will be defined which were missing in the previous version, e.g. how to process blank values and non-detects, but also details in the sampling method. This proposed inclusions are already used by the DioxinMonitoringSystem which also changed to outfit over the years.

History of the DioxinMonitoringSystem



Pic.1: 1990

Pic.2: 1993

Pic. 3: 1997

Pic. 4: 2002

In 1990 the first version of an automated sampling system based on the dilution method was developed.

In 1993 the first installation at 3 stacks was done at a hazardous waste incinerator using the final prototype G.16. Version G.18 provided first time full remote control capability in 1997.

In 2002, after several years of development the dilution method was perfectioned with the version G19. This device provides all purpose use, independently from the kind of emission gas to be monitored. *mCert* test is actual in progress in UK.

Advantages of the improved dilution method to sample persistent organic compounds

(1) The improved dilution method enables the isokinetic sampling at two positions in the stack. Especially organic components, which are distributed between gas and dust fraction were sampled representative.

(2) The dilution method enables the dry sampling of organic compounds. The improved dilution system enables the dilution of the gas with up to 10 times clean air. The conditions of sampling refer to the sampling of ambient air samples.

(3) With the dilution other interfering components like NO_2 and HCl which can react with the organic compounds were also diluted. Because of this the reaction speed (conversion of the sampled organic compounds) is reduced.

(4) Because of the dry sampling, no water is condensed during sampling. After the end of sampling only one dry sampling cartridge has to be transported to the laboratory. This is an important advantage especially for long time sampling periods.

Experimental

Persistent organic compounds have different volatility. Table 1 shows the vapour pressure of different compounds. A low temperature reduces the volatility of the compounds as table 1 shows.

Compound	Vapour pressure at 25°C (Pascal)	Vapour pressure at 100°C (Pascal)
OCDD	$1,1 \times 10^{-10}$	$2,4 \times 10^{-5}$
2,3,7,8 T_4CDD	$2,0 \times 10^{-7}$	$4,6 \times 10^{-3}$
PCB 153	$1,3 \times 10^{-4}$	
PCB 29	$1,3 \times 10^{-2}$	

Table 1: Vapour pressure of Persistent organic compounds

In a test run 1,0 m^3/h of flue gas was mixed with 4 m^3 /h of air. The mixed flue gas was sucked through the cartridge of the DioxinMonitoringSystem at a temperature of 40°C to determine the break through of the organic components, After 20 m^3 of flue gas the measurement was stopped.

Compound	First Polyurethane filter	Second Polyurethane filter	Measured breakthroug h after 2 filters	Calculated breakthroug h after 3 filters
Naphthalene	92 %	7 %	1 %	< 0,1 %
2',4,5 T_3CB	70 %	21 %	9 %	2,7 %
2,2',3,4,5 P_5CB	100 %	0%	0%	0 %

Table 2: Absorption efficiency of persistent organic compounds

Results and Discussion

The EN 1948 requires in chapter 8.3.4.1: The following parameters are required to be periodically recorded (at least every 15 minutes) to enable the validation of the sampling: velocity in duct, temperature in duct, flow

rate through sampling train, filter temperature, adsorbent temperature. The oxygen content shall be measured during sampling and recorded
Additionally chapter 8.3.4.2 and 8.3.5.1 require to store the results of the leak tests: It is recommended that the sampling train is leak checked both before and after changing sampling line. The final leak rate is recorded.
The DioxinMonitoringSystem, using the dilution method is able to sample the persistent organic compounds according to the EN 1948 standard. Especially organic components like naphthalene which can react with the flue gas components can be sampled with high efficiency.