

### DECS Dioxin Emission Continuous Sampling

What are dioxins and furans?

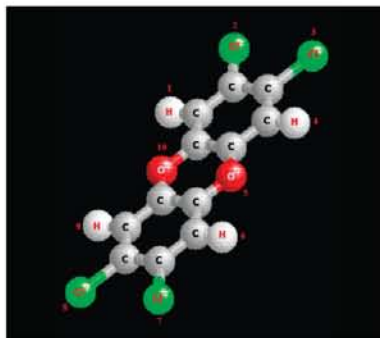
Dioxins, furans and PCB (polychlorinated biphenyls) are three classes of micropollutants classified as persistent and organic pollutants (POP, persistent organic pollutants), known at international level. Dioxins Furans and PCBs are halogenated aromatic compound, all made of carbon, hydrogen, oxygen and chlorine atoms. These compounds are divided in three families, depending on their molecular characteristics: 77 of them are polychlorinated dibenzodioxins (PCDD), 135 polychlorinated dibenzofurans (PCDF) and 209 polychlorobiphenyls (PCB).

The most studied dioxin, because believed the most dangerous, is the tetrachlorinated dibenzo-p-dioxins (2,3,7,8 TCDD) and is considered the reference dioxin.

Responsible of dioxin production, beyond wood combustion (domestic heating, accidental wood fire), caused by men activity are: incineration of urban and hospital waste, steel production from iron scrap and cement plants.

The first time the world heard about dioxin was in 1976 after the accident occurred at ICMESA in Seveso (Milan- Italy). Seveso case was the benchmark for all studies, followed after the disaster, to define and classify dioxins' and furans' toxicity. In 1997 the international agency for cancer research published the results on the valuation of TCDD toxicity. The verdict was guilty, so the molecule was accused of being carcinogenic, with special reference to sarcomas of soft tissues and leukaemia.

Dioxins are odourless and thermal



*Tetrachlorinated Dibenzop-dioxin  
2,3,7,8 TCDD molecule*



*Incineration plant*



*Cement plant*

stable molecules till 600°C, but insoluble in water and strongly liposoluble. Their stability ( they have a half life time of 7 years) makes possible an accumulation of them on the ground, and being capable of melting in the food chain fats it is said that dioxins are not breathed but are eaten. If eaten, dioxins can provoke serious damages to human immune, reproductive and endocrine systems. When attacked directly, the immune system reduces the lymphocyte B production, which causes a major weakness of the body towards virus and bacteria, exposing itself at the attack of important illnesses. In 1998 the health world organization lowered the daily amount of dioxin which is humanly tolerable in 1 picogram per kilo. Incinerators were obliged to use a dioxin limit concentration in gas which is 0,1 ng/m<sup>3</sup> as average of the 17 most dangerous dioxins.

### Sampling and determination of concentration of dioxins in gas

Nowadays, European regulations oblige incineration plants and alike classified plants to check their dioxins and furans emissions on a regular base. Dioxins and furans cannot be measured with real time analysers as of the state of the art of the technology. It requires sophisticated sampling technique and complex lab analysis.

For this reason, Environmental Authorities and Toxicology Research Institutes developed, over the last 30 years, standards to sample, to extract and to analyse dioxins in emissions and in ambient air.

Urban waste incinerators are typically required to check dioxins emissions 1 to 2 times per year with current techniques which require a stack test sampling of average 8 hours and lab analysis.

It seems clear that this approach keeps under control a very limited reality, being unable to catch anomalous situations and concentration peaks.

The periodical sampling of POP, family in which we find PCDD, PCDF, PCB and polycyclic aromatic hydrocarbon (PAH), can be carried out following the proceedings established by European regulations as described in the EN 1948 part 1 or by those established by US EPA 23.

The extraction of the sample will take place in laboratory with a gas-mass system, which means using a tumble gaschromatographer and a high resolution mass spectrometer (HRGC/HRMS).

Dioxins are found in gas in three phases:

- gaseous and condensable
- gaseous not condensable
- solid stage, concentrating especially in the finest dust.

While the EN 1948 establishes the distinct measure in each stage, the American authority establishes just two measures: the dust one and the other for not condensable gas, detained by a particular resin XAD2 or with polyurethane foam.

The European method EN 1948 admits three sampling techniques:

- filter condenser method
- dilution method
- cooled probe method

The American method EPA 23 only provide one sampling technique:

- filter condenser method.

### Continuous sampling VS periodical sampling

The standards in force concerning the dioxin emission sampling require a 8 hours sampling, which usually requires delicate and complicate equipment, a highly qualified staff and long preparation time. The periodical sampling as detailed in EN1948 and US EPA 23 is the only official validated method, but everybody understands that this approach supposes a stable process operation without transient conditions. Short time measurements taken between long periods of time do not provide representative and significant data.

The increasing awareness of the dangers of these compounds for human health generated a compelling need for a better understanding of dioxin stack emissions and, as a consequence, of long term samplings. Therefore based on such requirements TCR Tecora, leading manufacturer of stack testing instruments and environmental monitoring samplers since 1974, designed and produced DECS, a Dioxin Emission Continuous Sampler, which is a fixed system for stack emission for determination of dioxins and furans on long term.

### Dioxin Emission Continuous Sampler (DECS)

DECS (Dioxin Emission Continuous Sampler) is the solution of TCR

Tecora for the continuous emission sampling of dioxin, furans (PCDD/PCDF), PCB and other POP's. The system is permanently installed on stack for continuous sampling from 8 hours up to 30 days. According to EN 1948 and USEPA 23, DECS adopts the filter condenser method with adsorbing trap on wet gas.

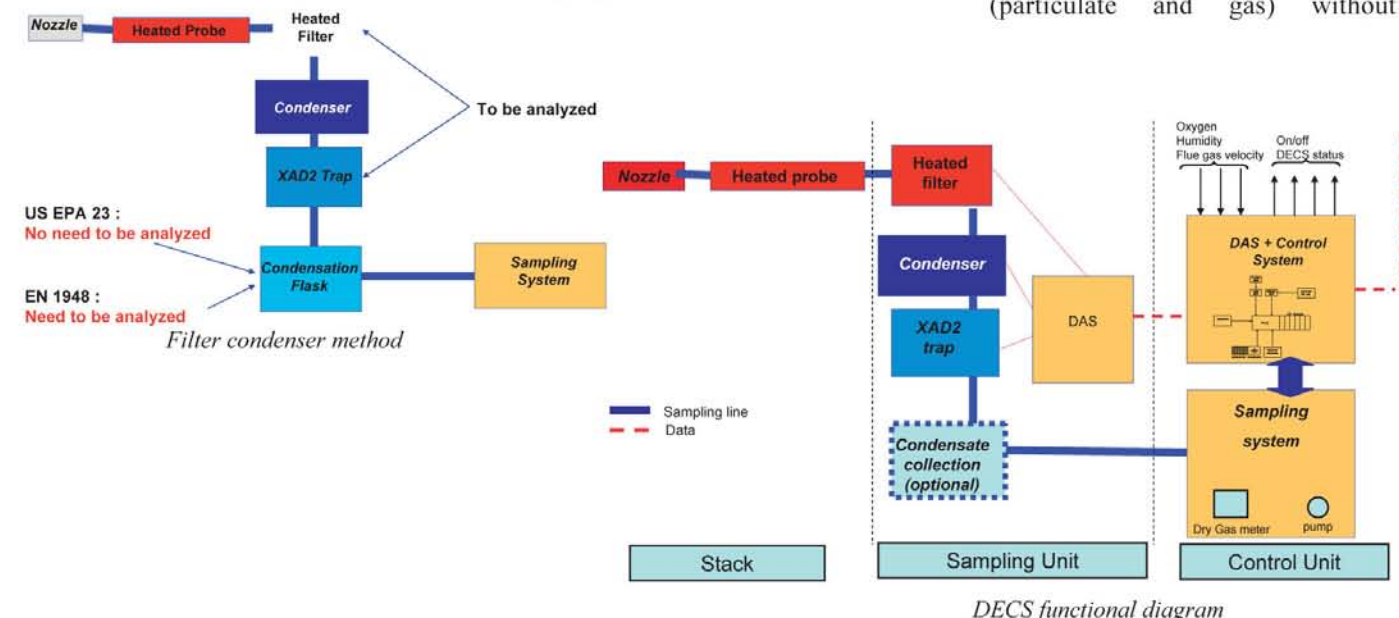
The filter condenser technique, which is the only one established by both methods, is the one that TCR TECORA selected many years ago, since when it started producing portable systems for stack testing based on ISOSTACK unit.

TCR TECORA was influenced to adopt this technique for other reasons:

- This technique allows to guarantee a temperature that is lower than 20°C on the adsorbing trap, which means maximum efficiency in the production activity and condensate separation.
- The heated probe with out stack filter allows to use the system even for sampling of hydrochloric acid, mercury and heavy metals, as requested by all methods in force with a side stream sampling, as requested by European regulations EN13285, EN 1911, EN 13211 and US EPA 29.

DECS consists of 2 units: the sampling unit and the control unit.

The sampling unit is the part to be mounted on the stack's sampling point and its aim is the collection of the sample in its two phases (particulate and gas) without



DECS functional diagram

modifying its composition.



The sampling unit can be mounted outdoor and it can get started anytime with no need of long preparation time. All the materials to which the flow stream comes in contact are glass and titanium.

The sampling unit includes the following devices:

- heated probe;
- particulate collection filter located in a heated box;
- condensing system;
- XAD2 adsorbing trap;
- Pitot tube.

The control unit is the user interface that controls all system's functions; it is usually located in a safe and easily accessible area.

Built in an industrial cabinet, it's connected to the sampling unit through pneumatic and electrical connections.



Control unit

DECS manages the sampling automatically, without man supervision. It requires for each sampling to define the sampling parameters with the friendly 10" colour screen and executes automatically probe cleaning, warm up, leak test, sampling for the defined duration and stop procedure covering standards requirements. On specific conditions like emergency shut down, anomalous operations as low operation load, can be defined a stand by condition. During stand by, the sampling line is isolated by the process with an air purging which protects the probe from contamination.

Available interfaces are a 10" LCD graphic monitor, a keyboard, a compact flash and a Internet/Ethernet connection.

Once the measurement is terminated, a summary report is produced, in order to calculate the concentration and evaluation of the measurement quality; a continuous record of the main parameters and anomalous situations it is also available. Extensive data log are available downloading with a USB key compact flash.



Operator panel

### Filter devices and Sample Management

TCR Tecora designed filter devices for the micro-pollutant capture, in order to obtain: tight sampling line, full protection from external contamination of the samples as well as easy to mount and dismount from respective receptacles. The titanium filter cartridge and adsorbant trap are supplied with plugs and transport case, in order to seal the sample, to arrange in a transport case for the lab delivery.

Filterholder for particulate matter is available in thimble form for long term sampling and with 47mm diameter flat filter for heavy metal and short term sampling.



Filter devices

### DECS Certifications

TCR Tecora obtained the mCERTs certificate for the DECS from CESI and more recently from SIRA UK.

The certification follows the protocol defined by the UK Environment Agency according to standards and procedures of the specification Performance Standards and Test Procedures for Automatic Isokinetic Samplers Version 2, September

2005.

The *Environment Agency*, the British institution for environmental protection, has designed the *Monitoring Certification Scheme (mCERTs)* to qualify environmental measurement systems which responds to quality and conformity criteria required by the Agency.

mCERTs is applicable for the monitoring systems certification, for people competences certification, for laboratories and audit consultants accreditation. This certification has the aim to guarantee the regulators that a certified equipment is capable to deliver reliable results, according to regulation requirements and the manufacturer specifications. At the same time, the end user is ensured that the mCERTs equipment is robust and compliant to standards and specification of the Environment Agency. The certification guarantees that the data measured are reliable and accurate and can be used for official communication in public.

It proposes to instrumentation manufacturers the independent evaluation of a recognised and reputable Organisation, facilitating the products introduction to British and international markets.



SIRA Certificate

TCR Tecora carried out independent field tests in collaboration with waste incinerators and cement plants to determine the overall capture efficiency of DECS system. The aim was to evaluate DECS filter condenser's efficiency, the residual dioxin content in the

condensate and to check capture efficiency in comparison with standard EN1948 test equipment.

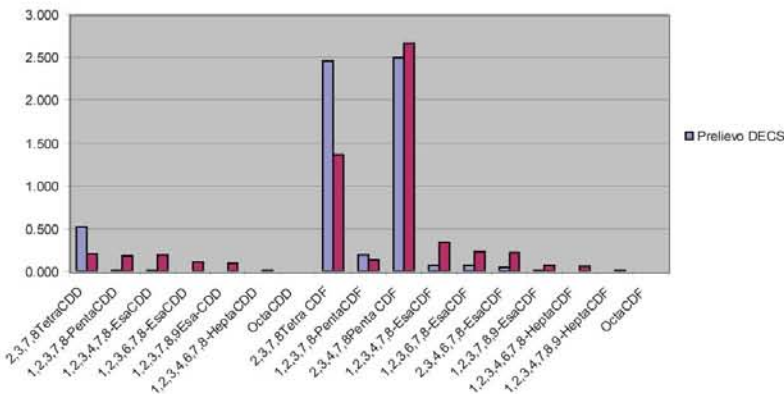
Over several tests was proved the ability of DECS to perform within the uncertainty accepted by the method when compared to EN1948 stack test equipment, to have residual dioxin in the condensate below or equal to the instrumentation detection limit. This last result eliminates any possible doubt about loss of compounds through the adsorbing material which could take place along long term sampling operations.

TCR Tecora with the scientific support of Italian research institute elaborated a protocol for the parallel sampling of DECS with EN1948 test equipment, for 8 hours and for long term sampling

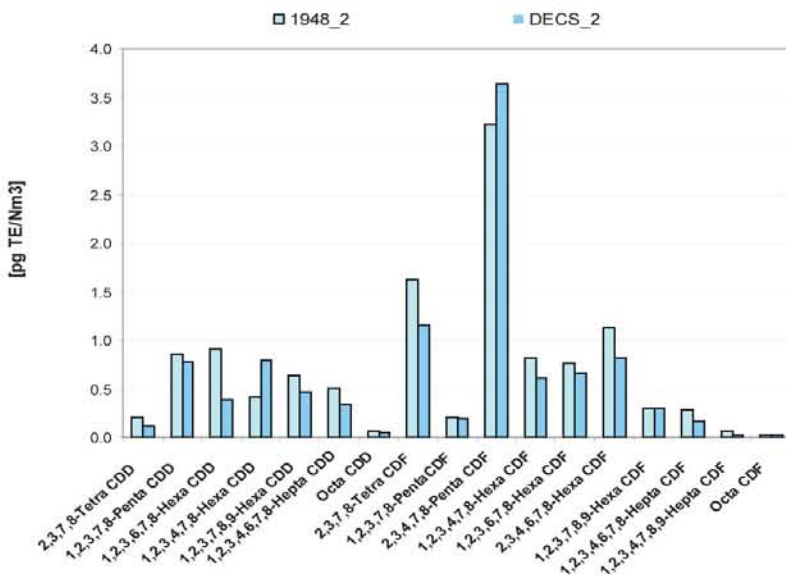


DECS sampling unit and EN1948 test equipment (TCR Tecora Isostack) during parallel sampling

confronto medie



One week DECS sampling vs average values of 3 8 hrs samplings using EN 1948 test equipment



Average values of 3 parallel samplings 8 hrs each with DECS vs EN1948 test equipment

TCR Tecora was established in Milan in 1974. Since more than 30 years the company designs and manufactures sampling and measuring systems for both immission and emission control in compliance with the most important international standards. Since 1998 TCR Tecora is ISO 9001 certified; this is a further commitment to supply high quality products toward Italian and foreign customers.