

## On-line monitoring of dioxin surrogates

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Polychlorinated dibenzo-p-dioxins and furans (PCDD/F) are formed in trace quantities in combustion processes such as waste incineration. In the last two decades, emission control technologies (i.e. secondary emission control devices such as absorbers) have been considerably improved, allowing nowadays the safe reduction of the PCDD/F stack emission level of municipal and hazardous waste incineration plants below 0.1 ng TEQ/m<sup>3</sup>. However, in many cases the PCDD/F are not destroyed but precipitated from the flue gas by filtering/scrubbing devices, leading to residue streams (fly ashes, absorbance material etc.) which partly are rather highly contaminated with PCDD/F. A more sustainable dioxin emission reduction approach would be the minimization of the dioxin formation processes itself. This should be achievable by an improved combustion process control, as it is known, that the formation of PCDD/F strongly depends on the quality of the combustion process. In order to realize a feed back control of the dioxin emission rate as well as for advanced dioxin formation research studies, a PCDD/F on-line measurement technology would be highly desirable. However, as the concentration of the 17 individual toxic PCDD/F congeners which need to be analyzed for the determination of the international toxicity equivalent value (I-TEQ) in the flue gases is very low, a direct on-line real-time measurement of the I-TEQ-value is not realisable. In the last decade concepts and techniques suited for on-line analyzing of PCDD/F surrogate compounds have been developed or are under development nowadays. The

session “On-line monitoring of dioxin surrogates” deals with recent developments in this field, covering rather basic studies on possible tomorrow’s detection techniques as well as more mature approaches. The session is divided into four parts, each containing two presentations:

- 1) In the first two presentations vacuum ultraviolet (VUV) – single photon ionisation mass spectrometric approaches (SPI-MS) for detection of dioxins or dioxin surrogates are presented.
- 2) The following two contributions deal with recent developments in the field of the laser based resonance enhanced multiphoton ionisation – mass spectrometry (REMPI-MS) for detection of PCDD/F and their surrogates.
- 3) The next two papers are dedicated to the determination of possible PCDD/F surrogate compounds for waste incineration flue gases.
- 4) Finally, the last two presentations in the session describe non-mass spectrometric concepts for recording of PCDD/F surrogate information, using the output of an ionisation cell or the information from the incineration plant monitors as potential surrogate signals.

In the following the contributed papers in the session are briefly introduced:

*Tonokura* et al. describe the laboratory application of a laser based VUV single photon-ionisation – time of flight mass spectrometer (SPI-TOFMS) for detection of chlorobenzene (MCBz). MCBz is known as a reliable surrogate for PCDD/F in flue gases of waste incineration plants. It is shown that MCBz can be ionised more efficiently than benzene and a detection limit in the low ppb region was achieved with the presented prototype.

The following paper by *Suzuki* et al. gives application results from a field measurement campaign at a waste incineration plant using a VUV-single photon ionisation mass spectrometer. In contrast to the system described in the previous paper, here a VUV-lamp is used for generation of the VUV-photons and a hybrid ion trap - time-of-flight mass spectrometric detector (IT-TOF) is used. Very good detection limits are achievable by this sophisticated set up and on-line monitoring results for trichlorobenzenes (continuous) and pentachlorofurans (discontinuous with enrichment unit) are shown.

The paper by *Uchimura* et al. reports on an one-colour resonance enhanced multiphoton ionisation time-of-flight mass spectrometric study (REMPI-TOFMS) on a tri- and a pentachlorodibenzofuran congener, respectively, using a GC-TOFMS coupling as inlet system.

*Kirihara* and co-workers have developed a multi-mirror photon accumulation system to enhance the sensitivity of the REMPI-TOFMS approach. Furthermore they implemented a previously described two-colour REMPI approach, using a tuneable laser pulse and a 213 nm laser pulse for excitation and ionisation in order to further enhance the sensitivity as well as to get access to the sharply structured origin region of the first electronic transitions of the higher chlorinated PCDD/F. An on-line detection limit of 4 ppt was achieved for 2,3,7,8-T4CDD.

In the following paper by *Oh* et al., the correlation of the chlorobenzene, chlorophenol and low chlorinated dibenzofuran/-dioxin concentrations in the flue gas of a municipal waste incineration plant are correlated with the measured PCDD/F I-TEQ values. Special emphasis was laid on determination of PCDD/F-surrogates which are accessible for REMPI-TOFMS on-line monitoring.

*Watanabe* and co-workers investigated the sum value of low and semi-volatile organic chlorine compounds as potential surrogates for on-line determination of the I-TEQ values. They added new experimental results to previously reported data and discuss the observed influence of the flue gas cleaning devices.

The paper of *Nakayama* et al. describes the development of a REMPI photo ionisation sensor cell for detection of aromatic compounds. The cell can be operated without a mass spectrometric (MS) detection system and thus might be an alternative to the expensive MS based approaches for special applications, where only a limited selectivity is required. A detection limit in the 100 ppt concentration range was obtained for pure monochlorobenzene seeded in nitrogen gas.

Finally *Nordsieck* et al. present the development of a multivariate model for describing of the PCDD/F concentration in the fly- and boiler ashes of municipal waste incinerators. The input variables used in the so called “sensor array” are easily measurable parameters which in most cases can directly obtained from the plant control system or by a REMPI photo ionisation sensor for polycyclic aromatic hydrocarbons (similar to approach described in the preceding paper).

In addition to the oral contribution also interesting poster presentations are belonging to the “On-line monitoring of dioxin surrogates” session. *Oser* et al. report on a REMPI-TOFMS laser ionisation mass spectrometer with a special membrane inlet for liquid samples. The measurement of the collection efficiency of semi and low volatile organic chlorine compounds is investigated by *Takakura* et al. *Muehlberger* et al. report on a novel, compact and rugged SPI - quadrupole mass spectrometer, which uses a special VUV-lamp instead of a laser, for detection of trace components in e.g. flue gases. *Zyaykina* et al. present correlation of REMPI-TOFMS and GC-MS data from thermal treatment of flue ashes. *Steiner* reports on the implementation of new European legislative requirements to the construction and operation of a long term PCDD/F sampling system. Finally, *Streibel* and co-workers present REMPI-TOFMS results on pyrolysis gases of organic material such as PVC.

In summary, the session gives a comprehensive overview on several of the current approaches towards a PCDD/F-surrogate on-line monitoring methodology. However, some interesting concepts for sequential monitoring of PCDD/F surrogates based on e.g. on-line GC-FID or on-line HPLC-GC-MS as well as an on-line monitoring approach based on chemical ionisation ion trap mass spectrometry (CI-ITMS) have been addressed in related special sessions in the preceding years.