New Results and Experiences of Continuous Dioxin Monitoring by Using of AMESA®

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Introduction

The continuous monitoring of dioxin and furan emissions of incinerators is a topic which has been discussed globally over the last several years. Even though a continuous on-line monitoring system would be the optimum solution, up to now no online-system is available which is able to give an information of the PCDD/PCDF emissions as TEQ value, as demanded by EN-1948[1] or the new EU directive for incineration of waste 2000/76/EC[2]. According last reports, such systems will be not available in the next few years.

Therefore, long-term sampling using AMESA® could close the gap between reality and target results. AMESA® provides more informations on dioxin emissions than the usual short-term collection of samples over a few hours on 1 – 3 selected days per year.

In Germany continuous emission measurement and control in accordance with §10 (1) of the 17th Federal Emission Control Ordinance (17. BImSchV)[3] must be carried out using a suitable (performance-tested) measuring device. Due to this regulation we decided to do a performance test for AMESA® by TÜV Rheinland in 1997.

Since the first installations of the TUV approved AMESA® systems in 1997, AMESA® became more and more as a standard for continuous dioxin control in Europe. More than 70 installations give a lot of information's. After starting of the continuous dioxin emission control in the Wallonia region with the 1st January 2001, in this area exist now experiences of the dioxin emissions of more than 3 years[4].

Since the start-up of this network more than 700 samples of duration of 2 weeks ware taken from 12 burners of household waste incinerators. After 20 occasions, in which the limit value of 0,1 TEQ ng/Nm^3 was exceeded in the first year 2001, this quantity was reduced to 9 occasions in year 2002 and 12 occasions in year 2003.

Therefore some plants had to be modernised to fulfil the regulations. Of course, these leaded at first to new investments, but after these investments, the operators had an instrument to calm down the public by showing continuously that their plants were running properly and the environmental stress was reduced.

This report will give you an introduction into the AMESA® system, realised applications, newest results and some remarks to the new version of EN-1948-1.

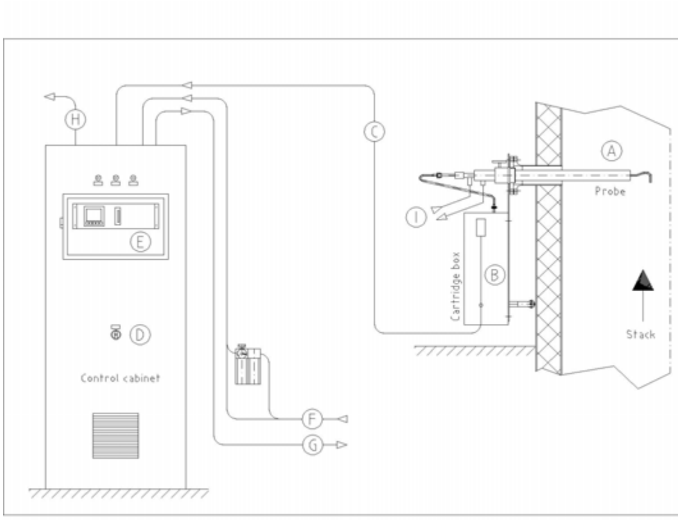
Material and Methods

The measurement principle which is used in the described system is known since several years as a possibility for long-term sampling of dioxins and furans[5]. The system was approved in 1997 by TÜV Rheinland[6] and validated against EN 1948, by comparison measurements with the cooled probe method. The performance test standard which was used followed the "German Guidelines for the Qualification Testing of Continuous Emission Monitors (CEMS)"[7], which were notified by the EU. In these guidelines are defined minimum requirements for CEMS in the qualification test and under chapter 1.7 requirements for Long-Term Sampling systems.

Contrary to the usual three single measurements every year, by means of continuous sampling over a period between 6 hours and 30 days, AMESA® ensures continuous documentation of dioxin/furan emission for each single sample.

This ensures that fluctuations in system operation and in the composition of fuels etc. are also recorded.

The functional principle of the system (see fig.1) is described in several publications[8]. In principle the used method complies with the cooled probe method of EN-1948 with the exception that the condensate flask is installed after the XAD-II cartridge and that therefore the condensate does not need to be collected and analysed. This is in accordance to US EPA method 23A. Additionally the plane filter for the dust collection is replaced by quartz wool included in the top of the XAD-II cartridge.



A	Cooled (< 70 °C) titanium probe for isokinetic extraction of a volume stream.
B	Measurement stream and condensate are drawn through the cartridge filled with adsorber resin (quartz wool as a pre-filter).
C	Measurement stream and condensate are drawn through the measuring gas line to the control cabinet.
D	Control cabinet with separation of the condensate by cooling (< 5 °C) and infinitely variable control of the isokinetical extraction.
E	User-friendly operation of AMESA® by menu dialogue in process controller. Data input for plant specific parameters and operation by means of keyboard and LCD-monitor. Analysis of the emission values by means of SRAM memory chip and analysis results.
F	Compressed air, power supply and input signal conduits.
G	Condensate drain and flue gas recycling
H	Signal output (optional)
I	Coolant connection (if $T_{Fluegas}$ > 70 °C)

Fig. 1 Functional principle

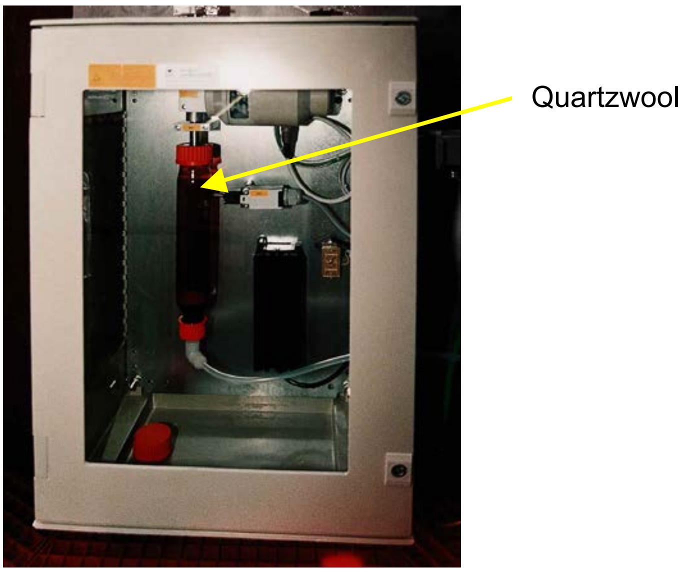


Fig. 2 Cartridge box incl. filled XAD-II cartridge

The cartridge containing the adsorbed dioxins and furans is evaluated together with the data medium in an accredited laboratory. By means of this process, dioxins and furans are separated from dust, the gas phase and the condensate in one adsorption step. This process not only registers dioxins and furans, but also further organic substances with a similar volatility and polarity.
Additionally a remote control software is available. With this equipment a world-wide control of the instrument via phone network is possible.

Results and Discussions
Since 1.1.2000 the dioxin emissions of all municipal waste incinerators in the Flemish region of Belgium are controlled continuously. After the introduction of the limit value of 0,1 ng-TEQ/Nm^3 six incinerators had to be closed, some others were modernised. Due to these efforts the total yearly dioxin emissions off all waste incinerators in the Flemish region could be reduced from 58,0 g TEQ in year 1995 to less than 1,0 g TEQ in year 2000. In different test series a good correlation of the results of AMESA® and manual sampling according EN-1948-1 could be obtained (see fig. 3)[9].

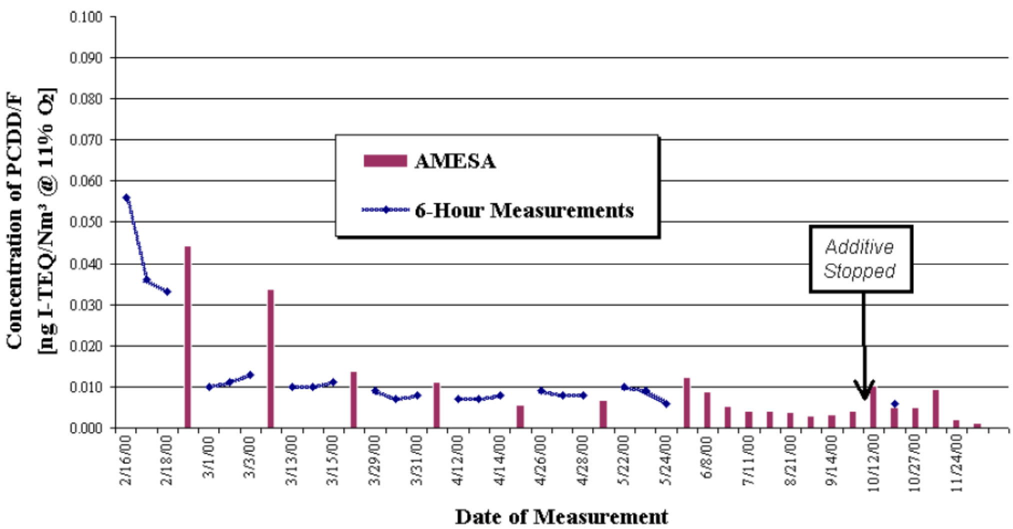


Fig. 3 The stack emissions of PCDD/F at IMOG and comparison between AMESA® results (14 days) and manual sampling (6 hours).

After starting of the continuous dioxin emission control in the Wallonia region with the 1st January 2001, there exist now experiences of the dioxin emissions of more than 3 years.
Since the start-up of this network more than 700 samples of duration of 2 weeks ware taken from 12 burners of household waste incinerators. After 20 occasions, in which the limit value of 0,1 TEQ ng/Nm^3 was exceeded in the first year 2001, this quantity was reduced to 9 occasions in year 2002 and 12 occasions in year 2003.
Due to the breaches some furnaces were permanently shut down during the year 2001. However several of them were restarted after modernisation and revision.
Most breaches were attributable to technical problems. It could be showed, that after solving the technical problems, a plant could run more than 2 years with acceptable low emission values. However this example showed, too, that still a long period of several months with low dioxin emission values do not guarantee low values for the complete year (see fig. 4). But after clarifying of the technical problems, it is possible, that such a plant is running well for a long time (see fig. 5 and 6).
After showing that the total dioxin emissions of the household waste incinerators of Wallonia region could be reduced in year 2001 to 0,69 g TEQ (from 64,9 g TEQ in year 1995 and 4,83 g TEQ in year 1999) an additional reduction by factor 10 in year 2002 (total 182 samples) to 0,067 g TEQ was achieved. Such values show the success of the introduction of the control network.

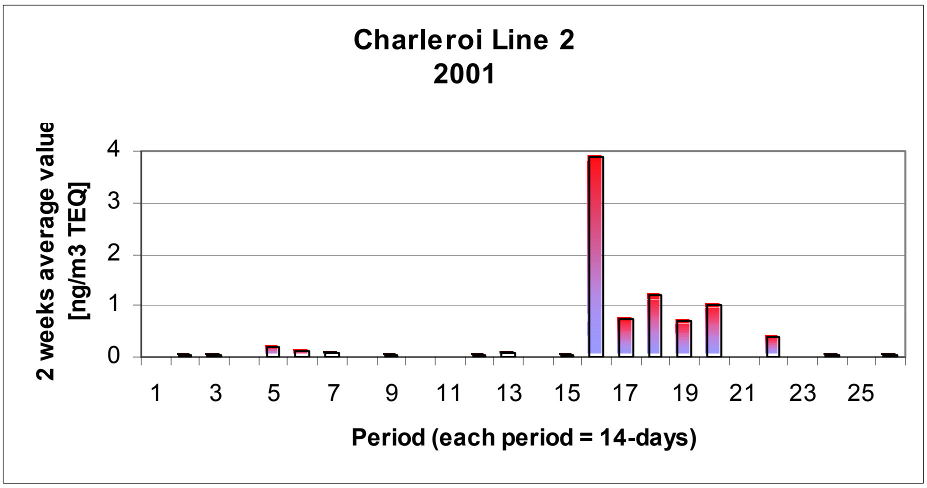


Fig. 4

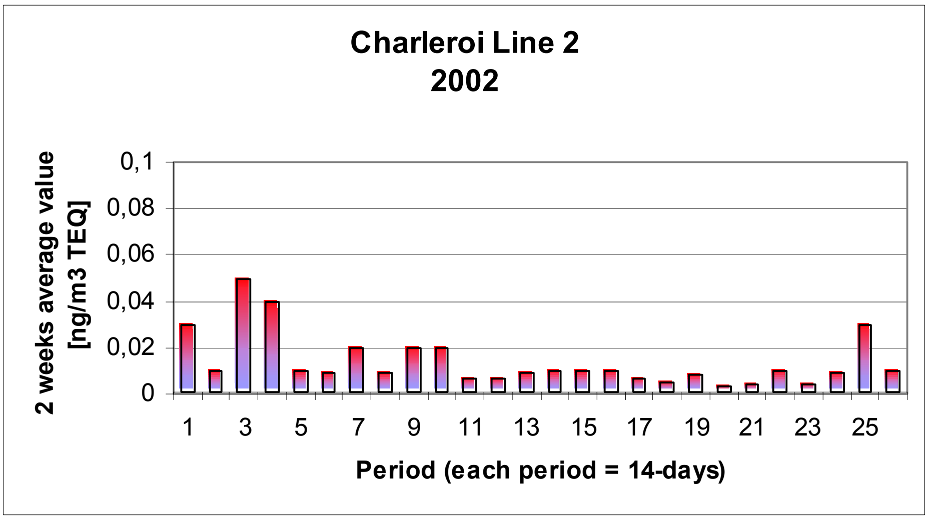


Fig. 5

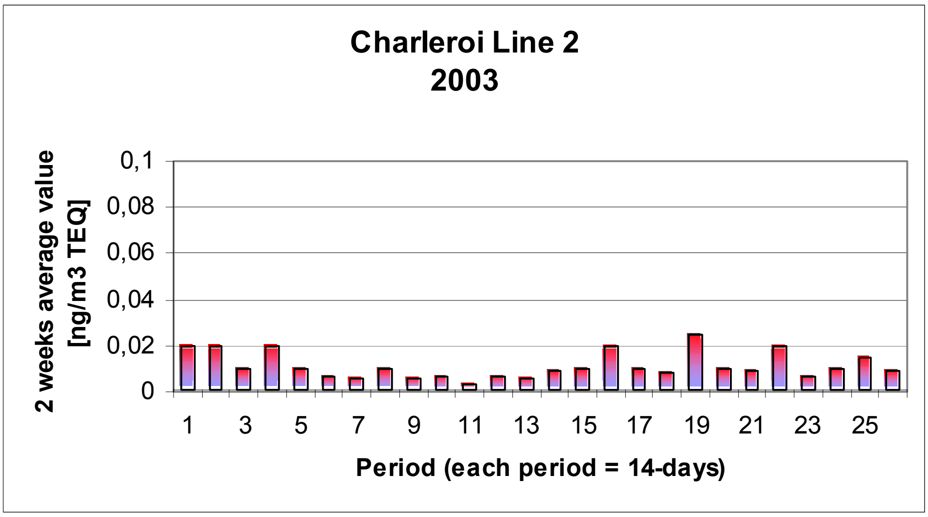


Fig. 6

Beside the installations in Europe first installations were also done in Asia. At first a performance test was done by TUV Rheinland Taiwan for the Taiwanese EPA. By this test could be detect a deviation between the AMESA® results and the results of the manual sampling (see fig. 7)[10]. These deviations were investigated as results of dioxin decompositions inside the probe.

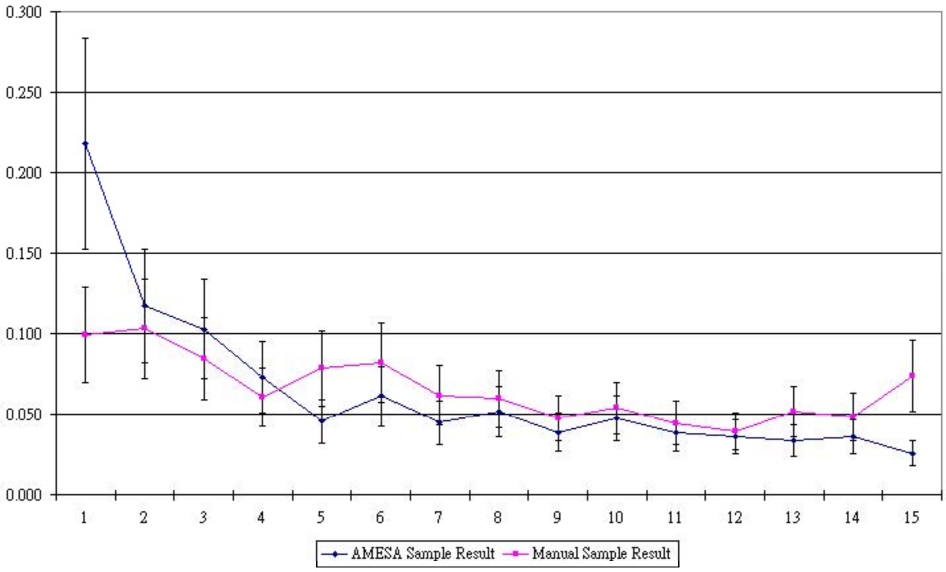


Fig. 7 Comparison of AMESA® and manual sampling according Taiwanese EPA method

As it is known, in contrary to the dilution and the filter/cooler method of EN-1948-1, by the cooled probe method, the inside of the probe is washed during the sampling by the created condensate. Therefore the risk of decomposition of dioxins inside the probe is quite smaller in comparison to the other two methods. Losses of less than 1 % by the used method were confirmed by different measurements (see fig. 8)[11].

	Glass tube	**1st XADII adsorber incl. quarz wool as solid filter**	**Conden-sate**	**2nd XADII adsorber**
ITE (NATO(CCMS) [ng/m³]	0,012	3,73	0,003	0,003
[%]	0,32	100	0,08	0,08

Fig. 8 Possible losses in the sampling line

However the results of the Taiwanese project showed that depending on the plant and flue gas conditions, the decompositions could be so high, that this effect is no more negligible.
Due to this effect different solutions were discussed. An overview about the different possibilities is showed in table 1.
According different experiences, we use, where it is necessary (up to now in less than 5% of the installations), the second solution as preferable solution, because the first solution is difficult to handle and the third solution contents too much uncertainties, which could vary also strong from plant to plant.

Solution	Advantage	Disadvantage
Cleaning of probe after each sampling by solvents	• Practice acc. the different international standards	• Time (30 – 60 min) and handling intensive
Usage of probe with changeable inner tube	• Follows the different international standards • Not so time (10 – 15 min) and handling intensive	• Still additional handling
Automatic probe cleaning by thermal desorption	• Fully automatic. • No manual handling.	• Does not comply any international standard • Time intensive (60 min) • No control about efficiency of cleaning process • => no control, if the thermal desorption of the PCDF/D does function uniform and therefore risk that the PCDD/F profile and the ITE value respectively, will be changed due to decomposition and/or synthesis of single congeners • After the desorption the inner probe wall could still by layered by dust, which could lead to non controllable adsorption and desorption conditions inside the probe for the following sampling periods

Table 1.

Standards and Directives

Since the European standard EN-1948 for the measurement of dioxins in emissions was established in 1996, a lot of experiences were collected over the past few years. To account for these experiences the CEN/TC 264 workgroup 01 is preparing a new version of the European standard EN 1948.

Even though our instrument AMESA® does not comply to the standard EN-1948-1, for us as supplier it is interesting, if modifications of this standard creates additional discrepancies to our instrument or if the adaption of some modifications would be helpful for long-term sampling, too.

One significant change of the new version is the removing of the maximum sampling time of 8 hours. This opens the standard theoretically for long-term sampling. However according to the EU Council Directive 2000/76/EC on incineration of waste the minimum sampling time is 6 hours and the maximum sampling time is 8 hours. The validation of the standard EN 1948 was performed for a sampling time of 6 h. This means, that as long as no intensive measurement campaigns were made to validate the standard for longer sampling periods, this standard is still a standard only for short term sampling of dioxins and furans.

According the new version, the sampling has to be done according to EN 13284-1, "The determination of low range mass concentrations of dust". This standard demands that the sampling has to be done at representative positions in the duct. Therefore a minimum of 1 sampling point is defined for small stack diameters, otherwise minimum 4 sampling points are necessary. Similar demands were also defined in the actual version of EN 1948-1. However it is known as a fact for continuous emission monitors (CEMS) to measure normally on only one representative sampling point. In general according the standard, such deviations are allowed, they have only to be mentioned in the measurement report. This

means that this change is no additional restriction for a fixed installed probe by long-term sampling to the existing version of the standard.
According the directive 2000/76/EC, all sampling and analysis of all pollutants including dioxins and furans as well as reference methods to calibrate automated measurement systems shall be carried out, as given by CEN-standards. The EN 1948 is the reference method in the EU member states by law. Therefore an automated sampling system like AMESA® has to be calibrated and/or validated by comparison measurements to EN 1948. This was done, as mentioned in this report, several times successfully.

Conclusion

The actual results of the Flemish and the Wallonia region of Belgium show the different advantages for both the public, environmental and the operator. If defects in the plant happen, which lead to higher dioxin emissions, these defects are recognised earlier and help to reduce the dioxin emissions. On the other side, if the values are constantly low, the public acceptance is higher.
Due to the high quantity of installations over the last few years we got a lot of experiences, which help us to recognise possible sampling problems fast and to use proofed solutions, like e.g. the changeable inner tube inside the sampling probe in case of decomposition problems.
The requirement of 2000/76/EC, that measurement methods as given by CEN-standards have to be used or that automated measurement systems have to be calibrated by reference measurements according CEN-standards, was fulfilled for AMESA® many times during the last few years.
There are different positive international movements for the introduction of long-term sampling of dioxin and furans like e.g. the conclusion of the EPA verification project of AMESA® in Taiwan and the actual project which is done by the Enviro Agency in UK.
ARPA in Italy and the US EPA are planning verification tests for this year and in France is running the ADEME supported Coper-Diox project with AMESA® since the year 2002.
In general we can conclude, that the international interest for long-term sampling of PCDD´s/PCDF´s is increasing and that by more and more installations of long-term sampling systems like AMESA® the dioxin emissions will be reduced world-wide in a strong way.

References

1. EN 1948: Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs – Part 1: Sampling (1996)
2. Directive 2000/76/EC of the European Parliament and the Council of 4 December 2000 on the incineration of waste, Official Journal of the European Communities, published 28.12.**2000**, page L332/91 – L332/111
3. Siebzehnte Verordnung zur Durchführung des Bundes-Immissionsschutzgesetzes (Verordnung über Verbrennungsanlagen für Abfälle und ähnlich brennbare Stoffe – 17. BImSchV), 23. Nov. **1990**, last revision dated 14. Aug. **2003**
4. http://environnement.wallonie.be/data/air/dioxines/menu/menu.htm
5. W. Funcke, H. Linnemann, Ch. Phillipp; Long-term-Sampling Method for Polychlorinated Dibenzofurans (PCDF´s) and Dibenzo (p) dioxins (PCDD´s) in Flue Gas of Combustion Facilities, *Chemosphere,* **1993**, 26, 2097-2101
6. Wilbring P, Gerchel B; TÜV report 936/805017B, **1997**
7. Federal Ministry of the Environment, Conservation and Nuclear Safety, Uniform Federal Practice for Emission Monitoring, Federal Ministry for the Environment circular dated June 8, **1998**-IGI3-51 134/3 (Report of the Government of the Federal Republic of Germany to the Commission of the European Community dated December 15, **1997**-Notification 97/26/D)
8. Ernst Becker, Jürgen Reinmann, Werner Rentschler, Johannes Mayer, Continuous Monitoring of the Dioxin/-Furan Emission of all Waste Incinerators in Belgium, Organhalogen Compounds, **2000**, Vol. 49S
9. Benoît de Montard, Gernot G. Pranghofer, Keith J. Fritsky, Destruction des Dioxines et Furannes: expériences récentes avec un système de filtration catalytique, présenté au Salon International POLLUTEC, décembre **2001**

10. Klaus W. Mehl, Arthur Huang, Jürgen Reinmann, Short-term and long-term dioxin sampling and analysis at a MSW incinerator in Taiwan, Organhalogen Compounds, **2003**, Vol. 60
11. W. Funcke, H. Linnemann, G. Bröker, K.-J- Geueke, Probenahme von polychlorierten Dibenzofuranen (PCDF) und polychlorierten Dibenzodioxinen (PCDD) in Abgasen mit einem Adsorptionsverfahren, Landesamt für Immissionsschutz Nordrhein-Westfalen, LIS-Berichte, Nr. 109, **1993**