MEASUREMENT OF MERCURY IN FLUEGAS

H.-R. Paur[1], J. Korell[1], Ch. Schrader[1],W.M. Winkler[3]

[1] Forschungszentrum Karlsruhe GmbH; Institut für Technische Chemie – Bereich Thermische Abfallbehandlung – Karlsruhe, Postfach 3640, 76021 Karlsruhe (Germany), paur@itc-tab.fzk.de.
[2] Seefelder Messtechnik GmbH & Co. Vertriebs KG, Mühlbachstrasse 20 , D-82229 Seefeld (Germany), .seefelder@t-online.de

Abstract
To determine the sum of all mercury species in flue gas by *continuous emission monitors* (CEM) different methods have been developed. Widely used is the condensation of flue gas and subsequent reduction of Mercury containing compounds into elemental Mercury, followed by measurement of gaseous Mercury at 254 nm. The reduction is performed in a wet chemistry system, by solutions of Stannous chloride or ascorbic acid and waste water is produced. Moreover higher sulphur dioxide concentrations in flue gas may increase the absorption at 254 nm and cause incorrect high Mercury readings.
To overcome the problems caused by cross sensitivity towards sulphur dioxide and by wet chemistry we have developed the novel Hg-CEM analyser. In this instrument Mercury compounds are decomposed by a catalyst at elevated temperature. The resulting gas containing elemental Mercury flows over an amalgamation trap, from which Mercury is desorbed by nitrogen in regular intervals. The concentration of Mercury in the gas is measured at 254 nm again.
The HgCEM instrument was extensively tested by German authorities and TUV-approval according to German and European regulations has been completed. In this paper we report our test measurements with the HgCEM at a waste incinerator. Long term operation experience with the instrument is reported.

Introduction

Despite efforts to avoid the use of Mercury in consumer products in Europe, low concentrations of the element and its compounds are emitted in the flue gas of many industrial high temperature processes. The main sources in Europe (1995) are coal combustion in power plants (89.2 t/a), residential heating (89.3 t/a), oil combustion (7 t/a), waste incineration (9.7 t/a), cement production (26.3 t/a), Lead and Zinc production (15.4 t/a), Caustic Soda production (41,3 to/a) and Pig-Iron production (10.21 t/a)[1].

Depending on flue gas compositions various distributions of elemental Mercury (Hg^0) and Mercuric Chloride ($HgCl_2$) have been reported by Hall and co-workers[2]. First generation Mercury CEM's used wet chemical reactions to convert Mercuric Chloride to elemental Mercury and subsequent measurement at 245 nm. Commonly used reagents to accomplish the reduction were Stannous Chloride, Sodium Tetrahydroborate and Ascorbic Acid. Due to the presence of reactors and tubings associated with wet chemistry the first generation Mercury CEMS suffered problems related to tubing pluggage, corrosion and inefficient conversion of mercuric chloride to mercury.

The continuous monitoring of Mercury emissions at German waste incinerators is required by the 17th BImSchV (Federal Imission Control Ordinance) of 1999[3]. Continuous monitoring is under discussion for combustion processes, which substitute fuel by using mercury containing wastes, such as the co-incineration of sewage sludge in coal-fired power plants or in cement kilns. Here we report on the development and testing of a novel Continuous Emission Monitor for Mercury (Hg-CEM) in flue gas of a waste incinerator.

Experimental

The HgCEM consists of the following components: Sampling system (probe and heated line), catalytic reactor, gold trap amalgamation unit and a UV Photometer. Fig. 1 shows the block scheme of the HgCEM System.

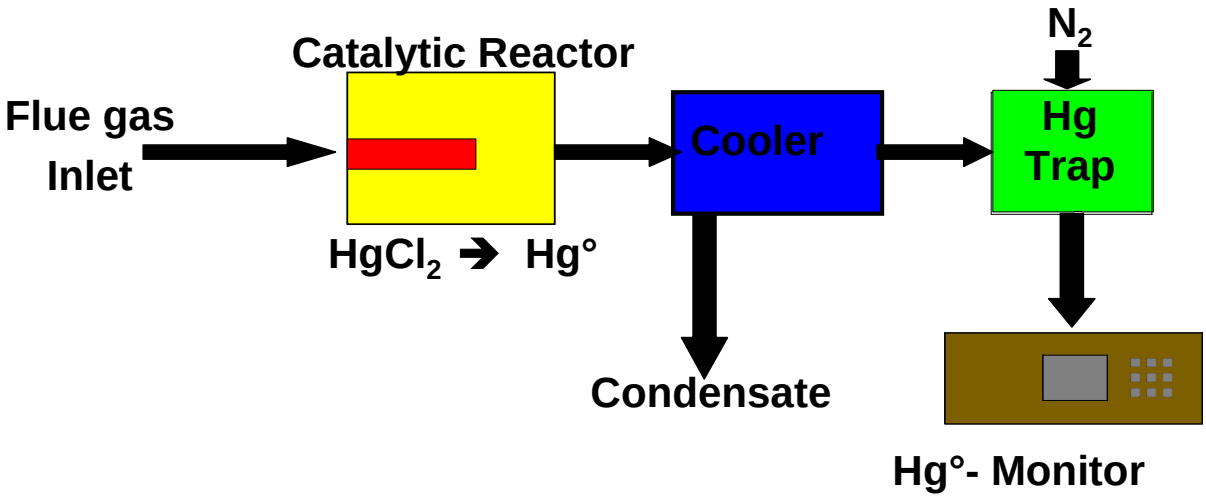

Figure 1: Block Scheme of the Continuous Emission Monitor for Mercury (Hg-CEM)

The sample probe extracts 2 to 3 litres per minute and transports it through a heated sampling line at 200 ºC. In order to prevent loss of mercury in the sampling line it is recommended that the line shall not exceed 150 feet. The thermocatalytic converter reduces mercury compounds to elemental mercury vapour. After the converter, Mercury exists only in the elemental form and hence memory effects due to adsorption in the sample lines are

Figure 2 : Continuous emission monitor HgCEM

reduced. The amalgamation unit consists of an integrated valve assembly, a gold trap and a calibration source for elemental mercury vapour. The valve assembly can be switched to a “continuous mode operation” in case of high mercury concentrations. By modifying the collection time associated with the Gold amalgamation unit it is possible to lower the detection threshold of the system. The UV photometer used for measuring the gas-phase concentration of elemental mercury consists of a fixed wavelength atomic absorption spectrometer at 253.7 nm wavelength. The photometer has a reference beam for lamp control and an electrodeless low-pressure lamp with long service life (>20000 hours). The entire system is functionally controlled by a microprocessor. All input is made through a water-resistant front panel keyboard with user-programmable keys (“soft keys”). A large TFT colour screen displays all system variables and measured values. The system components are used in a “swing design” compartment and can be very easily accessed. The most important components are housed in two 19” rack-mounted units each 3 units high.

Results and Discussion

The HgCEM unit was extensively tested in the laboratory and the specifications listed in Tab. 1 were verified during the TÜV-certification :

Table 1: Main Specifications of HgCEM.

- Measuring Ranges: 0 to 45 µg/m^3 and 0 to 75 µg /m^3
- Deviation from linearity: 2% of measuring range
- Detection Limit: 1 +/- 0,5 µg/m^3
- Availability better than 96%
- Service interval: 4 weeks
- Interference: No interference from SO_2, NO, NO_2, VOC and other compounds
- Zero Point: Automatic control and correction of zero point.
- Calibration: Automatic and manual calibration using permeation device

During the test at a German municipal solid waste incinerator two HgCEM units were operated in parallel over a period of 4 months. Figure 3 shows good agreement between

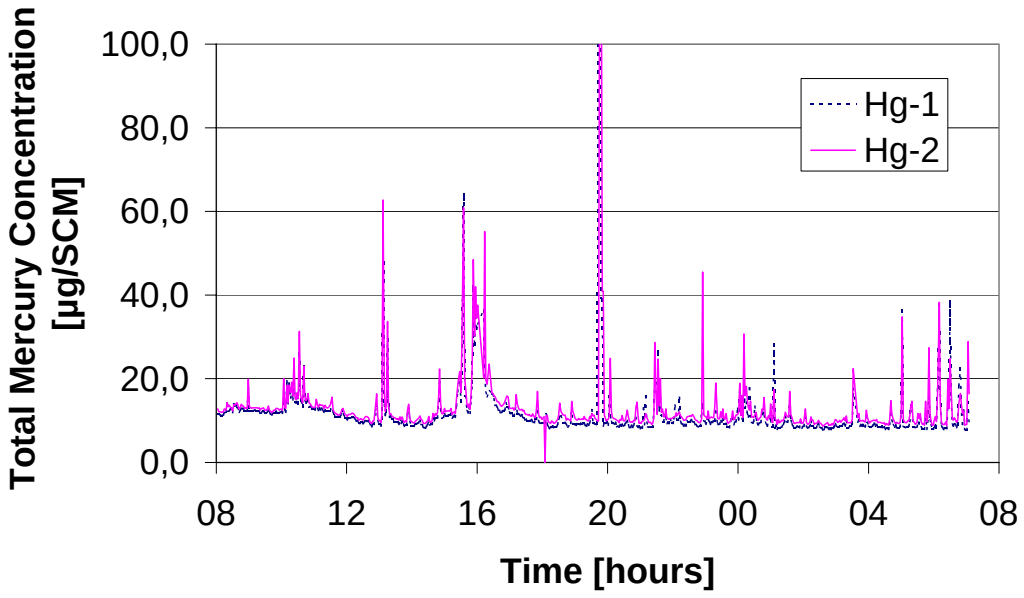

Figure 3: Total Mercury Concentrations measured over a 24 h period during continuous operation of two parallel HgCEM-units at a municipal

both units over a sampling period of 24 h. The measured data from two Hg-CEM show a relevant correlation with the manual samples obtained by VDI 3868 [4]

Conclusions

A continuous emission monitor for mercury in flue gas was tested in the laboratory and at a municipal solid waste incinerator. All requirements for certification of the HgCEM according to 17.BImSchV were satisfied.

References

1. European Commission-DG Environment – Working Group on Mercury (2001) http://europa.eu.int/comm/environment/air/background.htm#mercury

2. Hall, B., Schager, P. Lindquist, O., Water, Air Soil Pollution **56:** 3-14 (1991).

3. 17.BImSchV (1999) : Federal Immission Control Ordinance for Waste Incinerators

4. VDI 3868 „Messen der Gesamtemission von Metallen, Halbmetallen und ihren Verbindungen“ (1994)