

ON-LINE MEASUREMENTS OF FLUE GAS CONCENTRATIONS OF CADMIUM AND LEAD IN A CO-COMBUSTION IN A FLUIDIZED BED BOILER

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ABSTRACT

The operation of a new on-line toxic metal analyser was demonstrated in connection to a pilot-scale bubbling fluidised bed boiler during co-combustion tests of biomass and waste fuels. The analyser comprises a novel continuous sampling device combined with DC-plasma excited atomic absorption spectroscopy and Zeeman background correction. A continuous sample gas flow is extracted from a process duct through an electrically heated sample line into the analyser. In a mixing nozzle the sample gas is mixed with a nitrogen plasma jet, which is produced with a DC-plasma torch. Due to the mixing, the temperature of the sample gas raised up to 2300 K. At this temperature a substantial part of the vaporous heavy metal compounds and small aerosol particles are decomposed. The concentration of the free metal atoms is measured by atomic absorption spectroscopy and the flue gas concentration of the metal is calculated. The analyser is capable to measure toxic metal emissions on continuous basis in a wet and particulate laden flue gases at temperatures up to 1100°C. The detection limits of the prototype used in this work were 0.04 mg/Nm³ for Cd and 0.4 mg/Nm³ for Pb and the maximum measurement rate 1 s⁻¹. In the field demonstration, Cd and Pb concentrations were measured directly from the combustion chamber. The measured Cd and Pb concentrations depended strongly on fuel composition.

1. INTRODUCTION

Combustion of waste-based fuels has gained new popularity in industrial countries during last years. In past decades waste was mostly disposed into landfills and only a small portion of it, particularly hazardous waste, was burnt in incinerators. However, the shortage of available space has restricted the use of the landfills particularly in highly populated industrialised regions. But a far more significant reason for reducing of landfilling is serious environmental problems related to those sites. They have effects on the local environment such as poisoning of the soil and water reservoirs, but also global ones such as methane emission, which is one of the Green house gases (GHG).

In present days there is a strong international pressure to reduce the GHG emissions. Substituting fossil fuels in energy production partly by biomass-based waste fuels, such as municipal, agricultural and some industrial wastes, strongly reduces the net discharge of carbon dioxide and methane into the atmosphere. An efficient method to utilise the thermal energy content of these wastes is co-combustion in fluidised bed boilers. In modern facilities with combined heat and power production the energy conversion efficiency may exceed 90 %. In co-combustion waste-based fuels are burnt together with conventional ones such as biomass or fossil fuels. In fluidised bed combustors even heterogeneous waste fuels with a low heating value can be burnt. A main fuel (biomass or fossil fuels), which has a relatively high and constant heating value, is used to produce the base thermal load. A waste-based fuel with a varying heating value is used to produce additional energy. The varying thermal load does not induce problems, because the high heat capacity of the bed material smoothes thermal variations. Thus the operation of FB boilers can be optimised even for combustion of difficult waste fuels so that the energy production is maximised, but the emissions are minimised.

In the late 2000 the E.U. legislation for waste incineration changed notably [1]. Until then combustion of non-hazardous waste was allowed under the same regulations than conventional combustion. In the new waste incineration directive all types of waste incineration and co-combustion are controlled principally with the same regulations. This directive sets string emission limits for several gaseous species, particulates and 12

toxic metals (Hg, Cd, Tl, As, Cr, Co, Cu, Mn, Ni, Pb, Sb and V). It also requires frequent emission measurements and a close control of operation conditions.

Conventionally, toxic metal emissions are measured by wet chemical sampling and subsequent laboratory analysis. However, this is a laborious and time-consuming technique, which has also several uncertainties. There was a discussion to require continuous emission monitoring (CEM) for mercury in the new waste incineration directive. However, it was still abandoned because of a lack of suitable measurement methods. On contrary, in the U.S. CEMS for several metals (Hg, Cd, Pb, As, Be, Cr) will be required in the near future for hazardous waste incineration [2]. This evident need of CEMS for metals has stimulated development work of such measurement techniques. Main techniques studied for that purpose are microwave induced plasma [3,4], inductively coupled plasma [5-8], laser induced plasma [9-10], spark induced plasma [11], laser induced fluorescence [12-14], cavity ringdown spectroscopy [5] and X-ray fluorescence [15].

In this paper we present a versatile on-line toxic metal emission analyser, which is developed particularly for combustion research, but which can be utilised also for continuous emission monitoring. The constructed analyzer prototype was tested in connection to a 2 MW bubbling fluidised bed boiler. In the tests mixtures of plastic waste and wood chips were burnt. Cadmium and lead concentrations were measured directly from the combustion chamber to demonstrate the capability of the analyser.

2. MEASUREMENT METHOD

Vapour-phase and aerosol Cd and Pb emissions were measured by a new on-line analyser, named HEAMON [16]. The operation principle is illustrated in Fig. 1. A sample gas is continuously drawn through a heated sample line. The extracted gas flow is mixed with a hot nitrogen gas jet in a mixing nozzle that is integrally joined to the end of the sample line. The gas jet is generated by a DC-plasma torch. Due to the mixing the temperature of the sample gas is raised up to around 2000°C. At this temperature a substantial part of the heavy metal compounds is thermally dissociated. The degree of dissociation is determined using thermal equilibrium calculations.

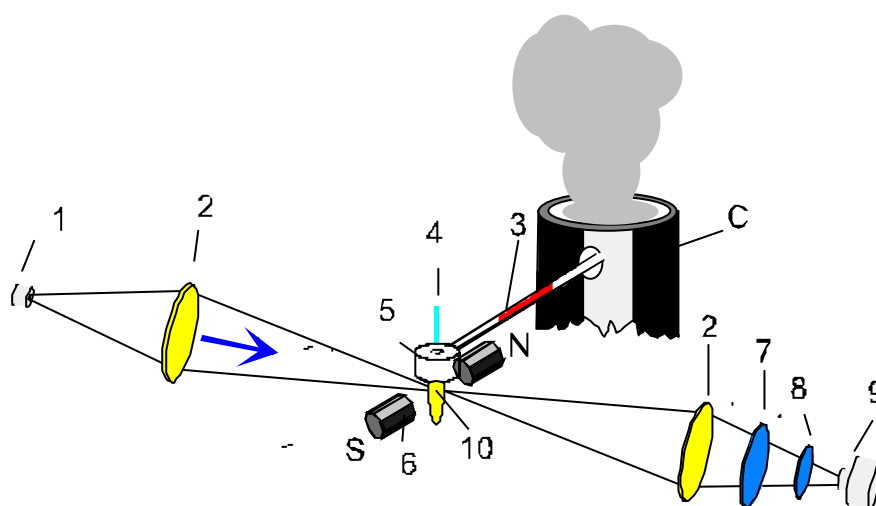


Figure 1. Schematic drawing of HEAMON: 1; light source, 2; lenses, 3; sample line, 4; plasma torch, 5; mixing nozzle, 6; magnet, 7; polariser, 8; line filter, 9; light detector and 10; plasma jet

The atom concentration of a specified metal in the gas jet is determined by atomic absorption spectroscopy aided by the elimination of background absorption using the Zeeman effect. The light source is a hollow-cathode spectral lamp containing the specified analyte metal. A separate lamp is needed for each analyte metal. Before traversing the gas jet, the light beam of the lamp passes through a polariser. The light is linearly polarised and rotating the polariser rotates the direction of polarisation. A magnetic field at right angles to the optical axis is applied across the gas jet. The magnetic field splits the degenerate energy levels of the metal atoms in the jet according to the Zeeman effect. Transitions to the different energy levels generated by the Zeeman effect are discriminated by the polarisation of incoming light. Light polarised in parallel to the magnetic field is absorbed both by analyte metal atoms and the background, whereas light polarised at right angles to the magnetic field is absorbed principally only by the background. The spectral absorbance of the metal atoms is determined from the difference between transmitted light intensities at these two polarisation states. By Beer-Lambert's law, the absorbance gives the analyte atom concentration in the gas jet. Finally, the metal concentration in the flue gas is calculated and expressed in desired units by taking into mixing, dissociation and correction coefficients.

The analyser performance was characterised in the laboratory. The detection limits of the prototype instrument used in this work were 0.04 mg/Nm³ and 0.4 mg/Nm³ for cadmium and lead, respectively. The maximum measurement rate is limited by the rotation speed of the polariser to 1 s⁻¹. The maximum temperature, to which the sample line can be heated, is 1100 °C, which is thus the highest allowed sample gas temperature to avoid condensation losses. A sample gas is not dried or filtered before analysis. Because of that, particles are also entered to the analyser. They will be detected to the extent they become vaporised and atomised in the mixing nozzle. The calculated upper size of the detectable particles is approx. 3 µm, which is also a typical upper size limit of particles passing through flue gas cleaning devices. Thus the analyser is capable to measure atmospheric toxic metal emissions without a need of any pretreatment of a sample gas prior to analysis. This simplifies the analysis and reduces significantly sample losses.

The measurement set-up comprised an analyser, a PC-computer, a suction pump and power supplies for the plasma torch, sample line heating and electronics. The analyser's measures are 60 cm x 40 cm x 30 cm (width, height and depth) and it weighs 40 kg. The analyser was connected to the combustion chamber using a standard flange (DN50), through which the sample line was protruded into the chamber.

3. EXPERIMENTS

The measurements were performed in a 2 MW pilot-scale bubbling fluidized bed reactor. A pilot plant consisted of a combustion chamber, a heat exchanger, which was connected to a local district heating network, an electrostatic precipitator and a bag house filter. The cross-section of the combustion chamber was 1.1 meters squared and the height 10 meters. The mean gas velocity was 2 m/s. Fluidising air was fed from the bottom of the reactor (41 % of the total air), secondary air through the burner (24 %) and tertiary air 1 meters above the bed surface (35 %). The HEAMON was mounted onto the combustion chamber's wall and the sample line was protruded into the chamber approximately 7 meters above the bed surface. The sample line temperature was adjusted to 750 °C, which was little above the maximum gas temperature in the sampling location. Test runs were made with four mixtures of low and high metal content fuels. The main fuel was wood chips (mixture of spruce bark and heartwood) and an additional fuel was plastic waste from a de-inking plant. The Cd and Pb concentrations of the fuels are shown in Table 1.

Table 1. Cd and Pb concentrations in the fuel ashes

Fuel	Cadmium (mg/kg)	Lead (mg/kg)
Wood Chips	5.14	65
Plastic Waste	43.8	815

The tests were made during one day burning one fuel mixture about two hours. Between the test points there was another two hours period to completely change the content of the fuel feeding system. For a reference purpose, toxic metal concentrations were also measured conventionally. However, the sampling directly from the combustion chamber would have been far too difficult and therefore the measurements were made from the flue gas duct at the temperature of 130°C. The operation conditions in the test points are shown in Table 2.

Table 2. Operation conditions and main flue gas constituents in the tests

Test No.	Fuel Mixture ¹	Heat Output (MW)	O ₂ (vol-% in dry gas)	H ₂ O (vol-%)	CO ₂ (vol-% in dry gas)
1	100/0	1.16	10	22.76	9.3
2	90/10	1.05	11	21.57	9.2
3	80/20	1.28	9.45	21.13	9.6
4	70/30	1.43	8.45	24.00	10.4

¹ wood chips/plastic waste in per cents calculated on energy basis

4. RESULTS AND DISCUSSION

Typical results of Cd and Pb concentration measurements are shown in Figs. 2 and 3, respectively. Measurement periods are indicated by arrows. Before and after a measurement period we measured a concentration corresponding zero absorbance. The detection limits are marked in figures by dashed lines. The concentrations and the detection limits are calculated in a dry gas and corrected to 6 vol-% oxygen. The average Cd and Pb concentrations measured by the HEAMON are summarised in a bar chart in Fig. 4.

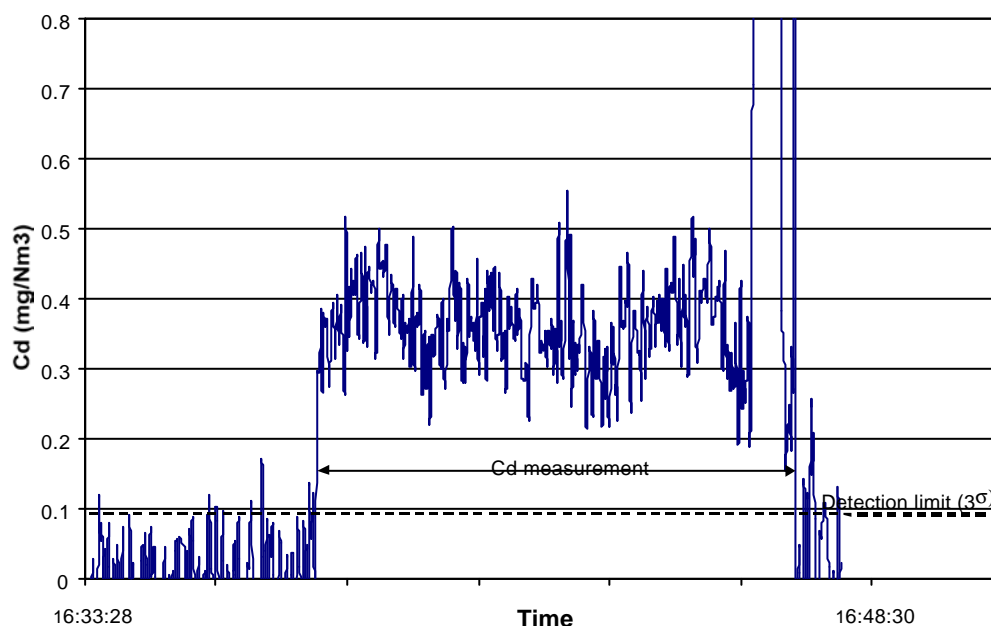


Figure 2. Cadmium concentration (in a dry gas and 6 vol-% oxygen) in the combustion of 80 % wood chips and 20 % plastic waste

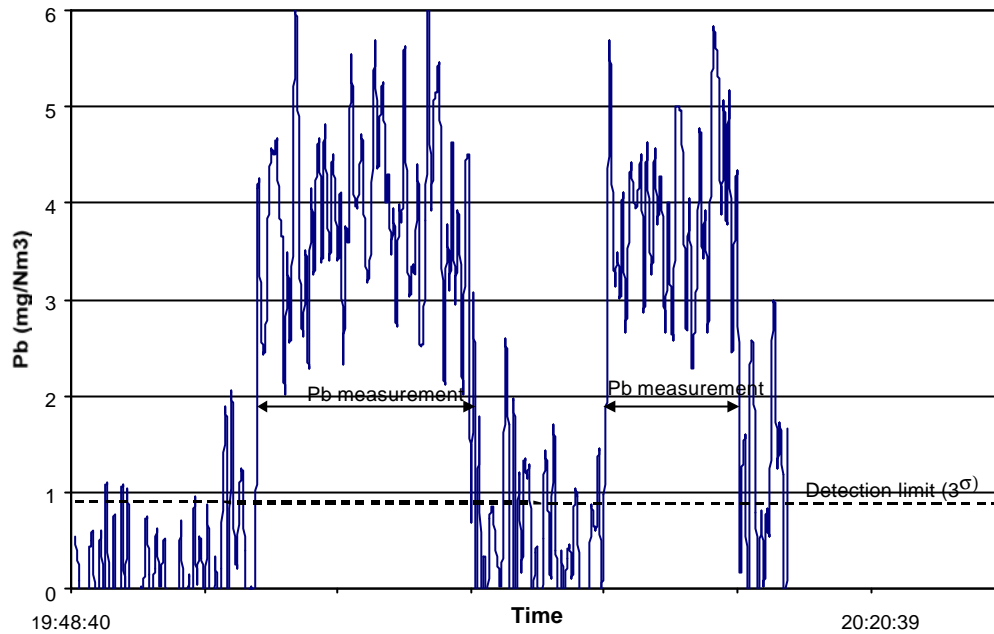


Figure 3. Lead concentration (in a dry gas with 6 vol-% oxygen) in the combustion of 70 % wood chips and 30 % plastic waste

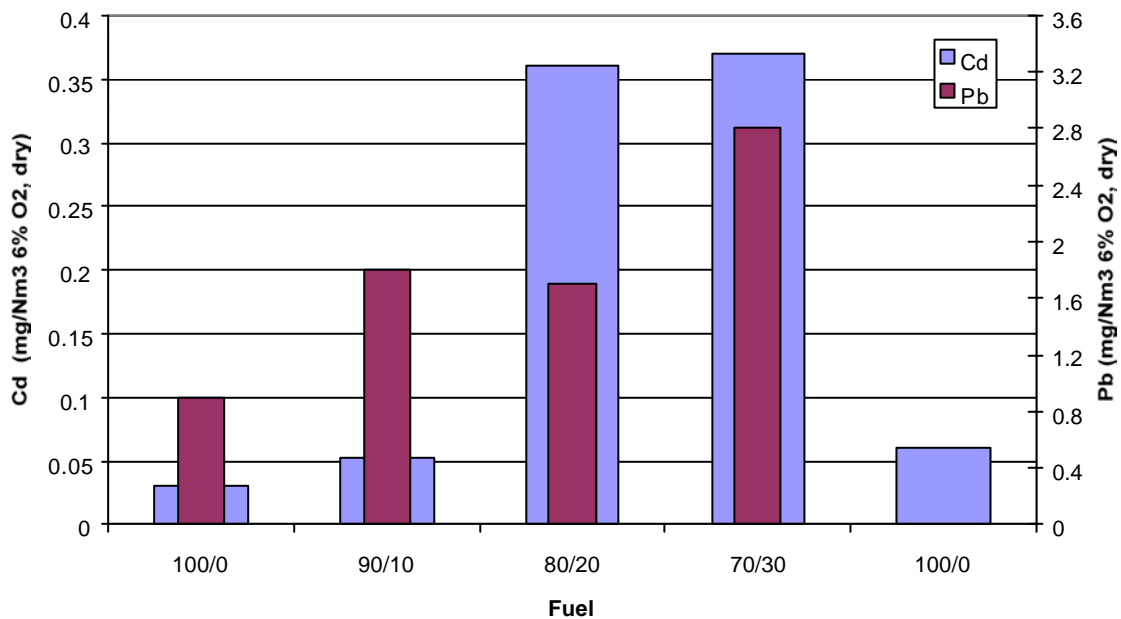


Figure 4. Average Cd and Pb concentration in a 2 MW BFB-boiler in co-combustion tests. The first number in x-values is the percentage of wood chips and the second one the percentage of plastic waste on energy basis.

The Pb concentration was above the detection limit in all the tests. Its concentration was increased with the increased share of plastic waste. This was a supposed behavior, because the plastic waste contained more metals than the wood chips. The plastic waste contained also a lot of chlorine (3 wt-%), which reacted with metals to form highly volatile metal chlorides.

The Cd concentration was below the detection limit in Tests 1-2. In Tests 3-4 the concentration exceeded significantly the detection limit being almost the same in both tests. After Test 4, the fuel feeder was once more filled with pure wood chips and after couple of hours the Cd concentrations was returned back to its low value as nicely shown in Fig. 5.

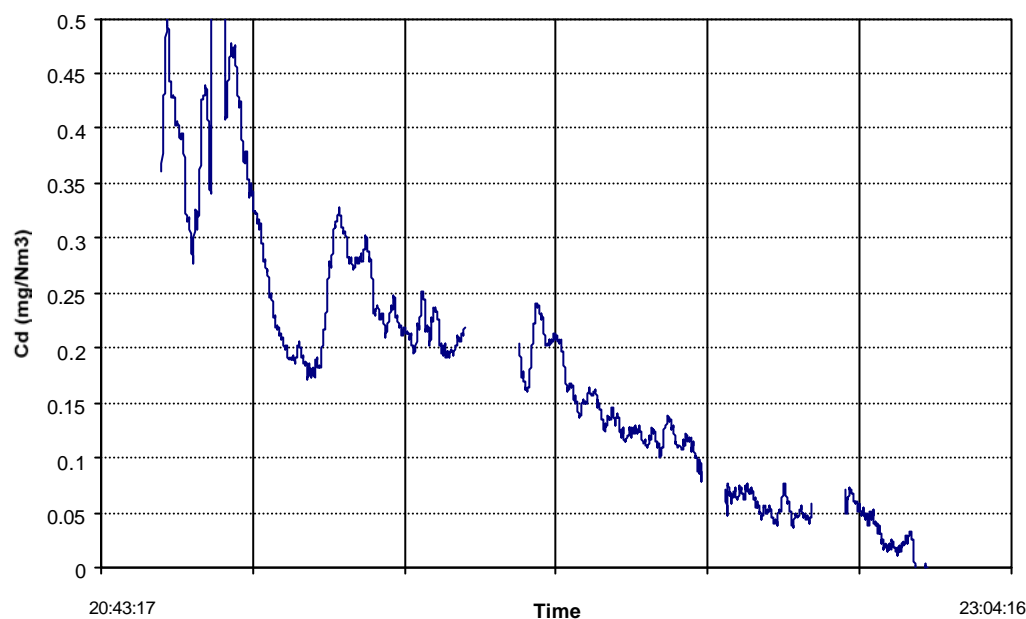


Figure 5. Decreasing trend of the Cd concentration when the plastic waste was replaced by wood chips

The Cd and Pb concentrations measured by a conventional method in the flue gas duct were much lower than what we detected in the combustion chamber. The Cd and Pb concentrations varied from 0.019 to 0.045 mg/Nm³ and from 0.241 to 0.671 mg/Nm³, respectively.

5. CONCLUSIONS

The operation of a new on-line toxic metal analyser was successfully demonstrated in co-combustion tests in a bubbling fluidised bed boiler. The analyser worked without noteworthy troubles at these extremely severe measurement conditions. Cd and Pb concentrations in the flue gas were observed to increase with the increasing share of the plastic waste in the feedstock. In several tests Cd and Pb concentrations were clearly below the detection limits, and even the highest observed concentrations were only three or four times the detection limits.

After the presented tests the analyser was modified in order to improve its performance. A new measurement algorithm based on digital signal processing was developed. A new magnet generating higher magnetic field induction, and thus more efficient background correction, was also constructed. Further, a low-noise photodetector and a signal amplifier were purchased. After these improvements, the detection limits as low as 0.01 and 0.05 mg/Nm³ were obtained for Cd and Pb at the laboratory conditions.

Further development of the analyser is in progress. The performance of the modified analyser will be demonstrated in field tests. The accuracy and repeatability of the measurement method will be systematically studied. Besides Cd and Pb, the ability of the analyser to measure other metals regulated by the new waste incineration directive, such as copper and manganese will be investigated. Finally, there is a lot to do to improve the hardware and software of the analyser so that it can be easily operated.

ACKNOWLEDGMENTS

This work was financially supported by the European Commission within the projects JOF3-CT95-0010 and JOR3-CT97-0191 and National technology agency (TEKES).

REFERENCES

1. Directive 2000/76/EU, Official journal of the European Communities L332, 28.12.2000
2. HWC MACT standard, Federal register, **64**, No. 189, 30.9.1999
3. P.P. Woskov., D.Y. Rhee, P. Thomas and R. Cohn, Rev. Sci. Instrum., **67**, No. 10, 3700, 1996
4. P.P. Woskov, K. Hadidi, P. Thomas, K. Green, G. Flores and D. Lamar, "Field test of a real-time calibrated microwave plasma continuous emissions monitor for stack exhaust metals", Report PSFC/RR-98-1, 1998
5. J. Plodinec, "Application of modern diagnostic methods to environmental improvement", Final report DIAL10575, 1998
6. C. Trassy, Proceedings of Continuous Emission Monitoring conference, p. 119, 1997
7. M. D. Seltzer and G. A. Meyer, Environ. Sci. Technol. **31**, No. 9, 2665, 1997
8. M. D. Seltzer, "Continuous monitoring of hazardous smokestack metal emissions using inductively coupled argon plasma atomic emission spectrometry", Proceedings of CEM99 International conference on emissions monitoring, Warwick, UK, 1999
9. M. Corsi, V. Palleschi, A. Salvetti and E. Tognoni, Proceedings of 5th international conference on combustion technologies for a clean environment, Lisbon, Portugal, 65, 1999
10. A. Ciucci, M. Corsi, V. Palleschi, S. Rastelli, A. Salvetti and E. Tognoni, Appl. Spectrosc., **53**, No. 8, 960, 1999
11. A.J.R. Hunter, S.J. Davis, L.G. Piper, K.W. Holtzclaw and M.E. Fraser, Appl. Spectrosc., **54**, No. 4, 575, 2000
12. U. Gottwald and P. Monkhouse, Appl. Phys. B, **69**, 151, 1999
13. X. Tong, R. B. Barat and A. T. Poulos, Rev. Sci. Instrum., **70**, No. 11, 4180, 1999
14. X. Tong, R. B. Barat and A. T. Poulos, Environ. Sci. Technol., **33**, No. 18, 3260, 1999
15. J. Cooper, B.E. Johnsen, J. Haye, S. Johnson, S. Bryson and W. Watson, "X-ray based multi-metals CEM for incinerators", Proceedings of international conference on incineration and thermal treatment technologies, Portland OR, U.S.A., 2000
16. Oikari R., Häyriäinen V., Parviainen T. and Hernberg R., A Method for Continuous Toxic Metal Emissions Measurement: Plasma Excited Atomic Absorption Spectroscopy, Submitted to Applied Spectroscopy, 2000

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