



## Introduction

Combustion sources are responsible for the majority of most atmospheric pollutant emissions, including particulates and metals. Industrial point sources, domestic combustion, and transport are all significant (Dore et al, 2005). The combustion of many fuels (for example coal, biomass, and waste) can lead to the release of potentially toxic metals, either by volatilisation of metal vapour, or entrainment of small metal-containing particles (Linak and Wendt, 1993). Concerns over the health effects of the emissions of particulate matter from combustion in general, and metals in particular, is continuing to increase, and one of the remaining challenges is to accurately identify and quantify the sources of this contamination.

The development of real-time monitoring of element and heavy metals species in gaseous samples is seen as a major challenge in both the understanding of industrial processes and in the measurement of emissions for legislative purposes. Without continuous and cost-effective sampling and analysis programmes, knowledge of the elemental emissions from industrial combustion processes will not be quantified and hence, it will not be possible to develop informed control strategies designed to minimise their emissions (Clarkson et al, 2003).

Experimental Continuous Emissions Monitoring (CEM) techniques, using a variety of analytical technologies, began appearing in the literature in the mid-1990's. Previously, there had been very little by way of multi-element continuous monitoring which may have been applicable to gaseous emissions (Poole et al, 2005). Conventional monitoring methodologies for metals involve the taking of discrete samples with subsequent laboratory based analysis, which means that the process is not monitored continuously, and that changes in concentration cannot be linked to their cause, in terms of fuel or process changes.

The work presented here focuses on the measurement of several metals in the gaseous emission from an municipal solid waste incinerator. These data were obtained from a state-of-the-art mobile laboratory-based continuous emission monitoring system using ICP-OES detection. This unique system, built in collaboration with Spectro A.I., is a self-contained laboratory that is designed to be used at industrial locations to measure metals in flue gases.

## Analytical Facility

### Description of the Laboratory

The Continuous Emission Monitoring Laboratory (CEML), designed and built in collaboration with Spectro AI, is a state-of-the-art self-contained mobile laboratory (figure 1). The laboratory comprises of a heated gas sampling system, which will extend 40m from the laboratory into an industrial plant, a gas-sampling interface, and a computer-controlled inductively coupled plasma – optical emission spectrometer (ICP-OES) detection system, with gas-phase calibration system. On site, the instrument is self contained, requiring only electricity, water, and sample supply, and periodic liquid argon refills (Cryoservice, Worcester, UK).

### Samples and Sample Collection

Using a 40m-heated sampling line (PTFE lined, i.d. = 12 mm) gas was isokinetically sampled from the flue stack at gas flow rates of 25-60 L min<sup>-1</sup> (figure 2). The sample line was operated at a temperature of 200°C. A low flow rate (0.125 - 0.24 L min<sup>-1</sup>) sub-sample was taken, using a double head, out of phase, peristaltic pump via a secondary sampling stage. This sample was mixed with carrier argon, and introduced to the analytical system, via an ultrasonic nebuliser, which allowed system calibration, and also standardisation of the water content of the gas.

### Instrumentation

All determinations were carried out using a Spectro Ciros ICP-OES (figure 1) with radial view configuration (Spectro AI, Kleve, Germany). The ICP torch was a custom built demountable torch with an injector i.d. of 1.8 mm, to allow the higher flow of coolant gas and higher power, needed to sustain the plasma during gas analysis.

### Calibration

The instrument was calibrated using a Spectro 2000 ultrasonic nebuliser (Spectro AI, Kleve, Germany) to introduce a semi-dry aerosol of metal salts. Calibrations were matrix-matched using carbon dioxide, oxygen, and nitrogen gases, supplied from on-board cylinders (BOC gases, Guildford, UK). Due to the constantly varying combustion gas composition, measurements were correlated to calibration conditions using linear regression analysis.



## Test Site Experimentation

The CEML was used to measure the metallic components of flue gas from a UK waste-to-energy plant (figure 2), with one reading every minute. The plant had 2 lines, each with an average hourly throughput of 10 tonnes. The grate type was reverse reciprocating, and the furnace walls were water cooled, providing heat to the energy recovery system. The temperature in the radiation shaft was kept between 850°C and 1100°C, with waste being added in response to falling temperature. The plant was operated with excess air, leading to an oxygen level in the combustion chamber radiation shaft varying between 6% and 14%.

Flue gas was treated in a hydrated lime and activated carbon dry scrubbing system. Fabric filters, designed to remove particulate matter down to a minimum of 5µm, collected the fly ash and scrubber products. An economiser, fitted before the scrubber system, reduced the flue gas temperature to 130°C at the bag filters. Standard 4" BSP sampling ports fitted in sections of ducting immediately prior to, and following, the gas clean-up system, were used in this work. Incinerator operating conditions are tightly controlled by EC legislation, and so atmospheric emissions are required to be extremely low (European Community, 2000/76/EC). Mandatory testing conducted by the plant showed that the clean-up system was consistently effective, always meeting legislative limits, despite the fact that the waste which is treated is highly inhomogeneous, and some of it can contain significant concentrations of volatile metals.

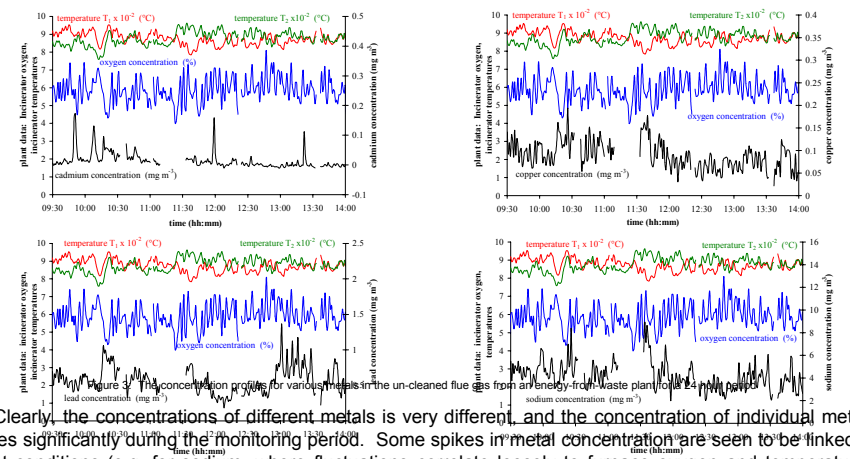
Thus the facility provided an ideal test-site for a continuous metals monitoring system. Firstly, measurements were made in contaminated gases, where maintaining instrument operation and obtaining data was extremely challenging, due to the level of dust (1-10 gm<sup>-3</sup>) and concentration of other pollutants. Secondly, measurements were made in the cleaned gas (at a different time), where accuracy at very low detection limits was required (~0.01 mgm<sup>-3</sup>), despite a continuously changing gross sample composition (oxygen, carbon dioxide, and water).



## Results and Discussion

### Un-Cleaned Flue Gas Monitoring

The results of continuous emissions monitoring of the un-cleaned flue gas, using the CEML, are shown in Fig 3, for various metals for a 4.5 hour period. Occasional gaps in the monitored results arise from un-avoidable down-time, necessary to ensure continued accurate monitoring in the contaminated gas matrix.

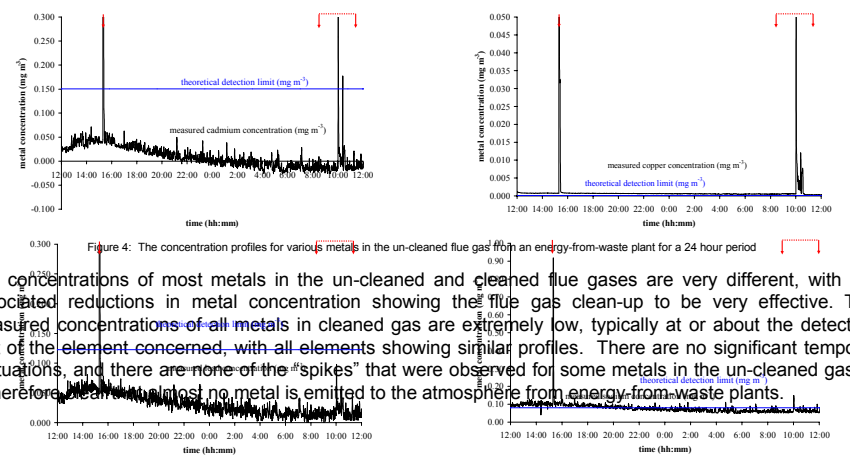


Clearly, the concentrations of different metals is very different, and the concentration of individual metals varies significantly during the monitoring period. Some spikes in metal concentration are seen to be linked to plant conditions (e.g. for sodium, where fluctuations correlate loosely to furnace oxygen and temperature). Other spikes in metal concentration (e.g. for cadmium) are apparently random, and are believed to correlate to changes in metal concentration in the waste feed, which is highly inhomogeneous.

The discrete peaks of high metal concentration for some toxic heavy metals (e.g. cadmium, mercury, and lead), clearly appear to correlate with specific sources of these metals in the waste feed. Therefore, better segregation of hazardous components of the municipal waste stream would help to significantly reduce the heavy metal impact of waste incineration.

### Emitted Flue Gas Monitoring

The results of monitoring the cleaned flue gases for a 24 hour period are shown in Fig 4 for various metals. Much longer continuous monitoring periods could be achieved in the cleaner gas matrix, without interruptions. The spikes indicated by the red arrows correspond to the addition of on-line calibration check standards, and do not represent actual metal emissions.



The concentrations of most metals in the un-cleaned and cleaned flue gases are very different, with the associated reductions in metal concentration showing the flue gas clean-up to be very effective. The measured concentrations of all metals in cleaned gas are extremely low, typically at or about the detection limit of the element concerned, with all elements showing similar profiles. There are no significant temporal fluctuations, and there are none of the "spikes" that were observed for some metals in the un-cleaned gas. It is therefore clear that almost no metal is emitted to the atmosphere from energy-from-waste plants.

## Conclusions

- A new mobile analytical system, based on ICP-OES analysis has been developed to enable the study of metal concentrations in a difficult and changeable flue gas matrix
- The CEML has been shown to work accurately, to a high degree of sensitivity, for numerous elements, despite the most challenging analytical conditions
- Measurements of un-cleaned flue gas have proven the existence of metal spikes, which can partly be related to changing waste input. Therefore, changing waste disposal practice for certain key items could significantly reduce the metal load in energy-from-waste plants
- Measurements of gases from a waste-to-energy plant have demonstrated the efficacy of the flue gas clean-up system in removing metal pollutant spikes. The emitted gas is essentially uncontaminated by metals, despite high concentrations in the un-cleaned gas
- More extensive measurements, of this and other industrial combustion processes, could lead to new information on metal volatilisation, which may lead to emission reduction strategies

## References

- Clarkson, P. J., Poole, D. J., Ruy, C. K., Sharifi, V. N., Swithenbank, J., Waarlo, H.-J., Ardel, D., Falk, H. Continuous Measurement of Metals in Flue Gas using ICP-OES, *Anal. Bioanal. Chem.*, 1993, **377**, 39-47.
- Dore, C. J., et al. UK Emissions of Air Pollutants 1970-2002, October 2004, UK National Atmospheric Emissions Inventory Report, The National Environmental Technology Centre.
- European Community Legislation, 2000/76/EC, on the incineration of waste, The European Community, 2000.
- Linak, W. P., Wendt, J. O. L., Toxic Metal Emissions from Incineration: Mechanisms and Control, *Prog. Energy Combust. Sci.*, 1993, **19**, 145-185
- Poole, D. J., Sharifi, V. N., Swithenbank, J., Ardel, D. Identification of Metal Concentration Fluctuations in Waste-to-Energy Plant Flue Gases – a Novel Application for ICP-OES, *J. Anal. At. Spectrom.*, 2005, **20**, 932-938.

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