Mercury in Crematoria Using Atomic Fluorescence Spectrometry

Anthropogenic emission of mercury into the environment continues to cause concern. Increasing control of atmospheric mercury emissions is resulting in the gradual overall fall in mercury emissions. UK annual mercury emissions are estimated to have fallen from 40.7 t to 6.9 t between 1982 and 2002.[1] In contrast to the overall fall, mercury emissions from crematoria have increased significantly. One estimate shows annual mercury emissions from UK crematoria more than doubling from 0.36 t to 0.82 t between 1982 and 2002 with little change in the number of cremations performed.[2] The increase in emissions is readily attributable to the use of amalgam fillings and, due to better dental health, a large decrease in the number of people edentate at the time of death. Estimates of the mass of mercury present in an average cremation vary significantly, with estimates generally between 0.9 g and 3.0 g.[2]. The mass present depends on dental health practices, thus varying with time period and with country.

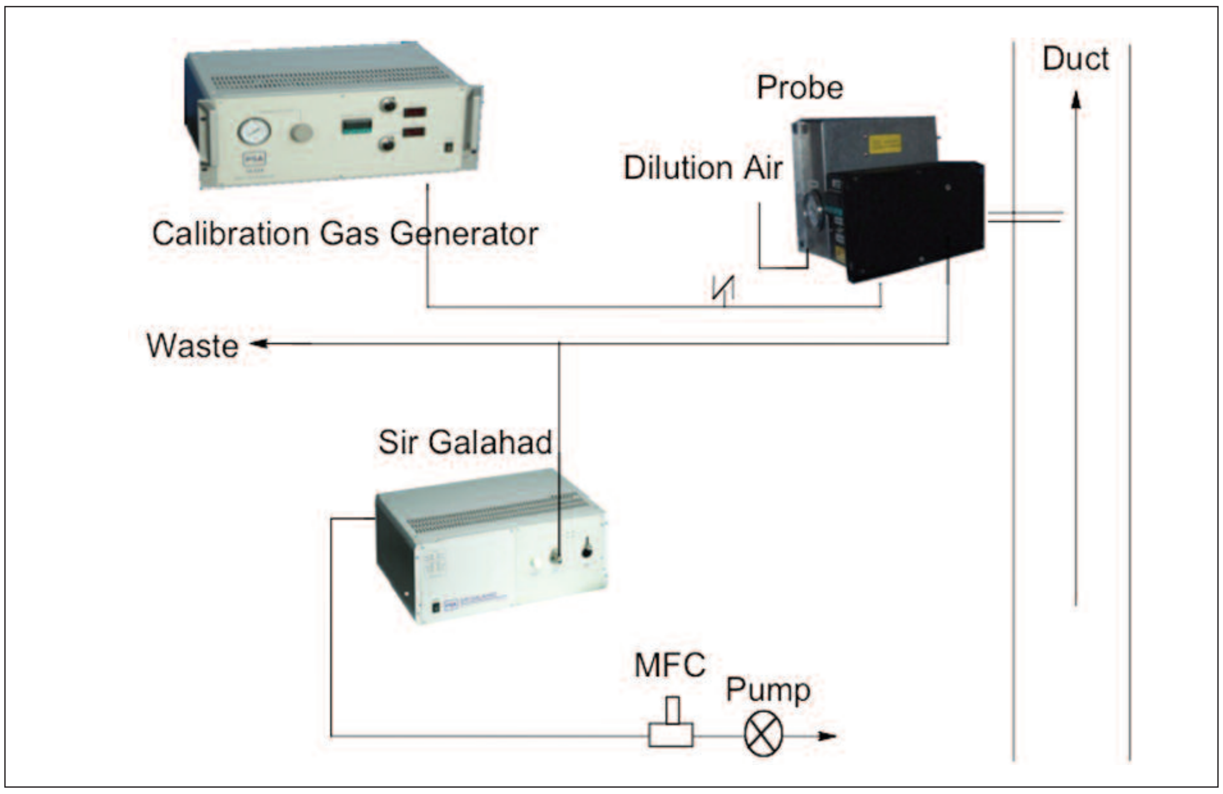

Figure 1: Schematic of apparatus

Mercury emissions during the cremation process are almost entirely due to the presence of amalgam fillings in the cadaver. This leads to very significant variation in the concentration of mercury emitted, in each cremation.

The P S Analytical Sir Galahad amalgamation-atomic fluorescence spectrometer is a proven technique for the determination of mercury in a wide range of gaseous media. This article summarizes the results of a study of mercury emissions on a single crematory stack at a UK crematorium and introduces a Hg CEM, specifically designed to continuously monitor mercury concentrations in cremation gases for regulatory purposes or online process control of mercury abatement equipment.

Instrumentation & Experimental

The PSA 10.680 system was designed to continuously monitor mercury emissions in incineration flue gas streams. For crematorium systems this consists of a PSA S123P100 heated dilution probe with pre-filter and thermo-catalyst. Sample gas was drawn into probe by an eductor-based dilution assembly and diluted 40:1 in compressed air. The probe is heated and all sample-wetted components are constructed with selected materials to avoid mercury losses. The diluted sample was drawn through the Sir Galahad amalgamation-AFS analyser by a mass flow controller (MFC) and pump assembly. The instrumentation was calibrated using the PSA 10.536 Calibration gas generator, calibration gas being introduced at the probe upstream of the filter. The apparatus is shown schematically in Figure 1 and a typical response in Figure 2.

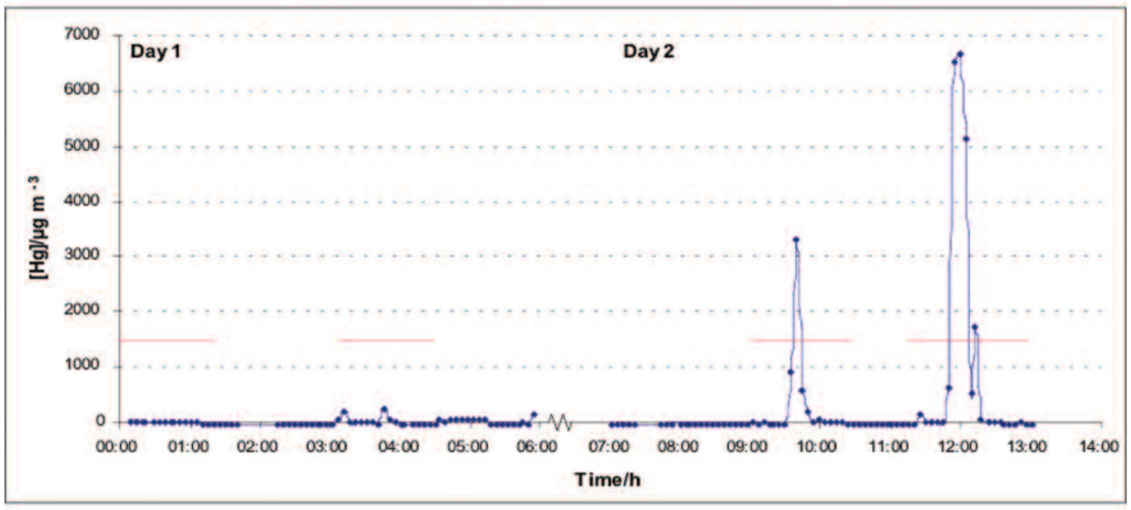

Figure 2: Typical mercury in crematory flue gas response. (Red lines indicate periods a cremation was in progress.)

To test for the presence of oxidised mercury in the flue gas, a side stream of the diluted sample gas was taken directly at the outlet to the probe and bubbled through an impinger containing 100 ml of 10 % potassium chloride solution connected as closely as possible to the sample probe. Flow control was by an MFC and pump downstream of the impinger. Sample was bubbled through the impinger for the duration of a cremation. This was repeated for the four cremations shown in Figure 2. The capture solutions were then treated with hydrochloric acid and potassium bromide-bromate and the mercury concentration determined by cold vapour AFS using the PSA 10.025 Millennium Merlin. Results are presented in Table 1.

Cremation No.	Mean Gas Phase Concentration		
	[Hg^{2+}] /μg m^{-3}	[Hg^{total}] /μg m^{-3}	Max. Oxidised mercury (%)
1	19.6	25.8	75
2	27.3	47.5	57
3	100.4	282.0	36
4	314.8	1094.5	29

Table 1: Speciation analysis for the four cremations

Discussion

The results shown in Figure 2 demonstrate the variability in mercury concentration that occurs in crematoria flue gases. Only minimal information is available about the deceased, making predictions of the mercury concentration for a particular cremation difficult.

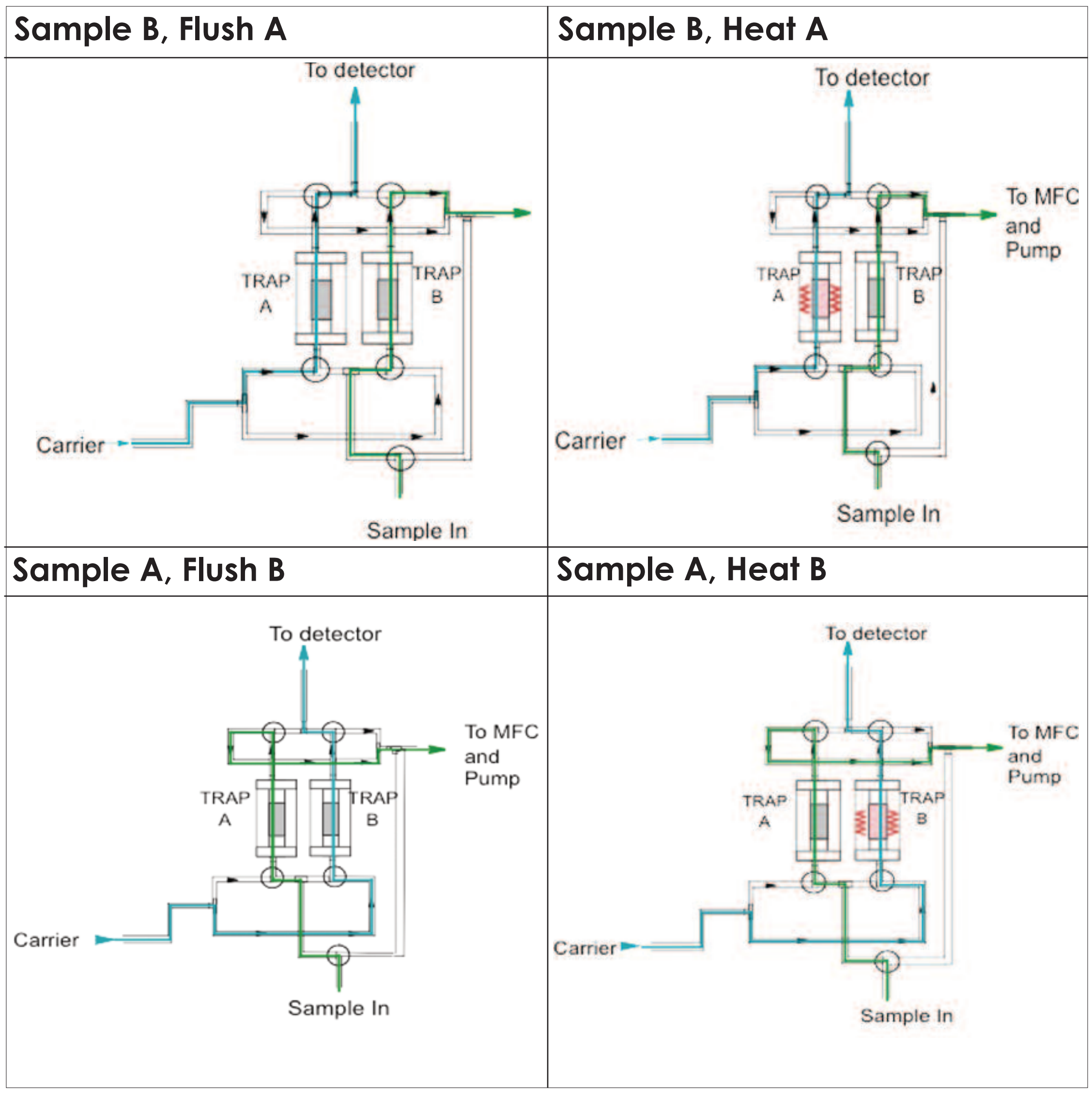

Figure 3: Schematic Diagram of the Sir Galahad

In the example presented here low levels of mercury observed for the first two cremations suggest that the deceased were edentate or had no amalgam fillings, whereas the 3rd and 4th cremations show high levels of mercury consistent with several amalgam fillings. Where mercury was present, it is emitted in a fairly short time period, approximately 40 min into the cremation cycle, this is consistent with the mercury remaining in the fillings until it evaporates during the combustion process. This tight time span of mercury removal is significant for any mercury abatement process employed, as the removal system must be able to handle spikes in concentration of several mg m^{-3}, with only background levels between spikes. Thus, process control of the abatement system with feedback from a mercury monitoring system could result in significant cost savings compared to running the abatement system continuously.

It is not possible in this case to estimate the mass of mercury emitted in each cremation as the volumetric flow in the flue had not been characterised. The data in Table 1 show that significant levels of oxidised mercury were present in the flue gas. The variation in oxidation may be due to differing levels of oxidising components, believed to be principally HCl, between the different cremations. That at least a quarter of the mercury present was oxidised has implications for any mercury abatement system due to the different chemistries of elemental and oxidised mercury. Oxidised forms of mercury are also water soluble and are therefore more likely to present a localized pollution of mercury during periods of precipitation compared to elemental mercury.

The various factors discussed above were accounted for when the Crematorium Hg CEM was designed. This system is described below:

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PSA Crematorium Hg CEM

The PSA Crematorium Hg Continuous Emission Monitor (CEM) consists of two principal components; a dilution probe (S123P100) and an analyser unit 10.665/10.680. The sample probe is designed to require minimal maintenance and to be as small and unobtrusive as possible for installation in awkward locations.

For system calibration and validation test purposes, elemental mercury calibration gas generated within the CEM is automatically introduced to the system upstream of the probe filter at flow rates suitable to totally displace the sample stream.

The diluted preconditioned sample is continuously delivered to the PSA 10.525F Continuous Sampling Sir Galahad analyser where the mercury concentration is continuously determined by amalgamation atomic fluorescence spectroscopy in less than 3 minutes per sample (a result is reported every 90 s). A carrier gas of compressed air is required.

Amalgamation-Atomic Fluorescence Spectroscopy

Hg is determined by the Sir Galahad analyser using amalgamation-atomic fluorescence spectrometry. Mercury is captured on the Amasil™ gold substrate by amalgamation, pre-concentrating the mercury and separating it from the sample matrix and thus overcoming potential interferences. Sample flow onto the Amasil tube is controlled by an MFC and pump arrangement to deliver an accurate sample volume to the analyser. Two Amasil™ tubes are used in parallel such that one tube is sampling while the other is being desorbed to ensure that any transient mercury spikes are determined. A photograph and schematic flow diagram is shown in Figures 3.

After sampling, the mercury collected is thermally desorbed into a carrier gas stream and subsequently delivered to a non dispersive atomic fluorescence spectrometer where mercury is detected at 253.7 nm. The combination of AFS with amalgamation offers excellent selectivity, an absolute detection limit of 0.1 pg and up to 8 orders of magnitude linearity.

Automation and System Integration

The system is designed to operate with minimal user intervention. The system can be operated unattended for several months, with internal QC checks performed automatically to ensure data validity. The system can readily be integrated with other data handling and control equipment using a variety of different communication protocols.

Conclusion

The mercury emissions from a crematory have been studied by amalgamation-atomic fluorescence spectroscopy. Mercury is emitted in a short period approximately 40 min into the cremation. The concentration emitted varies significantly but can be as high as several mg m^{-3}. Both elemental and ionic mercury are emitted during the cremation. The ratio of the two forms depends on the total level of mercury being emitted.

The PSA Crematorium Hg CEM has been presented, this system is specifically designed to determine mercury in crematorium flue gas for process control or regulatory purposes. The system is designed to operate with minimal user intervention.

References

1. National Atmospheric Emission Inventory, Emission Statistics by UNECE Source Category: Inventory Year 2006, AEA Technology, August 2008 (accessed online www.naei.org.uk Feb 2009)
2. N. Passant, Review of emission factors for mercury emitted from cremation, AEA Technology, June 2004