

PS ANALYTICAL

News Update 026

THE ON-LINE DETERMINATION OF MERCURY IN THE WASTEWATER INDUSTRY

Introduction

Due to current environmental concern there is increasing legislation regarding the discharge of mercury laden effluents to receiving waters. Consequently manufacturers are becoming more environmentally aware of the penalties associated with exceeding the consent limits for mercury in effluents. Wastewater can be divided into two categories: Domestic and Industrial.

Domestic Wastewater

Mercury may be present in domestic wastewater from a variety of sources, these can include clinical waste (dentists and hospitals) universities, light industry and household waste. Shock mercury loadings entering a wastewater treatment plant can have dramatic effects on the operating efficiency of the biological stages of water treatment. Anaerobic effluent treatment can be inhibited by excessive mercury levels, thus producing effluent of poor quality with high turbidity, BOD, COD, TOC etc and, of course, mercury.

Industrial Wastewater

There are a number of industries which utilise mercury directly such as the chlor-alkali industry, or that have mercury associated with their raw materials e.g. the smelting or waste incineration industries.

Chlor-Alkali Industry

The presence of mercury in chlor-alkali effluents is due to the consumption of the mercury flowing cathode during the electrolysis of brine.

Sulphuric Industry (Smelting Industry)

The presence of mercury in a smelting effluent is due to the association of cinnabar (HgS) with the sulphide bearing ores used in the smelting process.

Waste Incineration

The presence of mercury in a waste incineration plant effluent will vary dramatically according to the nature of the waste being disposed. The most common wastes undergoing incineration are sewage sludges, clinical wastes, chemical wastes and domestic garbage.

Justification for Wastewater Monitoring

Inevitably, treated wastewaters are discharged into rivers which can be used for drinking water abstraction and which also support a variety of aquatic life. Due to the toxicity and the bioaccumulation effects of mercury there is a range of legislation in place to monitor for the presence of mercury in such waters. As a result breaches of discharge consents will lead to heavy fines along with unnecessary adverse publicity. In certain incidents the regulatory authorities may impose strict criteria to which the manufacturer must adhere. This may include the requirement for more frequent monitoring or ultimately continuous monitoring to prevent further breaches of consent.

PS ANALYTICAL

UK: Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK

Tel: +44 (0) 1689 891 211 Fax: +44 (0) 1689 896009 E-mail: psa@psanalytical.com

USA: 1761 W. Hillsboro Blvd., Suite 318, Deerfield Beach, FL 33442, USA

Tel: +1 (954) 429 1577 Fax: +1 (954) 429 1601 E-mail: usa@psanalytical.com

www.psanalytical.com



Manual sampling

Any industry that has mercury in its wastewater is required to monitor their effluent several times over the day. A variety of sampling regimes can be used including grab and composite sampling.

However the limitations with these techniques include:

- Obtaining a representative sample from the same point each time.
- The manpower required each time for manual sampling.
- Contamination of the collected sample.
- Long turn-around times from sample collection to presentation of results

In certain industries plant malfunction and inefficient removal systems can lead to high mercury levels in the discharge effluent. When manual sampling techniques are employed situations may arise where high mercury levels in the effluent could go unnoticed. On a high throughput process this could lead to large volumes of contaminated effluent leaving the plant. Not only does this lead to a breach of consent limits but also raises a number of questions to the plant operator, for example:

- How much contaminated effluent has already been discharged?
- At what time did the contamination occur?
- Why did the contamination occur?:
 - Plant malfunction?
 - Removal plant malfunction?
 - Contaminated raw materials?

The PSA 10.223 on-line analyser is ideally suited to monitoring mercury effluents at low-level. By providing turnkey solutions to the customers monitoring requirements the PSA on-line analyser can provide the plant operators with a greater degree of confidence, control and compliance.

ON-LINE MERCURY MONITORING IN INCINERATION EFFLUENT

Background

A European waste incineration company was approached to investigate the possibility of configuring an on-line effluent monitoring system to their wastewater treatment process. The company processes its stack gas scrubber liquors in a wastewater treatment plant on-site. Wastewater treatment involves pH correction of the gas filtration effluent using calcium hydroxide from pH 2 to pH 9. This is then followed by the addition of FeClSO_4 polyelectrolytes to aid flocculation during sedimentation. TMT is also added to the sedimentation tanks to remove the majority of heavy metals as sludge. The settled sludge is then dewatered, dried and sent for landfill in specially lined landfill sites. The resulting wastewater is further treated by passing through sand beds and finally through activated carbon filter beds before discharge to the local river. A schematic diagram of the various stages of the waste incineration process is shown in Figure 1.

The company currently analyses their effluent for mercury approximately three times a day (at each shift changeover). This involves manual collection of the sample from the effluent outfall, transportation to the works laboratory, sample preparation and finally instrument calibration and subsequent determination.

The effluent sample is analysed using the EPA 7470 method for mercury in industrial wastewaters. This involves a two-hour digestion stage on a hot plate using a mixture of KMnO_4 , H_2SO_4 , and $\text{K}_2\text{S}_2\text{O}_8$ before being analysed using conventional cold-vapour AAS detection. The whole process can take as long as 5 hours before the mercury concentration in the effluent is known. In between analysis intervals, plant maintenance, wastewater treatment failures and variations in incoming waste composition are all factors



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which can lead to discharges of an effluent with a high mercury concentration leading to breaches of consent, possible prosecution and adverse publicity. Thus, the company expressed a desire to monitor their effluent on a continuous basis so that the necessary action can be taken when failures of the treatment process occur.

Analyser and sample location

The on-line instrument was located in a purpose built concrete analyser house located adjacent to main incineration plant. Figure 2 shows a photograph of the sampling point with the analyser house in the background. The analyser house was air conditioned at a temperature of 25°C, had an electronic heater for cold periods and was airtight from the surrounding atmosphere.

Two sample streams were plumbed to the instrument in ½" stainless steel. Each sample was delivered to a constant over-flow sampling system fitted with liquid level sensors. The first wastewater sample to be monitored was obtained from the inlet of an activated carbon clean-up system, here the sample underwent sedimentation involving treatment with TMT, small quantities of TMT flocculent matter were present in the sample. The second sample to be analysed was from the exit of the carbon beds and contained no visible particulate matter, this was the final discharge effluent to the river.

Gases

The instrument was plumbed with instrument air for activating the FI valve and also the dryer gas. Carrier and sheath gases were analytical grade nitrogen delivered from a bank of cylinders located outside the analyser house, cylinders were fitted with an automatic change-over unit.

Reagents

The customer's action level, the point at which the "contaminated" sample would be re-circulated to the wastewater treatment process for further polishing was 10 ng ml⁻¹. Hence mercury standards of 0, 5, 10 and 40 ng ml⁻¹ were prepared in the same matrix as the carrier solution, 0.5 litres of each standard were prepared and stored in HDPE bottles. 10.0 litres of each reagent were prepared, resulting in 7 days unattended operation.

Carrier stream: 10% v/v HCl in DDW

Oxidant: 0.05M potassium bromate/potassium bromide solution in DDW.

Reductant: 3.5% m/v Tin (II) Chloride in 10% v/v HCl in DDW.

Tap water was used for the cooling chamber.

All reagent and sample/standard flow rates were 0.8ml min⁻¹

Procedure

The instrument was set-up with the reagents for acidified bromination chemistry as shown in Figure 3. A simple analysis programme involving a four-point calibration of 0, 5, 10 and 40 ng ml⁻¹ Hg was performed. Once calibrated the instrument automatically performs twenty determinations on the inlet sample followed by two check standards of 10 ng ml⁻¹ and finally another twenty determinations on the outlet sample. This analysis cycle was then continuously repeated over 12-day period. The results from the instrument were then exported to the DCS via a two-channel 4-20 mA output.

Results

Calibrations

Figure 4 shows the variation of the instruments stability with respect to calibration variation over the 12 days. The mean calibrant peak height output have been grouped together to produce a mean calibration graph. The results show that the precision over the 12 days for both the 5 and 10 ng ml⁻¹ standards was less than 5%. Once again the reproducibility of the continuous re-calibration procedure was within 5%, i.e. the slope varied less than 5% over the test period.



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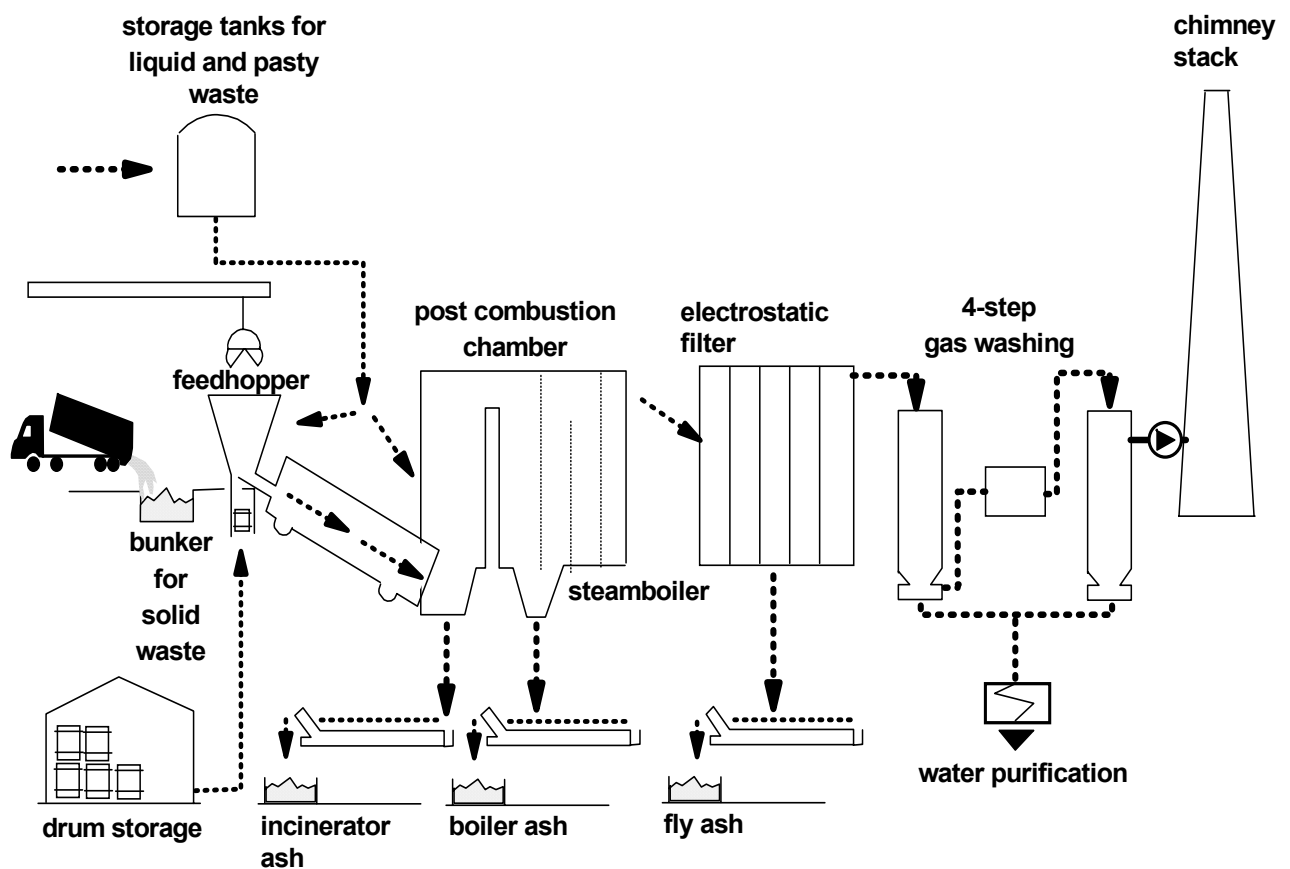
Conclusion

The typical results shown in Figure 6 illustrate the variation of both the inlet and outlet mercury concentrations over the test period. The results clearly show the efficiency of the carbon clean up system. The on-line monitoring system was set-up to export the results of each effluent stream to the control room where the appropriate action can be taken when discharge levels are exceeded.

With the rapid generation of results (every 7 minutes) the operators in the control room can take the necessary action and have a greater degree of confidence, control and compliance.

For further information on this or other on-line applications please contact P S Analytical directly.

Figure 1 Basic stages of the incineration process



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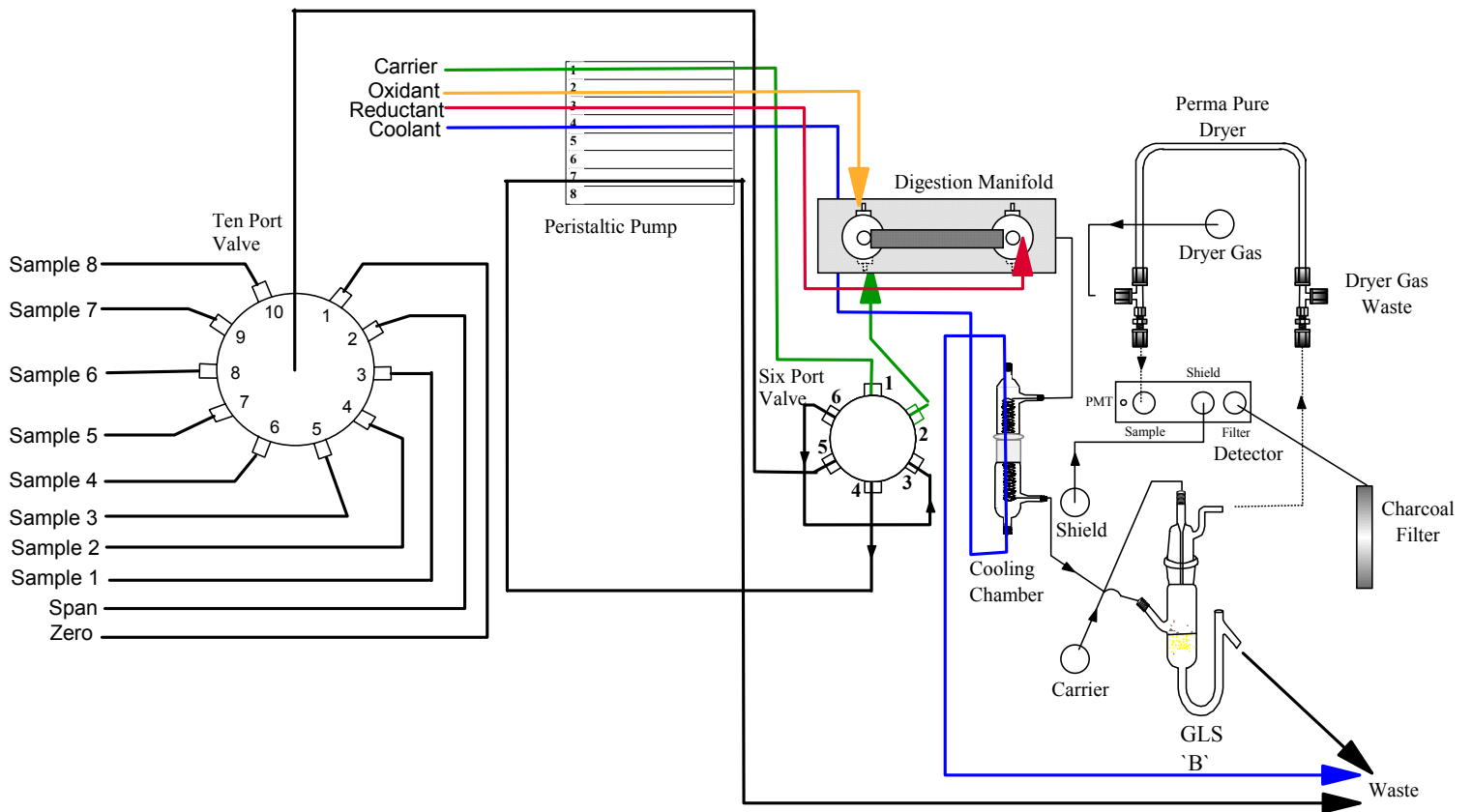
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Figure 2 Sampling point for treated incineration wastewater



Figure 3 Schematic diagram of wet section manifold configured for bromination oxidation



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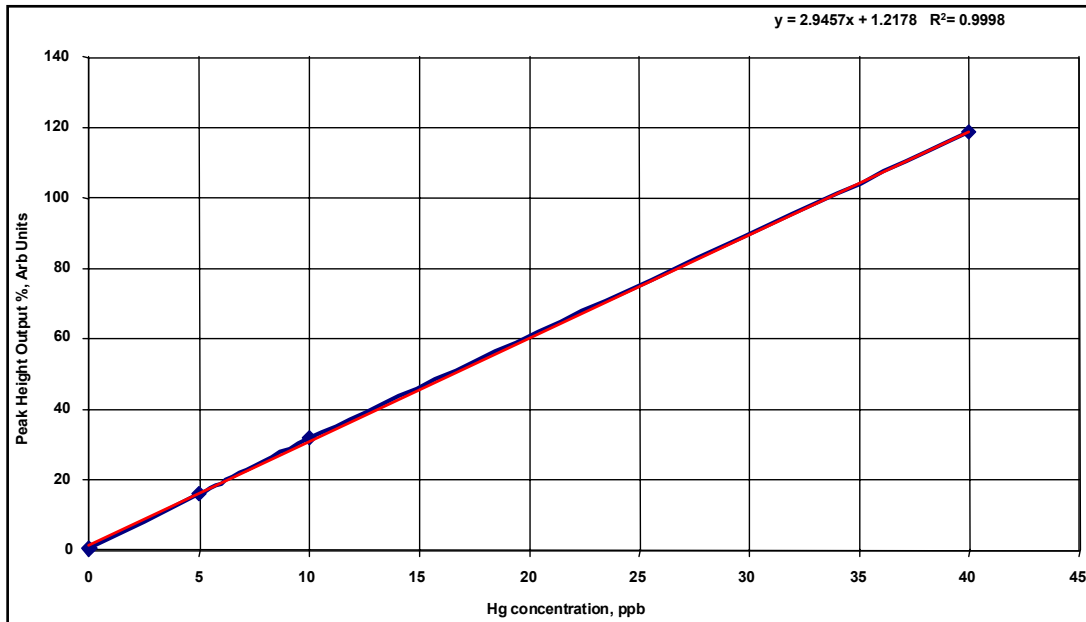
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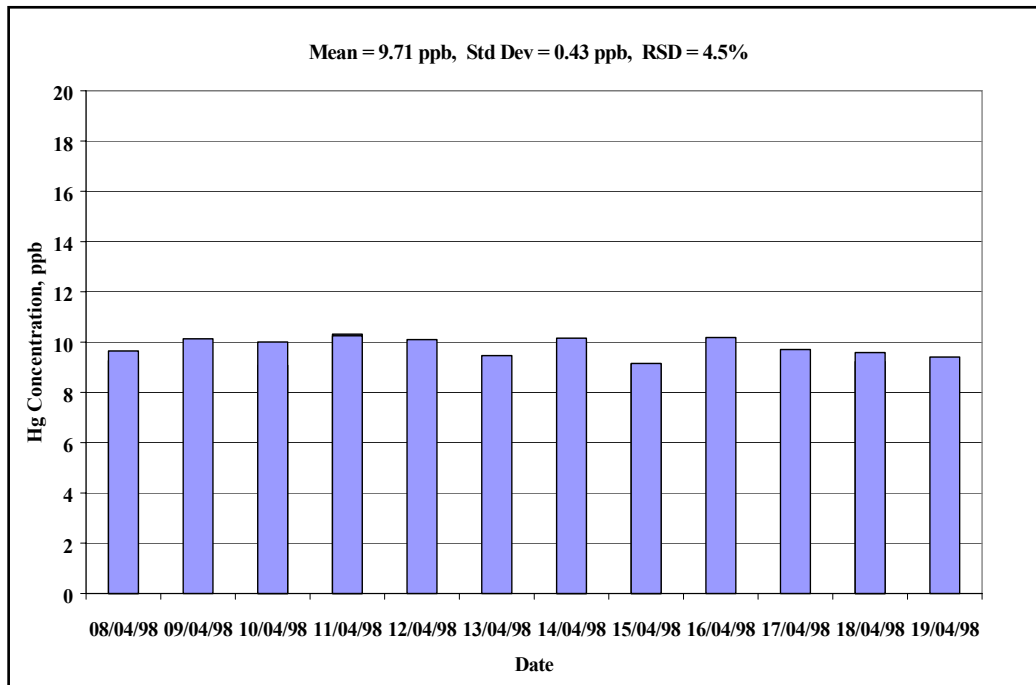
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Figure 4 Mean calibration slope over a 12-day period



QC Check Standards

Figure 5 Variation of 10 ng ml⁻¹ check standard over the test period



Wastewater Variation



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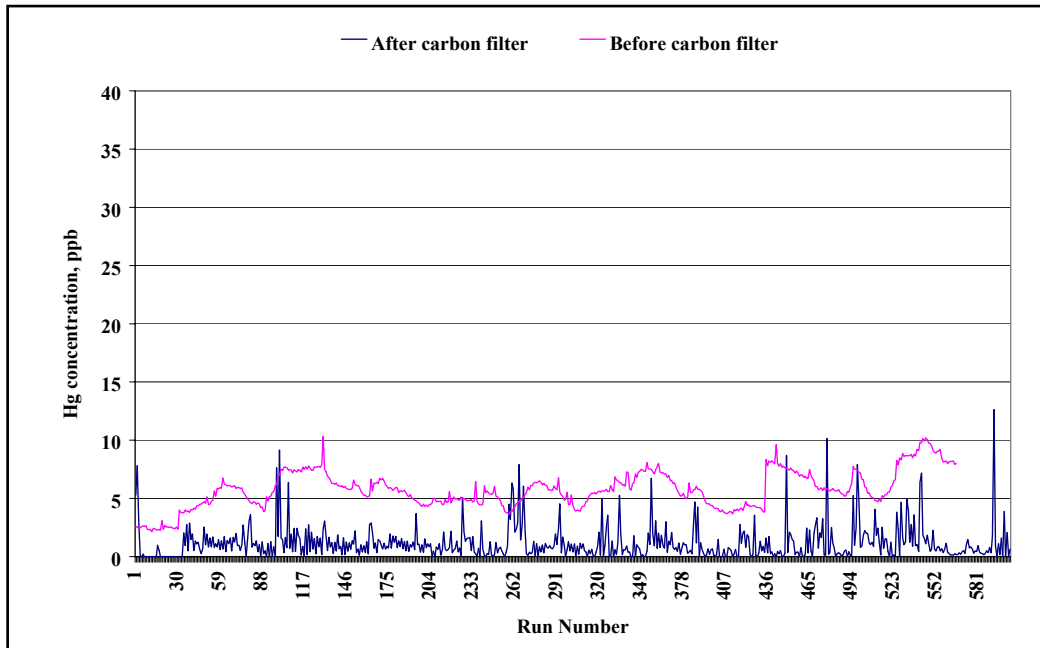
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Figure 6 Variation of both the inlet and outlet mercury concentrations over the test period



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