

Development of an online analyser to meet challenging new discharge limits for mercury in flue gas desulphurisation wastewater

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ABSTRACT

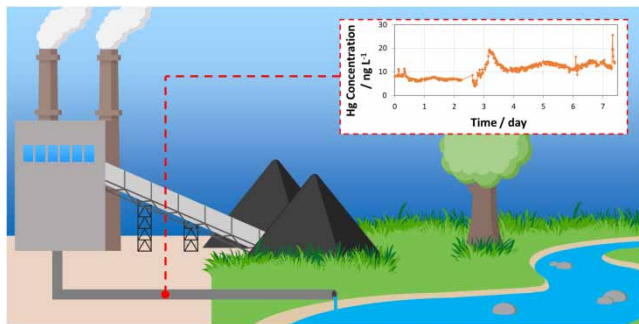
Anthropogenic emissions of mercury to the environment are of great concern due to its toxicity. The burning of coal contributes highly to Hg emissions and, as such, much lower effluent discharge limits for Hg in flue gas desulphurisation (FGD) wastewater have recently been proposed in the USA. Lower detection limits are required to meet the most demanding discharge limit of 10 ng L^{-1} . Therefore, in this work, a new analyser for online monitoring of Hg in FGD wastewater based on syringe injections of chemicals combined with gold amalgamation – atomic fluorescence spectrometry has been developed. The instrument has been validated against international standard method ISO 17852, as well as an interference study with extreme levels of salts majorly present in FGD water. Detection limits of 1.8 ng L^{-1} as well as accurate performance in an on-site field trial indicate that the methodology is fit to meet the new legislation.

Key words: effluent, FGD, mercury, wastewater

HIGHLIGHTS

- LOD of 1.8 ng L^{-1} and LOQ of 3.7 ng L^{-1} , with possibilities to further reduction by varying sample intake.
- Successful analysis carried out on-site with a constantly changing effluent Hg concentration.
- Interference study indicates the instrument is robust in high levels of extreme levels of salts present in FGD wastewater.

GRAPHICAL ABSTRACT



1. INTRODUCTION

Anthropogenic emissions make up the majority of mercury (Hg) releases into the environment (UN Environment 2019). Therefore, given the highly damaging effects of Hg to wildlife and human health (Syversen & Kaur 2012), it is vital that such Hg emissions are strictly regulated. Regarding aqueous emissions of Hg from industrial wastewater, unregulated

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discharge can be terribly damaging to wildlife and human health as ionic divalent mercury (Hg^{2+}) is converted by microorganisms to methylmercury (MeHg), one of the most toxic and most bioavailable forms of Hg (Gochfeld 2003; Syversen & Kaur 2012), which is then biomagnified through the food chain.

Fossil fuel burning is a major contribution to the global anthropogenic Hg emissions, where coal combustion alone contributes approximately 21% (UN Environment 2019). The global average Hg content of coal is 0.1 mg kg^{-1} (Yudovich & Ketris 2005) with China, USA, and South Africa showing elevated average coal Hg concentrations of approximately 0.2 mg kg^{-1} (Zhao *et al.* 2019). Combustion of coal thermally converts the mercury to volatile Hg^0 . The resulting flue gas cools down as it is carried along the process and Hg can either react with acid gases produced from the coal combustion, particularly hydrochloric acid (HCl), to form oxidised Hg, or can be adsorbed onto the unburned carbon particulates and fly ash as particulate bound Hg (Niksa & Fujiwara 2005). For coal with lower chloride content, halogenated powdered activated carbon (typically brominated) can be introduced to the flue gas to enhance the Hg^0 oxidation (Srivastava *et al.* 2006). Additionally, the conversion processes can be improved to >90% efficiency if selective catalytic reduction for NO_x gases is also used (Srivastava *et al.* 2006). Both oxidised and particulate bound forms of Hg are water soluble and can be subsequently removed from the flue gas through wet processes. Typically, Hg is preferentially removed during the flue gas desulphurisation (FGD) process, which is required to oxidise sulphur dioxide to soluble sulphate species to reduce SO_2 emissions. Most commonly, this is achieved using a wet limestone process (Córdoba 2015) or seawater at coastal locations (Huang *et al.* 2023). The solubilised Hg^{2+} can then be further treated using additional removal processes.

The most recent estimation of the global Hg emissions, carried out in 2015, showed that coal-fired power plants were responsible for approximately 54 tonnes of Hg emissions to water (UN Environment 2019). Effluent discharge limits are set by each country and based on the best available technology (BAT). In the European Union (EU), discharge limits for Hg range from 0.2 to $3 \mu\text{g L}^{-1}$ (EU 2017/1442). The USA currently has the lowest discharge limits following promulgation of a new regulation by the Environmental Protection Agency (EPA) (US EPA 2020) that came into force at the end of 2020. According to the Code of Federal Regulations (C.F.R. 40 § 423), previous discharge limits of 758 ng L^{-1} per day and an average of 356 ng L^{-1} within any 30-day period have now been drastically reduced to 103 ng L^{-1} per day and an average of 34 ng L^{-1} within any 30-day period. For an average 660-MW coal-fired power plant discharging approximately $0.3 \text{ m}^3 \text{ MWh}^{-1}$ FGD of wastewater (Han *et al.* 2020), the change in effluent discharge limit results in an annual maximum release of Hg to aquatic systems from approximately 0.6 to $0.06 \text{ kg year}^{-1}$. Additionally, power plants may elect to voluntarily meet even lower discharge limits as part of a voluntary incentives program. This limit, which was also reduced at the end of 2020, permits a maximum Hg discharge of 23 ng L^{-1} on any given day, and less than an average of 10 ng L^{-1} within any 30-day period (C.F.R. 40 § 423).

Such low discharge limits require much lower detection limits, which can be difficult to achieve due to the high variability of the FGD wastewater matrix. Though the BAT defines the discharge limits, power plants are by no means required to use the BAT, provided the removal process used complies with the set discharge limits. Typical processes used to treat FGD water for heavy metals include chemical precipitation with iron (US EPA 2015) or aluminium salts (Marcinowski *et al.* 2019), organo-sulphide precipitation (Sun *et al.* 2012; US EPA 2015; Masoomi *et al.* 2020), or hydroxide precipitation with wet limestone (Córdoba 2015; US EPA 2015), anaerobic biological treatment (EU 2017/1442; US EPA 2015), and adsorption onto activated carbon (EU 2017/1442). Therefore, development of an analyser capable of measuring Hg in any given FGD wastewater can be very challenging as different power plants may have substantially different FGD wastewater matrices due to differences in the types of coal, process conditions, removal systems, wastewater treatment processes, etc.

Determinations of Hg in waters are most commonly carried out with cold vapour (CV) generation coupled to either atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS), however the CV-AFS approach boasts lower detection limits compared to CV-AAS (Sánchez-Rodas *et al.* 2010). Typically, plants take daily composite samples and analyse them using standard methods, such as ISO 17852:2006, EPA 245.7 (US EPA 2005), and EPA 1631 (US EPA 2002). However, online determination of Hg is imperative, as offline grab-sample analysis can be slow and labour intensive, potentially leading to a delayed response to changing Hg concentrations due to lack of real-time data and noncompliance penalties being imposed. Previous analysers used for online monitoring of Hg in FGD wastewater were based on a continuous flow injection approach, which requires higher labour time and costs to operate due to the high volumes of reagents required and waste generated. Thus, a new, syringe-based batch process approach for online Hg monitoring has been developed here that is capable of accurate quantification of total Hg at the lowest discharge limit of 10 ng L^{-1} through preconcentration of Hg with gold amalgamation. Such design has been utilised to massively reduce reagent consumption by injecting precise

volumes of reagent only when required, while also maintaining accurate quantification of total Hg at the lowest discharge limit of 10 ng L⁻¹. This work highlights that the new instrumentation provides accurate and precise determinations of low-level Hg in various real FGD wastewater samples, as well as excellent performance on-site at a coal-fired power plant operated under real-world conditions.

2. MATERIALS AND METHODS

2.1. Chemicals

Deionised water was produced by an Elga Purelab Option DV35 (15 MΩ cm; Elga, UK). HCl (NORMATOM[®], 34–37%; VWR, UK) was used for acidification of samples and standards. Ten thousand mg L⁻¹ of Hg²⁺ standard was purchased (Fisher Scientific, UK) and was diluted sequentially to a working standard of 100 μg L⁻¹ in 0.6 M of HCl. Further dilutions were prepared in 0.6 M of HCl. A 1,000 mg L⁻¹ of stock solution of methylmercury chloride was prepared by diluting the compound (Fluorochem Ltd, UK) in methanol. Subsequent dilutions were carried out in 0.12 M of HCl. A 1,000 mg L⁻¹ of stock solution of ethylmercury chloride was prepared by diluting the compound (Johnson Matthey GmbH, Germany) in methanol. Subsequent dilutions were carried out in 0.12 M of HCl. Bromide–bromate solution (0.1 N; Merck, UK) was used as an oxidising agent. Excess bromine was reduced using 20 g L⁻¹ of hydroxylamine hydrochloride (SpectrosoL[®]; BDH, UK) online, or 100 g L⁻¹ of L-ascorbic acid (99 + %; Alfa Aesar, UK) offline. The reductant was tin(II) chloride dihydrate (AnalaR NORMAPUR; VWR, UK) prepared in 1.2 M of HCl at concentrations of 40 g L⁻¹ online, or 20 g L⁻¹ offline. Soda-lime (Sofnolime[®], RG grade; Molecular Products, UK) was used to trap acid gases prior to gold amalgamation.

Magnesium chloride (>95%; Sigma Aldrich, UK), calcium chloride (technical grade; Sigma Aldrich, UK), potassium nitrate (ACS Reagent grade; Sigma Aldrich, UK), sodium sulphate (ACS Reagent grade, 99 + %; Sigma Aldrich, UK), sodium hydrogen sulphide (technical grade; Sigma Aldrich, UK), sodium chloride (99.5%; Sigma Aldrich, UK), potassium hydrogen phthalate (Puriss grade; Fluka, UK), iron chloride hexahydrate (99 + %; ACROS, UK), aluminium chloride hexahydrate (99 + %; ACROS, UK), boric acid (ACS Reagent grade, 99.5 + %; Sigma Aldrich, UK), and ammonium carbonate (ACROS, UK) were chemical salts used for an interference study. TMT-15[®] (15% (m/v) 1,3,5-triazine-2,4,6-trithiol trisodium salt; Sigma Aldrich, UK) was an organo-sulphide compound used for the interference study.

2.2. Instrumentation

Online measurements were carried out with the Hg analyser developed (PSA 10.226; PS Analytical, UK). A CV-AFS (PSA 10.025 Millennium Merlin; PS Analytical, UK) was used for offline analysis of samples.

Online filtration of wastewater samples was carried out using a fast-loop self-cleaning filter (PSA L225A210; PS Analytical, UK) with a 100-μm filter insert. Whatman[™] filter papers (41, Ashless, 90 mm diameter; Fisher Scientific, UK) were used for offline sample filtrations.

2.3. Samples

Seven influent and effluent FGD wastewater samples were obtained from various coal-fired power plants in the USA. The plants burned bituminous or subbituminous coals and had operating capacities within the range of 2,150–2,850 MW.

2.4. Sample preparation and analysis

2.4.1. Online Hg analysis

Samples were filtered offline before analysis using the analyser except for the field trial, where live sample was filtered online across an external filter panel prior to being introduced to the sample line. All reagents and samples were transferred through the system using a syringe. A diagram of the instrument set-up is given in [Figure 1](#).

A sample aliquot of 2.5 mL was added to a quartz UV digestion vessel, followed by 2 mL of 6 M of HCl and 1 mL of bromide/bromate solution. The sample was then diluted to 20 mL using deionised water and allowed to digest for 15 min. Excess bromine was reduced using 1 mL of hydroxylamine solution. The digest was then transferred to the gas–liquid separator (GLS), where 1 mL of tin(II) chloride reductant was added and the Hg purged from solution with argon carrier gas at 350 mL min⁻¹ through a PermaPure[®] membrane, soda-lime trap, and collected on a gold trap for 5 min. The gold trap was then heated for 15 s, and the Hg evolved was carried to the AFS detector for quantification.

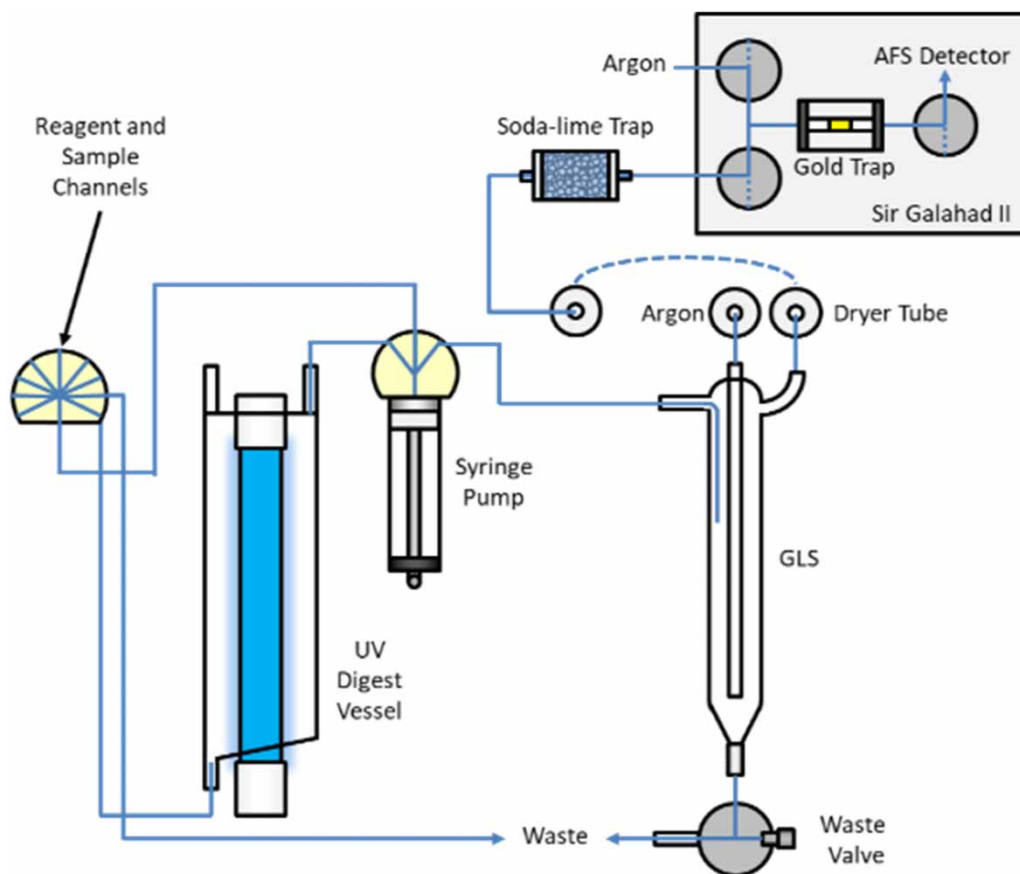


Figure 1 | Schematic representation of the PSA 10.226 online Hg analyser.

2.4.2. Offline Hg analysis

Offline analysis of FGD wastewater samples was carried out in accordance with ISO 17852:2006. To 45 mL of wastewater sample, 2.5 mL of HCl and 2 mL of bromide/bromate solution was added. The samples were allowed to react for 1 h. The excess bromine was reduced with 500 μ L of L-ascorbic acid solution before analysis with AFS.

3. RESULTS AND DISCUSSION

3.1. Development of an online Hg analyser

3.1.1. Collection time for gold trapping

Gold amalgamation coupled to AFS detection was employed to increase sensitivity and, thus, reach much lower detection limits. The time required to purge the Hg from solution was evaluated to ensure maximum sensitivity. Monitoring the Hg signal by analysing Hg^{2+} standards while bypassing the gold trap showed that a 5-min collection time quantitatively purges Hg up to absolute mass of 2 ng of Hg (equivalent to 10 mL of a sample containing 200 ng L^{-1} Hg^{2+}), which is sufficient for the analysis of Hg in FGD wastewater.

3.1.2. Development of analysis method for total Hg in FGD wastewater

Acidified bromide/bromate digestion was employed for the measurement of Hg in FGD wastewater, similar to previously validated offline wastewater analysis methods such as ISO 17852:2006 and EPA 245.7. The reaction was carried out in a quartz digest vessel in the presence of UV light to assist acidified bromine digestion of the sample matrix. To reduce the excess bromine formed, 0.1 mL of hydroxylamine was required to successfully decolourise the digest. However, this volume was increased to 1 mL as a precaution to ensure the excess bromine was reduced to avoid potential interferences once transferred to the GLS. As a secondary precaution, a soda-lime trap was added before the gold trap to remove any halogens from the

carrier gas stream. Calibrations were able to be carried out using varying volumes of one Hg^{2+} standard between 2.5 and 15 mL, which reduces overall preparation time and allows for more space on the reagent introduction valves for additional samples or QC standards.

Optimisation of the digestion time and sample dilution was carried out using four different FGD wastewater samples. Samples were spiked online with 0.25 ng Hg absolute mass. Results are presented in Table 1.

Spike recoveries were assessed based upon a pass criterion of 90–110%. A good recovery of 96.3% was obtained for one FGD wastewater sample using a high sample volume of 10 mL and a short digestion time of 5 minutes. However, all other FGD samples tested required a much lower sample volume and longer digestion times to obtain acceptable spike recoveries. Spike recoveries within 90–110% were obtained for all samples using a 2.5-mL sample volume with a 15-min UV digestion time. Therefore, this method was employed as standard for all FGD wastewater samples. However, it should be noted that it may be possible to use higher volumes or shorter digestion times for FGD streams where higher frequency or lower detection limits are required.

3.1.3. Conversion of organic Hg species

Bromination serves to also ensure conversion of any organic Hg species to Hg^{2+} before the reduction step. The conversion efficiency of UV-assisted bromination was assessed for varying digestion times using 2.5 mL of a 50 ng L^{-1} standard of either MeHg or ethylmercury (EtHg). Results are presented in Figure 2.

Recoveries for EtHg were consistently between 98 and 103%, which indicates complete conversion of the EtHg compound to Hg^{2+} regardless of digestion time. Conversely, recoveries for measurements of MeHg increased with digestion time, which implies that MeHg is more difficult to break down compared to EtHg. Recoveries of greater than 90% were obtained for

Table 1 | Optimisation of digestion time based on the recovery of a Hg^{2+} spike standard for four FGD wastewater samples

Wastewater sample	Sample volume (mL)	Digestion time (min)	Measured conc. (ng L^{-1})	Spike recovery (%)
FGD 1	10	1	8.86 ± 0.61	79.2 ± 2.3
	10	5	8.66 ± 0.26	96.3 ± 4.4
FGD 2	2.5	10	23.1 ± 0.9	50.3 ± 8.4
	2.5	15	44.8 ± 1.8	90.3 ± 2.4
	2.5	20	46.4 ± 0.5	94.1 ± 4.0
FGD 3	2.5	10	20.8 ± 0.9	55.9 ± 1.8
	2.5	15	22.9 ± 0.2	93.1 ± 3.1
FGD 4	2.5	15	7.20 ± 0.58	93.2 ± 2.2

Errors are given as standard deviation of three replicates.

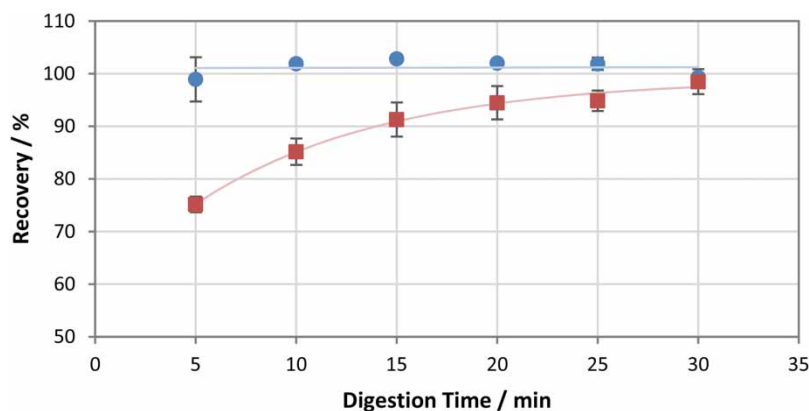


Figure 2 | Recovery of Hg obtained for UV-assisted digestion of 50 ng L^{-1} MeHg (red, square) and EtHg (blue, circle) standard solutions. Error bars represent one standard deviation of three replicates.

digestion times of 15 min and above. It is worth noting, however, that the MeHg present in FGD wastewater makes up only a small fraction of the total Hg. One study of four coal-fired power plants in Ohio, America, observed influent and effluent MeHg concentrations at approximately two orders of magnitude less than that of the total Hg (ORSANCO 2013). However, it is possible that other wastewater streams may contain higher levels of organic Hg species.

3.1.4. Reagent stability

For online monitoring systems, reagents with longer lifetimes are desirable as it lowers the overall maintenance due to less frequent preparation of chemicals. The main reagent of concern regarding stability was the tin(II) chloride reductant, which required frequent preparation due to aerial oxidation of Sn^{2+} to Sn^{4+} . To improve the lifetime of the reductant, aerial oxidation was reduced by continuously purging the reductant with argon gas at 70 mL min^{-1} . A stability study was carried out by analysing 2.5 mL of a 100 ng L^{-1} of Hg^{2+} standard with and without an argon purge (Figure 3).

The efficiency of Hg^0 generation was greatly reduced when the reductant solution was left open to air, as indicated by the immediate decline of Hg recovery to less than 90% after just 1 day. Using argon gas to remove contact of the solution with air vastly improved stability of the reductant, giving recoveries of Hg within 90–110% over the 14 days tested.

Stabilities of the other reagents were tested by leaving them open to air 60 days before use. Two Hg^{2+} calibration standards were prepared in borosilicate bottles at concentrations of 100 and 10 ng L^{-1} . The standards were measured against a calibration generated using freshly prepared reagents. After 60 days, analysis of the 100 and 10 ng L^{-1} standards using the old reagents gave 102.5 and 102.8% recovery, respectively, which indicates that these reagents used for the online digestion have a high stability and are suitable for online monitoring.

3.2. Method validation

3.2.1. Detection limits

Detection limits were established by the analysis of blanks against a calibration. Limit of detection (LOD) and limit of quantification (LOQ) were calculated by addition of three and 10 times the standard deviation to the blank concentration respectively. Instrument detection limit (IDL) considered only three times the standard deviation. However, these limits do not consider the sample matrix, which may be significantly more difficult to analyse than a pure standard. In this case, a method detection limit (MDL) was also calculated by the multiplication of the t -statistic (at 99% confidence) with the standard deviation of sample, as defined in the Code of Federal Regulations (C.F.R. 40 § 136). To be valid, the native Hg concentration must be <10 times that of the MDL. Results are presented in Table 2.

Similar LODs and MDLs were obtained, suggesting that the presence of the sample matrix had minimal effect. Results indicate that a detection limit of 1.8 ng L^{-1} can be achieved using 2.5 mL of sample, however, this can be vastly improved to $<0.5 \text{ ng L}^{-1}$ using a larger volume of sample. Here, this was carried out using 10 mL of sample diluted to 20 mL in the digest vessel, which may not work for all FGD samples; however, there may be scope to scale up the volumes of digest reagents and dilution if lower detection limits are required. However, the LOQ of 3.7 ng L^{-1} is well below the lowest effluent

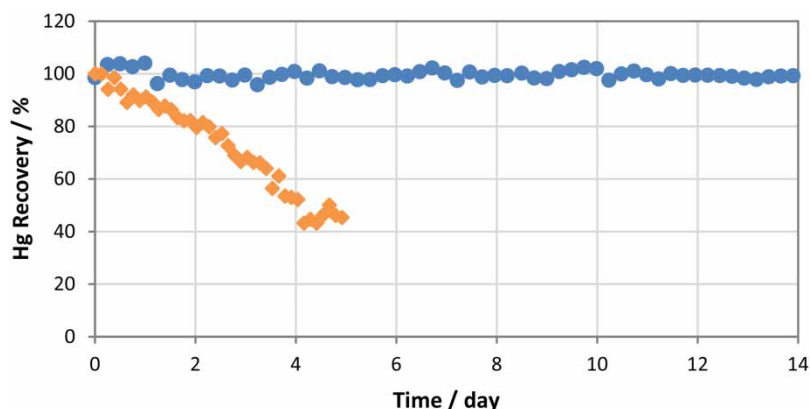


Figure 3 | Recovery of a 100 ng L^{-1} Hg^{2+} calibration standard using tin(II) chloride reductant open to air (orange, diamond) and under argon purge (blue, circle).

Table 2 | List of detection limits determined for the online Hg analyser

Detection limit	Number of runs	Hg mass (pg)	Hg conc. for 10 mL sample (ng L ⁻¹)	Hg conc. for 2.5 mL sample (ng L ⁻¹)
LOD	10	4.5	0.45	1.8
LOQ	10	9.3	0.93	3.7
IDL	10	2.1	0.21	0.84
MDL	8	4.5	–	1.8

limit of 10 ng L⁻¹ proposed by the EPA, which further enhances reliability as concentrations obtained below the effluent limit are both detectable and quantifiable. The IDL indicates that the contribution of the instrument noise to the detection limit is approximately half. This implies that the detection limit may be improved by up to half by improving the blank concentration (i.e., using higher quality reagents).

3.2.2. Validation of the method against ISO 17852

Validation of the online Hg analyser was carried out against ISO 17852:2006, whose scope states it may be applied to industrial wastewater measurements. In total, seven samples of FGD wastewater were measured. The wastewater samples were also spiked at different concentrations of Hg²⁺ to encompass a range of concentrations up to 50 ng L⁻¹. Results were compared using a scatter plot with orthogonal regression (Figure 4).

The slope of 1.0259, which is close to the expected value of 1, showed no significant systematic bias at a 95% confidence interval (Z -score = 0.647, p = 0.518). Additionally, the intercept of +0.4286 ng L⁻¹, which is close to the expected value of 0, showed no significant bias at a 95% confidence interval (Z -score = 0.460, p = 0.646). Therefore, the online analyser has been shown here to perform well for the analysis of Hg in FGD wastewater and has been successfully validated against an international standard method.

3.2.3. Further validation with uncertainty budget

Uncertainty budgets were calculated using a bottom-up approach for the measurement of an FGD wastewater sample and the measurement of spiked standards in 5% HCl (see Supplementary material). The expanded uncertainty for the measurement of Hg in FGD wastewater was estimated here to be 15.4% (Supplementary material, Table S1), which is within a similar order of magnitude to previously published expanded uncertainties for wastewater measurements, such as from a proficiency test

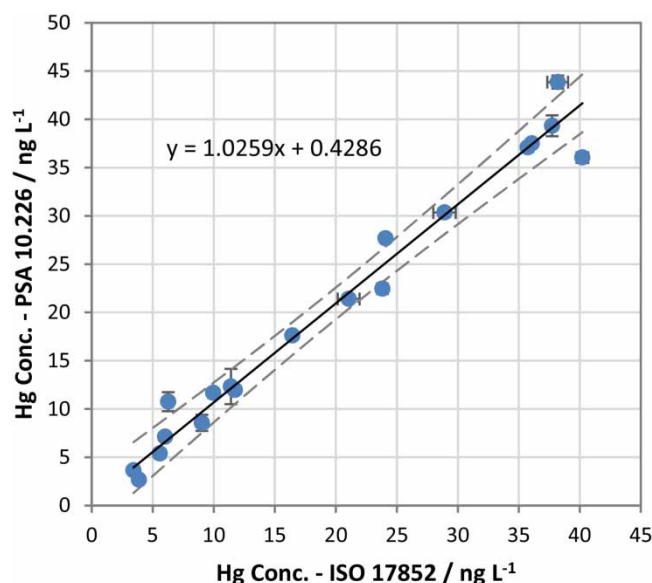


Figure 4 | Total Hg concentrations for FGD wastewater samples measured using the online Hg analyser (PSA 10.226) and standard method ISO 17852 compared using orthogonal regression. Error bars represent one standard deviation of three replicates. Associated confidence interval bands (95%) are displayed (grey dotted line).

for routine laboratory measurements (Pereyra *et al.* 2013) and the development of a thermal decomposition/amalgamation AAS method (Fletcher *et al.* 2020). This further validates the instrument for its intended purpose. The expanded uncertainty for a Hg^{2+} standard was much lower at 5.4% (Supplementary material, Table S2) due to the absence of sample matrix. This value therefore gives an indication of the theoretical best uncertainty obtainable under the conditions tested.

3.2.4. Field trial

A field trial was conducted using the online Hg wastewater monitor at a coal-fired power plant in the US. The analyser monitored the effluent FGD wastewater stream over 7 days. A 100- μm fast-loop filter panel was inserted into an effluent sampling line to remove large particulate matter that may cause blockages within the system. The results from the field trial are shown in Figure 5. High frequency of sample measurements was prioritised during the trial to obtain as much data as possible. The wastewater stream from this site was analysed offline during the initial development phase (Table 1, FGD 1). Therefore, a 10 mL of the sample volume with a 5-min UV digestion time was able to be used throughout the trial, giving a sample frequency of four results per hour. An online spike measurement (equivalent to 20 ng L^{-1} additional to the sample concentration) was performed automatically using the system every five measurements to assess accuracy. Pass criteria for the spike recoveries were set to 80–120% recovery.

The results indicate that the analyser was able to successfully monitor a continuously changing wastewater stream over 7 days. A notable decrease in Hg^{2+} spike recovery was observed after 2.5 days of measuring. This decrease occurred after a short period of plant shut-down. When shutting the instrument down, the reagent lines were moved to a water container and rinsed by priming the lines once with 5 mL. Upon restarting the instrument, the reagent lines were moved back to their respective containers, however the reagents were not primed before restarting. Therefore, the spike recovery decreased for four measurements but returned to within 80–120% recovery thereafter while the dead volume of water in the tubing was overcome.

3.3. Interference study

Due to the complex and highly variable composition of FGD wastewater matrix, it is important to consider the different components that may cause interferences with Hg analysis. Potential interferences, which may hinder the digestion or reduction of Hg steps, were tested by diluting the interferent in deionised water over a range of concentrations. Recovery of Hg was

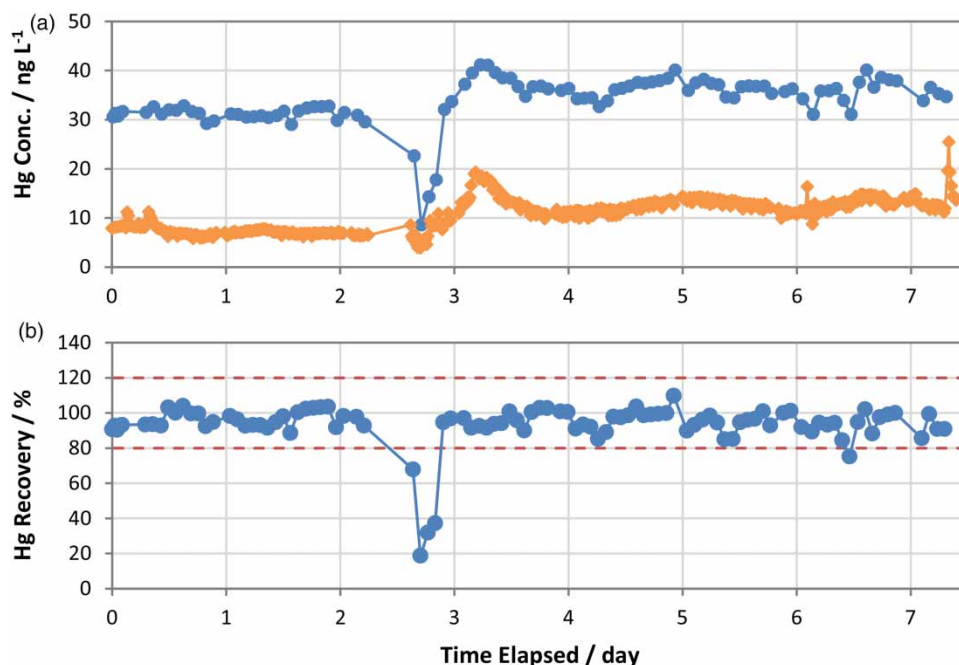


Figure 5 | Results of 7 days of online monitoring of FGD wastewater for (a) concentrations of native Hg in FGD wastewater (orange, diamond) and online Hg-spiked FGD wastewater (blue, circle), and (b) the Hg spike recovery results. The red dotted line indicates the Hg spike recovery criteria of 80–120%.

assessed by spiking the salt solutions with $100 \text{ ng L}^{-1} \text{ Hg}^{2+}$. Interference from each compound was tested separately to determine which anions, cations, or organics may affect the Hg measurements. The range of concentrations of the major elements, anions, and cations present in FGD wastewater, and the range of each tested in this study, has been given in Table 3 and the results from the main interferents are presented in Supplementary material, Figure S1.

The Hg recovery for all anions and cations listed gave Hg recoveries of 90–110% using the online UV digestion method (Supplementary material, Figure S1). Therefore, the online Hg analyser is capable of quantitatively measuring Hg in FGD wastewater, even in the presence of extreme levels of different dissolved salts observed in literature.

Total dissolved solids (TDS) were tested using sodium chloride. Over the saline concentrations tested (up to 286 g L^{-1}), recoveries of Hg between 90 and 110% were obtained (Supplementary material, Figure S1) and with high precision. Therefore, the instrument provides reliable results for total Hg, exceeding the range of TDS observed in literature works (Huang *et al.* 2013; Andalib *et al.* 2016; Conidi *et al.* 2018; Zheng *et al.* 2020). In addition, total Hg in sodium chloride solutions close to saturation were successfully analysed, which suggests that the instrument may also be suitable for Hg monitoring of other processes with extremely high salinity, such as saturated brine from storage caverns or produced water from oil and gas production and sea water.

Interference of high total organic carbon (TOC) concentration in samples was tested using standards of potassium hydrogen phthalate (Figure 6), as this compound is typically used as a standard for TOC measurements (Potter & Wimsatt 2012).

The recovery of Hg was observed to decrease using the UV digestion method, while also giving very high variability in the results obtained (Figure 6(a)). The TOC study was repeated with the UV light turned off. Under this condition, recoveries of Hg within 90–110% were obtained with much lower variability. Given that the compound used is a salt of phthalic acid, which is an organic acid, it could be that the loss of Hg observed under UV light was due to photochemical vapour generation of Hg^0 in the digest vessel, which could then be evolved from solution during the digestion and lost. However, it would be

Table 3 | Concentration range of major components of FGD wastewater and the concentration range of each component assessed for interferences in this study

	Unit	Range tested using PSA 10.226	Range in FGD wastewater	References
pH	–	–	3.5–8.2	a, b, c, d, e, f, g
Conductivity	mS cm^{-1}	–	26.5–65.8	a, b, c, e, f
TDS	mg L^{-1}	26,600–286,000	7,500–121,000	d, e, f, h
TOC	mg L^{-1}	102–1,970	13.8–121	a, b, e, f, g, i
Aluminium	mg L^{-1}	2.57–15.1	0.006–10.3	c, j
Ammonia (as N)	mg L^{-1}	2.47–19.9	0.220–13.2	g, h, j
Boron	mg L^{-1}	106–832	31.5–723	a, b, d, i, j
Calcium	mg L^{-1}	419–5,880	384–5,080	c, d, e, i, j
Chloride	mg L^{-1}	744 – 42,381	1,120–24,200	a, b, c, d, h, i, j
Iron	mg L^{-1}	30.9–211	0.050–130	a, b, j
Magnesium	mg L^{-1}	2,100–14,500	145–9 050	c, d, e, i, j
Nitrate/Nitride (as N)	mg L^{-1}	56.7–1,140	0.095–345	a, b, c, d, e, g, h, i, j
Potassium	mg L^{-1}	158–3,770	–	–
Sodium	mg L^{-1}	125–7,170	477–1,970	c, e, i, j
Sulphate	mg L^{-1}	262–15,000	750–13,300	a, b, c, d, e, g, h, i, j

^aBogacki *et al.* (2018).

^bMarcinowski *et al.* (2019).

^cStaicu *et al.* (2017).

^dHuang *et al.* (2013).

^eConidi *et al.* (2018).

^fZheng *et al.* (2020).

^gWei *et al.* (2017).

^hAndalib *et al.* (2016).

ⁱKoenig & Liu (2004).

^jEPRI (2013).

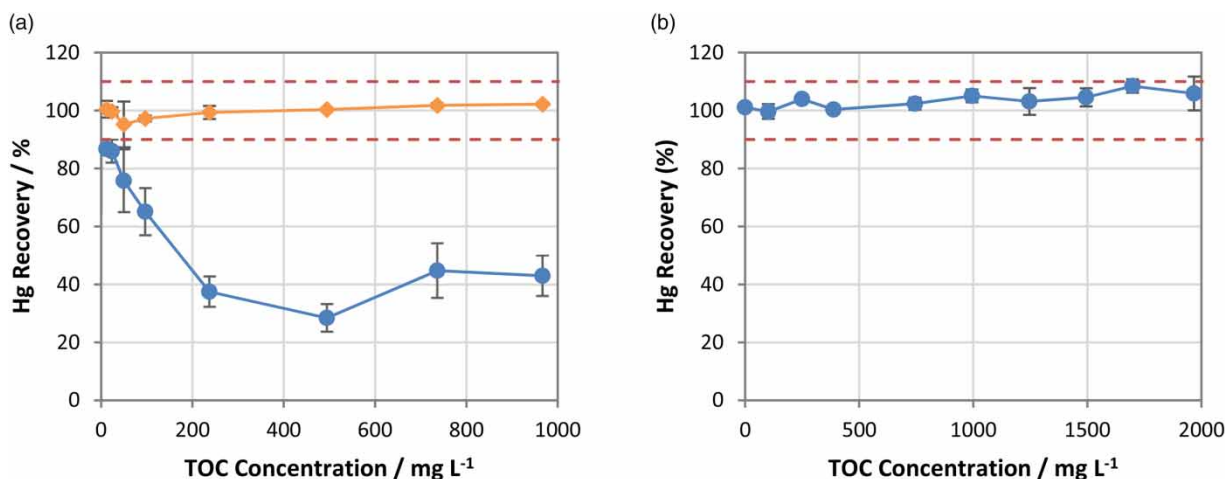


Figure 6 | Recovery of 100 ng L⁻¹ Hg in (a) potassium hydrogen phthalate standards with UV on (blue, circle) and off (orange, diamond) during digestion and (b) real FGD wastewater matrix with additional potassium hydrogen phthalate added. Red dotted lines indicate the threshold of 90–110% recovery of Hg. Error bars represent one standard deviation of four replicates.

expected that the use of bromide/bromate oxidant would convert any generated Hg⁰ back to Hg²⁺ and keep it in solution. Alternatively, the UV reaction with the potassium hydrogen phthalate could generate species which could interfere with the tin(II) chloride reduction step, cause modification on the surface of the gold trapping material, or cause quenching of atomic fluorescence.

The TOC interference study was repeated in the presence of a real FGD wastewater sample and using UV digestion to determine if elevated TOC levels would be problematic during normal operation of the instrument. Under these conditions, recoveries of Hg within 90–110% were observed for TOC levels as high as 1,970 mg L⁻¹ (Figure 6(b)). It was likely that the FGD wastewater matrix was suppressing the effect of phthalate. Therefore, given this context, it can be assumed that high TOC levels will not cause an interference with the measurement of total Hg in FGD wastewater. However, elevated levels of TOC may cause interferences during analysis of less complex water streams, such as river or seawater.

In addition to interferences from major contaminants in FGD wastewater, some plants may add sulphides (such as organo-sulphides) as part of their process to maximise removal of Hg. The most commonly used organo-sulphide for Hg removal is TMT (US EPA 2009), widely available as TMT-15[®] – a 15% solution of the organo-sulphide salt. Another sulphide that has previously been used in water treatment processes is sodium hydrosulphide (NaHS) (US EPA 2013). The influence of these compounds on Hg recovery is presented in Figure 7.

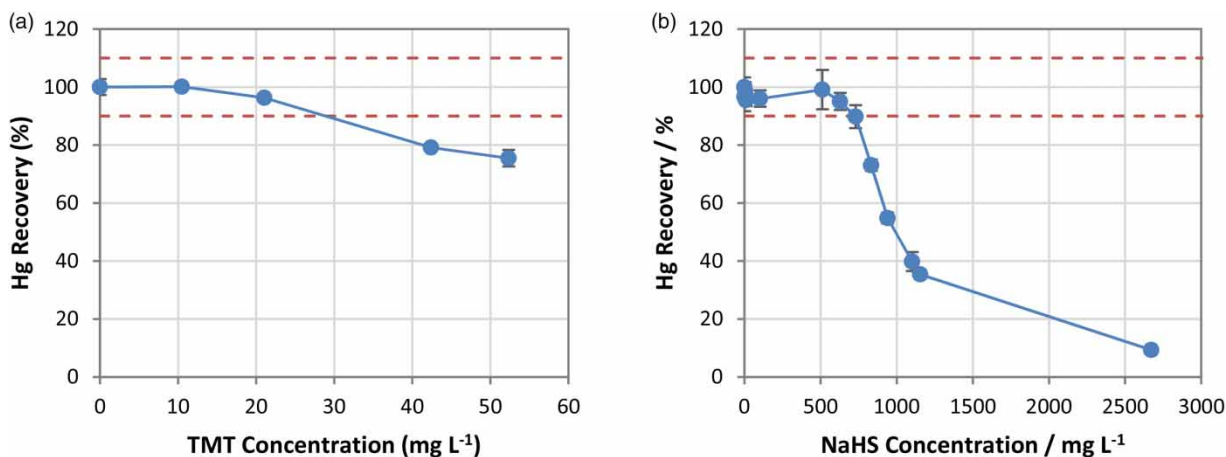


Figure 7 | Recovery of 100 ng L⁻¹ Hg²⁺-spiked standards containing (a) TMT and (b) NaHS. Error bars represent one standard deviation of four replicates.

Concentrations of TMT tested ranged from 10.5 to 52.3 mg L⁻¹ (equivalent to 70.0–330 µL L⁻¹ TMT-15[®]). Hg recoveries between 90 and 110% were observed for tested TMT concentrations up to 21.1 mg L⁻¹. However, a noticeable decrease in recovery of Hg was observed as the TMT concentrations were increased further. Therefore, the method may require to be altered to provide accurate results in FGD wastewater treated with greater TMT concentrations, either by employing longer digestion times or with the addition of higher volumes of oxidant to break the Hg-organo-sulphide complex more easily.

NaHS decomposes to gaseous hydrogen sulphide (H₂S) under acidic conditions. The resulting H₂S may cause measurement issues due to sulphur poisoning of the gold trap, as has been previously observed (Ferrara *et al.* 2000). The online method used can accurately measure total Hg in NaHS concentrations up to 730 mg L⁻¹. Analysis of QC standards directly following measurements of higher NaHS concentrations gave 90–110% recovery, which may indicate that the suppression observed is due to the interference in the release of Hg from solution rather than poisoning of the gold trap as recoveries improved instantaneously, even following 2,700 mg L⁻¹ NaHS. Sulphur poisoning of the gold trap likely did not occur due to the use of a soda-lime trap inline, which captures acidic gases.

4. CONCLUSION

A new instrument for online monitoring of Hg in FGD wastewater has been successfully developed in house and on-site at a coal-fired power plant. The use of gold amalgamation, combined with the batch digestion approach, provides high sensitivity, allowing for low detection limits that can achieve the most demanding legislative value of 10 ng L⁻¹. Results of the interference test and the validation against ISO 17852:2006 demonstrate the great robustness of the analyser, especially given the challenging nature of the FGD wastewater matrix, as well as its potential for alternative monitoring applications in future. The analysis method validated here has the capacity to generate two results per hour, which provides a good frequency of analysis for routine monitoring. However, the work here has demonstrated that the frequency may be improved to four results per hour after assessment of the matrix. The instrument also offers the ability to increase the quantity of reagents used for digestion if required.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

REFERENCES

- Andalib, M., Arabi, S., Dold, P. & Bye, C. 2016 *Mathematical modeling of biological selenium removal from flue gas desulfurization (FGD) wastewater treatment*. *Water Environment Federation* **2016** (11), 228–248.
- Bogacki, J., Marcinowski, P., Majewski, M., Zawadzki, J. & Sivakumar, S. 2018 *Alternative approach to current EU BAT recommendation for coal-fired power plant flue gas desulfurization wastewater treatment*. *Processes* **6** (11), 229.
- Commission Implementing Decision (EU) 2017/1442 of 31 July 2017 Establishing Best Available Techniques (BAT) Conclusions, under Directive 2010/75/EU of the European Parliament and of the Council, for Large Combustion Plants. Available from: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32017D1442> (accessed 4 December 2020).
- Conidi, C., Macedonio, F., Ali, A., Cassano, A., Criscuoli, A., Argurio, P. & Drioli, E. 2018 *Treatment of flue gas desulfurization wastewater by an integrated membrane-based process for approaching zero liquid discharge*. *Membranes* **8** (4), 117.
- Córdoba, P. 2015 *Status of Flue Gas Desulphurisation (FGD) systems from coal-fired power plants: Overview of the physico-chemical control processes of wet limestone FGDs*. *Fuel* **144**, 274–286.
- EPRI 2013 *EPRI Comments on Proposed Effluent Limitations Guidelines Rule*. EPRI, Palo Alto, CA. 3002002231.
- Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E. & Pirrone, N. 2000 *Volcanoes as emission sources of atmospheric mercury in the Mediterranean basin*. *Science of the Total Environment* **259** (1–3), 115–121.

- Fletcher, S., Miranda, A., Paiva, J., Benoliel, M. J. & Almeida, C. M. M. 2020 Optimization and in-house validation of the TDA-AAS method for mercury control in water and wastewater treatment plant sludges. *Analytical Methods* **12** (45), 5503–5513.
- Gochfeld, M. 2003 Cases of mercury exposure, bioavailability, and absorption. *Ecotoxicology and Environmental Safety* **56** (1), 174–179.
- Han, X., Liu, M., Yan, J., Karellas, S., Wang, J. & Xiao, F. 2020 Thermodynamic analysis of an improved flue gas pre-dried lignite-fired power system integrated with water recovery and drying exhaust gas recirculation. *Drying Technology* **38** (15), 1971–1987. <https://doi.org/10.1080/07373937.2019.1607871>.
- Huang, Y. H., Peddi, P. K., Zeng, H., Tang, C.-L. & Teng, X. 2013 Pilot-scale demonstration of the hybrid zero-valent iron process for treating flue-gas-desulfurization wastewater: Part i. *Water Science and Technology* **67** (1), 16–23.
- Huang, M. H., Chen, W. H., Trinh, M. M. & Chang, M. B. 2023 Mass flows and characteristic of mercury emitted from coal-fired power plant equipped with sewer flue gas desulfurization. *Sustainable Environment Research* **33**, 8. <https://doi.org/10.1186/s42834-023-00168-9>.
- International Organization for Standardization 2006 *Water quality – Determination of mercury – Method using atomic fluorescence spectrometry (ISO 17852:2006)*. June 2006.
- Koenig, A. & Liu, L. 2004 Autotrophic denitrification of high-salinity wastewater using elemental sulfur: Batch tests. *Water Environment Research* **76** (1), 37–46.
- Marcinowski, P., Bogacki, J., Majewski, M., Zawadzki, J. & Sivakumar, S. 2019 Application of aluminum-based coagulants for improving efficiency of flue gas desulfurization wastewater treatment in coal-fired power plant. *E3S Web of Conferences* **108**, 02006.
- Masoomi, I., Heidel, B., Schmid, M. O. & Scheffknecht, G. 2020 Effect of additives on mercury partitioning in wet-limestone flue-gas desulfurization. *Clean Energy* **4** (2), 132–141.
- Niksa, S. & Fujiwara, N. 2005 Predicting extents of mercury oxidation in coal-derived flue gases. *Journal of the Air and Waste Management Association* **55** (7), 930–939.
- ORSANCO 2013 *Investigation of Mercury and Methyl Mercury Discharges From Flue Gas Desulfurization Systems at Four Coal-Fired Power Generation Facilities on the Ohio River*. Cincinnati, OH.
- Pereyra, M. T., Lista, A. G. & Fernández Band, B. S. 2013 Quantification of uncertainty in mercury wastewater analysis at different concentration levels and using information from proficiency test with a limited number of participants. *Talanta* **111**, 69–75.
- Potter, B. B. & Wimsatt, J. C. 2012 USEPA method 415.3: Quantifying TOC, DOC, and SUVA. *American Water Works Association* **104** (6), 358–369.
- Protection of Environment, C.F.R. 40 § 136 Revised as of June 30, 1986 (1984)
- Protection of Environment, C.F.R. 40 § 423. e-CFR current as of Feb 2021. Available from: <https://www.ecfr.gov/> (accessed 13/02/2021).
- Protection of Environment, C.F.R. 40 § 423 Revised as of July 1, 2018 (1982).
- Sánchez-Rodas, D., Corns, W. T., Chen, B. & Stockwell, P. B. 2010 Atomic fluorescence spectrometry: A suitable detection technique in speciation studies for arsenic, selenium, antimony and mercury. *Journal of Analytical Atomic Spectrometry* **25** (7), 933–946.
- Srivastava, R. K., Hutson, N., Martin, B., Princiotta, F. & Staudt, J. 2006 Control of mercury emissions from coal-fired electric utility boilers. *Environmental Science and Technology* **40** (5), 1385–1393.
- Staicu, L. C., Morin-Crini, N. & Crini, G. 2017 Desulfurization: Critical step towards enhanced selenium removal from industrial effluents. *Chemosphere* **172**, 111–119.
- Sun, M., Hou, J., Tang, T., Lu, R., Cheng, L. & Xu, X. 2012 Stabilization of mercury in flue gas desulfurization gypsum from coal-fired electric power plants with additives. *Fuel Processing Technology* **104**, 160–166. <http://dx.doi.org/10.1016/j.fuproc.2012.05.008>.
- Syversen, T. & Kaur, P. 2012 The toxicology of mercury and its compounds. *Journal of Trace Elements in Medicine and Biology* **26** (4), 215–226. <http://dx.doi.org/10.1016/j.jtemb.2012.02.004>.
- UN Environment 2019 *Global Mercury Assessment 2018*. UN Environment Programme, Chemicals and Health Branch Geneva. Switzerland. Available from: <http://www.unep.org/gc/gc22/Document/UNEP-GC22-INF3.pdf>.
- US Environmental Protection Agency 2020 40 CFR part 423 steam electric reconsideration rule. *Federal Register* **85** (198), 64650–64723.
- U.S. Environmental Protection Agency 2005 *Method 245.7: Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry (EPA-821-R-05-001)*.
- U.S. Environmental Protection Agency 2009 *Steam Electric Power Generating Point Source Category: Final Detailed Study Report (EPA 821-R-09-008)*.
- U.S. Environmental Protection Agency 2013 *Optimization Review French Gulch/Wellington-Oro Mine Site Water Treatment Plant Breckenridge, Summit County, Colorado (EPA 542-R-13-013)*.
- U.S. Environmental Protection Agency 2015 *Technical Development Document for the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category (EPA-821-R-15-007)*.
- U.S. Environmental Protection Agency 2002 *Method 1631 Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry (EPA-821-R-019)*.
- Wei, C., He, W., Wei, L., Ma, J. & Li, C. 2017 The performance and microbial communities of biodegradation-electron transfer with sulfur metabolism integrated process for flue gas desulfurization wastewater treatment. *Bioprocess and Biosystems Engineering* **40** (10), 1543–1553.
- Yudovich, Y. E. & Ketris, M. P. 2005 Mercury in coal: A review. Part 1. Geochemistry. *International Journal of Coal Geology* **62** (3), 107–134.

- Zhao, S., Pudasainee, D., Duan, Y., Gupta, R., Liu, M. & Lu, J. 2019 A review on mercury in coal combustion process: Content and occurrence forms in coal, transformation, sampling methods, emission and control technologies. *Progress in Energy and Combustion Science* **73**, 26–64.
- Zheng, L., Jiao, Y., Zhong, H., Zhang, C., Wang, J. & Wei, Y. 2020 Insight into the magnetic lime coagulation-membrane distillation process for desulfurization wastewater treatment: From pollutant removal feature to membrane fouling. *Journal of Hazardous Materials* **391** (January), 122202. <https://doi.org/10.1016/j.jhazmat.2020.122202>.

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