DETERMINATION OF DISSOLVED ELEMENTAL MERCURY IN SURFACE AND INDUSTRIAL WATERS

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DOLOČANJE RAZTOPLJENEGA ELEMENTARNEGA ŽIVEGA SREBRA V POVRŠINSKIH IN INDUSTRIJSKIH VODAH

Doktorska disertacija

Supervisor: Prof. Dr. Milena Horvat

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Abstract

Mercury (Hg) is a toxic metal that occurs naturally in the Earth's crust principally as the ore cinnabar, HgS, but centuries of human activities such as mining and fossil fuel burning have been mobilizing increasing amounts in the atmosphere, oceans, and terrestrial systems. It is emitted to the atmosphere from a variety of natural and anthropogenic sources after which it redistributes globally via a complex combination of chemical, physical, and biological processes throughout the atmosphere and the rest of the environment. Due to its volatility and long residence time, it can travel long distances and is therefore considered a global pollutant. The recently signed global treaty "Minamata Convention" acknowledged the negative impacts of mercury on humans and ecosystems at the global scale and it primarily aims at the reduction of mercury emissions, particularly from current anthropogenic sources. Among these, coal burning power plants represent the greatest source, followed by other industrial sectors using high temperature processes. In recent years clean technologies have been developed, which significantly reduced the emissions of Hg(0) into the atmosphere. In the coal burning sector wet desulphurisation equipment (WFGD) with forced oxidation has shown to be very effective. Removal efficiency is commonly monitored by Hg measurements in the emitted flue gas, but these measurements are costly and time-consuming. These methodologies are still not fully optimized therefore comparability of the results is questionable.

In the WFGD systems elemental Hg is oxidized and trapped in the slurry solution; however, a small fraction of dissolved elemental mercury (DEM) leaves the WFGD and is emitted to the atmosphere through the stack gas. It has been suggested that by accurate and continuous measurements of DEM in the slurry solution it is possible to follow the oxidation/reduction processes in the WFGD slurry and estimate the quantity of Hg emitted to the flues gas. In order to simplify the protocol for checking the emissions of Hg(0) through the flue gas, we proposed the determination of DEM in the scrubber solution as a measure of Hg removal efficiency.

In natural waters Hg exists in different forms such as inorganic mercury (Hg(II)) compounds, dissolved elemental mercury (DEM), mono methyl mercury compounds (MeHg) and dimethyl mercury (DMeHg). These forms can be present in dissolved forms and/or adsorbed on suspended particles. DEM and DMeHg are gaseous forms at room temperature and are present as dissolved gaseous Hg (DGM) forms. While DMeHg is rarely found in natural waters, DEM can represent a significant fraction (up to 50%) of total Hg in surface waters. The evasion of DEM as Hg(0) from surface waters represents one of the most important sources of elemental Hg in the global atmosphere. Hg(II) compounds are frequently named "reactive mercury (RHg)" which is an operationally defined fraction of mercury determined after reduction of Hg(II) in aqueous solution by stannous chloride. The methods for DEM determination in surface waters as well as RHg have not been standardized as yet.

The main objective of the present PhD was to develop and validate a simplified semi-continuous method which enables DEM and RHg measurements in both natural waters and in the the scrubber solution of the WFGD.

Analytical methods used for determining DEM are conventionally based on the removal of Hg(0) by purging, pre-concentration on gold and detection by either cold vapour atomic absorption (CV AAS) or atomic fluorescence spectrophotometry (CV AFS). At present there is no agreed protocol for the measurement of DEM in aqueous samples. A new method has been developed in this work which is based on continuous stripping of DEM by mercury free nitrogen in a flow injection mode and detection by CV AAS. The partitioning of Hg(0) between aqueous and gas phases is largely dependent on the composition of the former. Moreover, calibration using the standard addition method was not possible due to the reactivity of DEM and RHg introduced from calibration solutions. Calibration is therefore done by reference measurements using a manual method for DEM involving quantitative removal and CV AFS detection. DEM was then determined in the water sample by applying the partitioning factor. The optimized method is precise, sensitive and linear over a wide concentration range. It has provided comparable results with the manual method when applied on board a research vessel in the Mediterranean Sea (20 to 50 pg L^{-1}) and during a pilot laboratory scale experiment on industrial aqueous media from wet flue gas desulphurisation equipment (2 to 300 ng L^{-1}).

By adding an additional line in the system which enables a flow of tin chloride (used as a reducing agent) to be introduced continuously into the system, the method was successfully adopted and applied also for RHg measurements in the scrubber solution. The existing manual method was used as a reference method along with the semi-continuous one. Good comparability of the data was obtained regardless of the sample matrix. We were able to track changes in Hg chemistry depending on different physical/chemical factors of the natural and industrial water media (scrubber solutions). Such measurements have not been conducted yet in scrubber solutions of WFGD due to large difficulties related to the sample matrix. The intention of this PhD, however, was not to discuss the parameters affecting the chemistry of Hg in aqueous media but to demonstrate the ability of the analytical method to accurately track the changes. In natural waters this is important in order to better estimate Hg(0) emissions from water surfaces into the atmosphere and to determine the availability of Hg(II) to be methylated. In the scrubber solutions, the accurate determination of DEM and RHg can be used as a tool to improve the efficiency of cleaning technologies.

The PhD also addressed some aspects of the analytical protocol that contribute considerably to the uncertainty of the results. These include the (i) stability of DEM and RHg in aqueous samples, (ii) passivation of gold traps used for preconcentration of Hg(0) prior to detection on CV AAS, and (iii) calibration using gaseous Hg at saturated conditions and Hg(II) in aqueous media.

(i) As both species, DEM and RHg, are unstable, their stability in relation to storing conditions including temperature and exposure to light and the addition of storage agents was studied. The tested water matrices included: freshwater and seawater samples and scrubber solutions. The results showed good performance for freshwater samples and a maximum of three hours was found to be not critical for DEM measurements when stored in glass bottles in dark conditions. The use of HNO_3 and $AuCl_3$ as agents for preserving the samples demonstrated the oxidation of Hg(0) into Hg(II) and the formed Hg(II) was stable for 2-3 days. Preservation of RHg and DEM is therefore not possible.

(ii) The most widely used material for mercury pre-concentration is gold-coated silica oxide which tends to be passivated over extended period of time. This results in irreproducible and lower signals during measurements. It was found that this is

due to inhomogeneity of the coating of the surface and reactivity of SiO_2 substrate at higher temperatures. A new substrate, alumina, was used and coated with a nano-layer of Au and was tested with very promising results; however, longer time testing is needed to ascertain the resistance towards passivation. The obtained results were very promising, but further work is needed. As humidity was found to affect the performance of gold traps and the measurement system, various drying procedures were tested, among which soda lime traps showed best results.

(iii) Recent detailed studies have shown that Hg(0) measurements are questionable due to systematic biases in calibration. Several empirical equations are available to describe the vapour pressure of mercury at a given temperature, which is the basis for calibrating Hg instruments. The agreement between these equations differs by 5% or more. In order to remove the dependence of mercury vapour measurement on these empirical equations, and to provide stability, comparability and coherence for mercury vapour measurements, the calibration in present work was also done by Hg(II) calibration solution certified for Hg content. The results obtained by two methods provided comparable results; therefore instrument calibration was mainly done with Hg(0) vapour.

Povzetek

Živo srebro (Hg) je strupena kovina, ki je naravno prisotna v zemeljski skorji. Dejavnosti, kot so rudarjenje Hg, kurjenje fosilnih goriv, ter raba Hg v industrijskih procesih in produktih so mobilizali večje količine Hg atmosfero, vode, in kopenske ekosisteme. Zaradi kompleksnih biogeokemijskih procesov v okolju in prehanja med vodo, kopnim in zrakom je Hg prisoten povsod. Ker je elementarni Hg hlapen pri sobni temperaturi in se v atmosferi zadržuje dalj časa, lahko z zračnimi masami potuje na dolge razdalje, zato Hg uvrščamo med globalna onesnažila. Pred kratkim podpisana globalna konvencija imenovana "*Minamata Convention*" izpostavlja negativne vplive Hg na zdravje ljudi in ekosistemov na globalnem nivoju, zato je zmanjševanje emisij Hg v atmosfero med prioritetnimi nalogami. Med pomembne vire, ki prispevajo Hg v atmosfero, spadajo kurjenje fosilnih goriv, zlasti premoga, ter ostale visokotemperaturne tehnologije, kot na primer cementarne in livarne. V zadnjih letih so bile razvite čiste tehnologije, ki so bistveno zmanjšale emisije elementarnega Hg (Hg(0)) v ozračje. Med te spadajo tudi postopki za mokro razžvepljevanje dimnih plinov (RDP). Učinkovitost odstranjevanja se običajno spremlja z meritvami Hg v dimnih plinih, vendar so te meritve drage in zamudne. Prav tako so te metode še vedno v razvoju, zato je primerljivost rezultatov rezultatov še vedno vprašljiva.

V sistemih WFGD se Hg(0) oksidira in se zato zadrži v raztopini, le majhen del le-tega zapusti WFGD in se nato sprošča v ozračje skozi dimnik. Ker je Hg(0) v plinastem stanju se v tem procesu razporedi med plinsko in vodno fazo. S natančnim in kontinuirnim merjenjem razstopljenega elementarnega Hg (*dissolved elemental mercury – DEM*) je možno spremljati procese oksidacije in redukcije Hg v razstopini RDP. Namen te naloge je bil zato razviti enostavno metodo za merjenje DEM in Hg(II) v raztopini RDP kot potencialnega indikatorja uspešnosti odstranjevanja Hg v RDP.

V naravnih vodah Hg obstaja v različnih oblikah, kot so anorganske Hg spojine (Hg(II)), raztopljeni elementarni Hg (DEM), mono metil spojine (MeHg) in dimetil Hg (DMeHg). Te oblike so lahko prisotne v raztopljenih oblikah in / ali adsorbirane na suspendiranih delcih. DEM in DMeHg sta hlapni obliki pri sobni temperaturi. DMeHg se redko nahaja v naravnih vodah, DEM pa lahko predstavlja pomemben delež (do 50%) celotnega Hg v površinskih vodah. DEM iz površinskih vod prehaja v ozračje, zato predstavljajo vodne površine enega najbolj pomembnih virov Hg v globalno ozračje. Hg(II) spojine pogosto imenovane kot "reaktivno živo srebro (RHG)", predstavljajo operativno frakcijo Hg, ki se določa tako, da se v vodnih razstopinah dvovalentne spojine Hg reducirajo z $SnCl_2$, nastali elementarni Hg pa določamo z metodo atomske absorpcije hladnih par (CV AAS). Metode za določanje DEM v površinskih vodah, kot tudi RHG še niso standardizirane.

Glavni cilj doktorskega dela je bil razviti in potrditi enostavno kontinuirno metodo za določanje DEM in RHG v naravnih vodah in razstopininah RDP.

Analitske metode, ki se uporabljajo za določanje DEM običajno temeljijo na odstranjevanju Hg(0) s prepihovanjem, pred-koncentriranjem na zlato, desorpcijo s segrevanjem zlatih pasti in uvajanjem par Hg(0) v detektor, ki lahko bazira na atomski absorpciji ali fluorescenci hladnih par Hg(0) (AAS HP ali AFS HP). Metodologije za določanje DEM niso standardizirane, zato je primerljivost rezultatov vprašljiva. Metoda, ki je bila razvita v tem delu, temelji na kontinuirnem pretočnem sistemu, kjer pretoku

tekočega vzorca dodajamo dušik. V pretočnem sistemu se Hg(0) razporedi med tekočo in plinsko fazo, po ločitvi teh dveh faz pa elementarni Hg prehaja v AAS HP detektor. Razporeditev Hg(0) med vodno in plinsko fazo je v veliki meri odvisna od sestave razstopine. Kalibracija sistema z uporabo metode standardnega dodatka ni bila možna zaradi reaktivnosti Hg(0) in Hg(II). Za umerjanje pretočne kontinuirne metode smo zato morali uporabiti referenčne meritve, ki bazirajo na kvantitavnem odstranjevanju Hg(0) iz razstopine. DEM pa smo potem izračunali z uporabo faktorja porazdelitve. Optimizirana kontinuirna metoda je natančna, občutljiva in linearna v širokem razponu koncentracij. Uporabnost metode smo testirali na krovu raziskovalne ladje v zahodnem delu Sredozemskega morja, kjer smo potrdili uporabnost metode pri koncentracijah med 20 do 50 pg/L. Medotodo smo uporabili tudi pri obratovanju pilotne laboratorijske naprave za RDP, kjer smo potrdili premerljivost rezultatov DEM v razponu med 2 do 300 ng/L.

Metodo smo optimizirali tudi za merjenje Hg(II) ali RHg v raztopini tako, da smo v pretočni sistem dodali še dodatno linijo za vnos kositrovega klorida, ki se uporablja kot reducent. Nastali Hg(0) smo nato merili po principu DEM. Rezultate smo primerjali z referenčnimi meritvami, ki smo jih dobili s kvantitaivnim prepihovanjem reduciranega Hg na zlato past in detekcijsko metodo AFS HP.

Metodi za merjenje DEM in Hg(II) smo uporabili za spremljanje prisotnosti obeh oblik v pilotni napravi RDP. Spremljanje prisotnosti obeh oblik je namreč pomembno za razumevanje vpliva različnih fizikalno/kemijskih dejavnikov v razstopini RDP, ki ograjo ključno vlogo pri odstranjevanju Hg v teh napravah. Tovrstne meritve se v praksi ne izvajajo zaradi kompleksnosti povezanih z matrico vzorca. Natančno razumevanje teh procesov v RDP sicer presega obseg tega doktorskega dela, vendar lahko z gotovostjo potrdimo, da se je analizna metoda pokazala kot priemerna za sledeneje prisotnosti Hg(0) in Hg(II) v razstopini RDP pri pilotnih poskusih.

Doktorsko delo pa obravnava tudi nekatere pomembne vidike analitskega protokola, ki bistveno prispevajo k negotovosti rezultatov. Ti vključujejo (i) stabilnost DEM in RHG v vodnih vzorcih, (ii) učinkovitost zlatih pasti, ki se uporabljajo za predkoncetracijo Hg(0) in (iii) aspekte pravilne kalibracije.

(i) Obe obliki Hg, DEM in RHG, v vodnih vzorcih sta nestabilni. Pravilno vzorčenje in shranjevanje je zato ključnega pomena za pravilnost rezultatov. Preučevali smo časovno stabilnost pri različni temperaturi in izpostavljenosti dnevni svetlobi. Testirali smo stabilnost DEM in RHG v sladkovodnih in morskih vodah ter raztopinah RDP. Obe obliki sta stabilni pri vseh preiskovanih vzorcih v temi do največ treh ur. Uporaba kislin, kot je HNO_3 z dodatkom $AuCl_3$, ki jih priporoča literatura, ni priporočljiva saj prihaja do oksidacije Hg(0). Analize DEM in RHG je torej potrebno opraviti v najkrajšem možnem času oz. na mestu vzorčenja.

(ii) Zlato, ki je nanešeno v tankem sloju na nosilcu, kot je SiO_2, je v analitiki Hg najbolj pogosto v uporabi. Žal pa pri daljši uporabi teh pasti prihaja do pasivacije, kar posledično vodi do nižjih in neponovljivih meritev. V tem delu smo zato pripravili nove pasti, kjer je zlato naneseno na Al_2O_3. Dobljeni rezultati so bili izjemno ponovljivi ter neobčutljivi na vlago. Pasivacije pasti v okviru tega doktorskega nismo zaznali, kar kaže na veliko potencialno uporabnost teh pasti pri praktičnem delu v bodoče.

(iii) Večina sistemov za kalibracijo detektorjev za merjenje Hg uporablja Hg(0) paro, ki jo odvzamemo z natančnim volumnom iz zaprtih naprav pri določeni temperaturi. Empirične enačbe, ki definirajo koncentracijo Hg pri določenem parnem tlaku in temperaturi, ki so podlaga za umerjanje Hg instrumentov, kažejo odstopanja med 5 do 8%. Pri našem delu smo preverili kalibracijske naprave z umerjenjem po dveh metodah: s Hg paro ter vodnimi raztopinami certificiranih refenčnih materialov. Naklona umeritvenih premic za obe metodi sta bili identični, zato smo zaradi enostavnosti večino meritev umerjali s Hg(0) paro.

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Abbreviations

CRM	. . .	Certified Reference Material
CV AAS	. . .	Cold Vapour Atomic Absorbance Spectrometry
CV AFS	. . .	Cold Vapour Atomic Fluorescence Spectrometry
EPA	. . .	Environmental Protection Agency
ESP	. . .	Electrostatic Precipitators
FF	. . .	Fabric Filters
WFGD	. . .	Wet flue gas desulphurization
IC-ICPMS	. . .	Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry
ICP-AES	. . .	Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS	. . .	Ion Chromatography-Inductively Coupled Plasma Mass Spectrometry
LSFO	. . .	Limestone Forced Oxidation
NAA	. . .	Neutron Activation Analysis
NIST	. . .	National Institute Of Standards And Technology
SCR	. . .	Selective Catalytic Reduction
UNEP	. . .	United Nations Environment Programme
GMOS	. . .	Global Observation system
CNR	. . .	Italian National Research Council
SLT	. . .	Sodalime trap
Hg(0)	. . .	Elemental mercury
Hg(I)	. . .	Mercurous ion (Hg_2^{2+})
Hg(II)	. . .	Mercuric ion (Hg^{2+})
Hg_p	. . .	Mercury particulate
LOD	. . .	Limit of detection
LOQ	. . .	Limit of quantification
THg	. . .	Total mercury
DGM	. . .	Dissolved gaseous mercury
DEM	. . .	Dissolved elemental mercury
DMeHg	. . .	Dimethyl mercury
MeHg	. . .	Methyl mercury
RHg	. . .	Reactive mercury
FLPE	. . .	Fluorinated High-density Polyethylene
PETG	. . .	Poly Ethylene Tetraphthalate Copolyester
FEP	. . .	Teflon bottles
PC	. . .	Poly carbonated
HCl	. . .	Hidrochloric acid
HNO_3	. . .	Nitric acid

Chapter 1

Introduction

Mercury is considered a global pollutant (Fitzgerald et al., 2007, Pirrone et al., 2009) due to its ability to undergo long−term transport in the atmosphere, its transformations between different species, and its ability to enter and accumulate in the food chain. It exists in several chemical forms in different environments (air, water, soil, living organisms).

The most common form of Hg in the atmosphere is elemental mercury (Hg(0)). Inorganic mercury (Hg(II)) and mercury bound to particles (Hg_p) are also present, but at much lower concentrations. Hg(0) in the atmosphere is rather stable, therefore it can travel long distances before it is oxidized and deposited. Hg(II) and Hg_p have shorter lifetimes compared to Hg(0) and enter aquatic and terrestrial environments where they undergo transformation processes. Mercury is toxic in all forms. Toxicity depends on the chemical form, route and mode of exposure (inhalation vs. ingestion; acute vs. chronic), dose and susceptibility of a person. The damage caused by MeHg is irreversible, which is not the case for inorganic Hg. Because of its toxicity, Hg is probably the most studied of all trace elements in the environment. Since the early 1960s, growing awareness of environmental mercury pollution (e.g., the Minamata tragedy resulting from MeHg poisoning) has stimulated the development of more accurate, precise and efficient methods of determining mercury and its compounds in a wide variety of matrices (Horvat, 2005).

In uncontaminated natural aquatic systems, Hg is present at trace levels (Horvat et al., 2003) ranging from a few pg L^{-1} to few ng L^{-1}. The chemical form of Hg in aquatic systems is strongly influenced by redox conditions, pH, and the concentrations of inorganic and organic complexing agents (Ullrich et al., 2001, Whalin et al., 2007). Other factors such as temperature, solar radiation, chemical composition (in particular salinity), the presence of suspended matter and microorganisms, also play important roles. As a result, Hg in aquatic systems exists in a variety of forms: monomethyl mercury, MeHg (with a chemical formula of CH_3Hg^+), Hg bound to particles (Hg_p), inorganic Hg forms (Hg(II)) so-called reactive mercury (RHg) and dissolved gaseous mercury (DGM) forms: dimethylmercury (DMeHg) and dissolved elemental mercury (DEM). MeHg is considered the most toxic form of Hg in the environment due to its ability to enter the food chain where it bioaccumulates and biomagnifies (Fitzgerald et al., 1991). The consumption of fish is the primary source of MeHg exposure to humans (Mergler et al., 2007). RHg in water is not yet very well defined but it is considered as the easily accessible divalent mercury fraction available for reduction and/or complexation (Liang et al., 2013). When reduced, Hg(II) is converted into Hg(0), which represents the predominant gaseous form of Hg in the water media (DEM). The species which this research focuses on are the DEM and RHg as primarily important in the biogeochemical cycle of Hg.

The presence of DEM in water was proved by Sanemasa et al., 1971 when checking the solubility of Hg related to temperature by applying Henry's low. Due to its high Henry's constant and the presence in the atmosphere, DEM is basically the primary constituent of DGM (about 95 %) compared to DMeHg. The volatilization of Hg(0) from water surfaces represents an important Hg flux for many aquatic systems (Costa and Liss, 2000, Costa and Liss, 1999) and it has important biogeochemical implications because it can not only decrease mercury half-life in the water, but also affects its wider geographical dispersion to other environments (Poulain et al., 2006). DMeHg is reported to be the dominant organic form of Hg in deeper waters (Horvat et al., 2003, Kotnik et al., 2007) and it is not found in surface waters due to transformations while 'traveling' toward the surface.

There is a biogeochemical cycle of Hg in the environment by which the mentioned species interchange between atmospheric, aquatic and terrestrial environments (Selin et al., 2009, Mason et al., 2002, Lamborg et al., 2002). Processes such as oxidation/reduction reactions, complex formation, phase transitions, biodegradation, and surface and heterogeneous interactions with aerosols, clouds, snow, and ice convert mercury from one species to another. Physical mechanisms such as wind flux, runoff, and dry and wet deposition transport elemental and oxidized mercury species from one place to another. After being released to the environment, there are no boundaries for Hg transport. Evasion of Hg from surface waters represents an important source of Hg in the environment.

Despite natural sources, emissions from the combustion industry are of great concern. The combustion processes account for more than 80% of the anthropogenic mercury emissions to the atmosphere. In recent years clean technologies have been developed that significantly reduce the emissions of Hg through stack gases (Pavlish et al., 2003). It has been shown that wet desulphurisation equipment can also effectively remove Hg (Stergaršek et al., 2010, Stergaršek et al., 2013). The removal efficiency depends on a variety of factors and it is achieved by modifying the chemistry of the scrubber solution.

Frequent measurements of Hg in aqueous environments are of high importance in following Hg chemistry. The existing analytical methods for DEM are classified as manual (discontinuous) methods and semi-continuous methods, which are automated. The conventional manual method consists of purging a certain volume of water sample and the resulting Hg(0) is pre-concentrated on gold (Au) traps for further quantification by CV AFS as more sensitive than CV AAS. The same is applied for measurements of Hg(II), with the difference that a reducing agent such as tin chloride ($SnCl_2$) is added to the sample prior to purging. Usually the analysis time with the manual method is longer than the changes in DEM chemistry in a certain water system. Therefore, methods with higher frequency of measurements are required. For this reason, semi-continuous methods have been developed and applied for DEM measurements in different natural water matrixes (freshwater and seawater). They are based either on the equilibrium between gaseous and liquid phases or on quantitative removal of DEM from the solution. The first do not assure quantitative removal of DEM but measure the concentration of Hg(0) stripped in the gaseous phase which is further converted into DEM concentration in the aqueous phase by applying appropriate mathematical models. To our knowledge, none of the semi-continuous/continuous methods has been applied to conduct DEM and RHg measurements in the scrubber solution of a WFGD.

The purpose of the present PhD was, therefore, to optimize and improve the analytical procedures for the determination of the mentioned species in two applications: in natural surface waters and in the wet flue desulfurization slurry solution. Firstly, an overview of the Hg cycling in the environment is described together with Hg sources in the environment. In addition, we review the analytical techniques used for mercury speciation in surface water samples. Important issues related to the stability of these species in different water matrixes, possible interferences and the pre-concentration techniques used

for Hg measurements are elaborated. Measurements of DEM and RHg in natural waters are important for better estimations of emission rates and the contribution into the atmosphere. However, the only intervention that can be made is reducing Hg emission from anthropogenic sources. Therefore, investigations of Hg behaviour in industrial settings of TPPs equipped with e WFGD system for Hg removal are important. Nowadays, in order to monitor Hg removal efficiency, continuous measurements (CEM) of Hg in stack gas are required by the legislation. CEM systems are not yet fully optimized, resulting in costly and time-consuming measurements. In the case of a wet FGD, mercury speciation can serve as a diagnostic tool for the removal efficiency. To our knowledge such methods have not yet been optimized and applied. Therefore, a semi−continuous method for measuring DEM and RHg in aqueous media was developed and optimised during the PhD. The method is applicable to a wide range of concentrations, from a few tens of pg L^{-1} up to several tens of ng L^{-1}. Moreover, the semi−continuous method detects changes in DEM concentrations in response to physico−chemical factors affecting oxidation−reduction processes in aqueous media, which is useful in environmental and industrial applications. The method is highly sensitive to the composition of the aqueous phase and to the presence of particles, which significantly reduces the partitioning of Hg(0) between gaseous and liquid phases. Direct calibration of the method using standard addition of DEM is not possible for most water samples because of significant losses of Hg(0) due to oxidation, adsorption on particles or changes in solubility.

1.1 Mercury Emission Sources

Hg entering the environment is of natural, anthropogenic or re-emission origin. Once in the environment, Hg cycles between air, soils and waters until it is eventually removed from the system through burial in deep ocean sediments and mineral soils (UNEP/AMAP report, 2013).

Although a lot of work has been done in approaching an accurate estimation of Hg emissions, there are still a lot of uncertainties since the range of the reported values vary from 5500 to 8900 t y^{-1} of emitted Hg (Mason et al., 2012). A detailed description of the major natural and anthropogenic contributions to the atmosphere is given in Figure 1.1.

Natural sources of Hg into the atmosphere are those that arise from natural processes without any anthropogenic intervention. Natural sources of Hg are volcano eruptions, natural volatilization from the ocean surfaces, natural weathering of mercury-containing rocks, and geothermal activity, both of which allow Hg to continuously escape into air and waters. According to the global mercury assessment report by the United Nations Environmental Programme (UNEP, 2013), current Hg emissions to the atmosphere from natural sources are estimated at 80-600 t y^{-1} (Mason et al., 2012), corresponding to about 10 % of total global emissions.

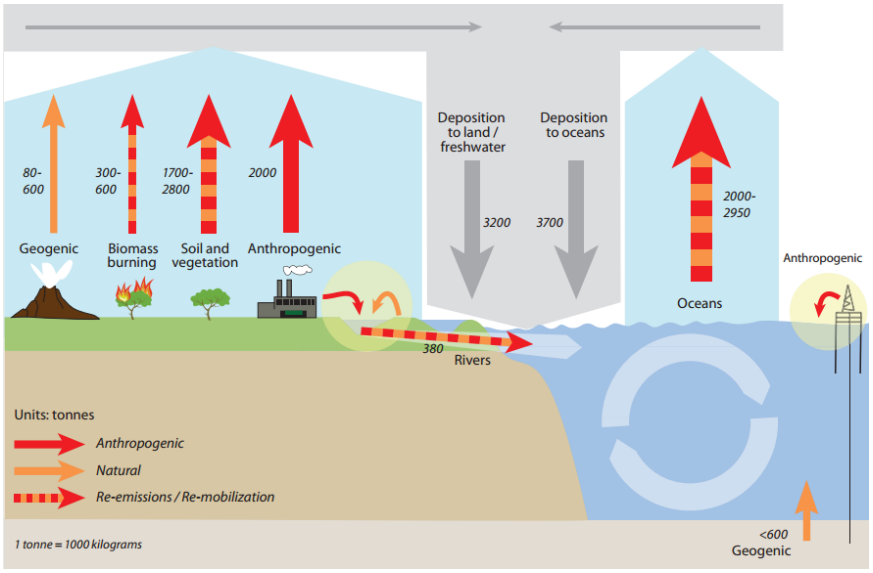


Figure 1.1: Components of the global mercury cycle and the global Hg budget (AMAP/UNEP 2013).

A recent work reported rivers to be an important source of Hg to marine ecosystems, contributing to about 30% of atmospheric inputs (Amos et al., 2014).

Human activity has increased the mobilization of mercury into the environment, raising the amounts in the atmosphere, soils, fresh waters, and oceans. Anthropogenic emissions represent around 30 % of the total amount of Hg entering the atmosphere annually and include: coal burning, mining, smelting and production of iron and non-ferrous metals, cement production, oil refining, artisanal and small-scale gold mining, wastes from consumer products, amalgam dental fillings, the chlor-alkali industry and vinyl monomer industry (UNEP, 2013). Anthropogenic sources are responsible for about 2000 t y^{-1} and the main contributors are artisanal gold mining with about 37.1 % and coal combustion with about 16 % of total annual emissions. The contribution of the Cl-alkali industry is about 1 % while emissions from dental fillings during human cremation represent less than 1 % of all anthropogenic sources (Gaffney and Marley, 2014).

Besides natural and anthropogenic sources, *re-emission* is also a source of Hg into the atmosphere. Re-emission includes Hg releases to the atmosphere from past natural and anthropogenic releases. Estimations of current annual re-emissions to the atmosphere are in the range of 4000-6300 t y^{-1} (Mason et al., 2012) where about 300 t y^{-1} are released due to the evasion of Hg(0) from water surfaces, mainly from oceans. Re-emissions are responsible for 60 % of yearly emissions to the atmosphere (UNEP, 2013). Controlling anthropogenic Hg emissions therefore reduces present-day emissions and also acts to reduce (future) re-emission.

1.2 The Global Cycle of Mercury

After being released into the environment, Hg forms interchange. This leads to the Hg biochemical cycle by which MeHg and Hg(II) compounds, DMeHg and Hg(0) may interchange in the atmospheric, aquatic, and terrestrial environments. Hg cycling in the biosphere is very complex and depends on numerous environmental parameters (Morel et

al., 1998). All mercury forms can be converted into one another by methylation, demethylation, reduction and oxidation processes (Whalin et al., 2007, Monperrus et al., 2007,Celo et al., 2006, Morel et al., 1998). A simplified scheme of the Hg cycle in the environment, transformation pathways in aquatic environments, and the exchange with the atmosphere and sediment is given in Figure 1.2:

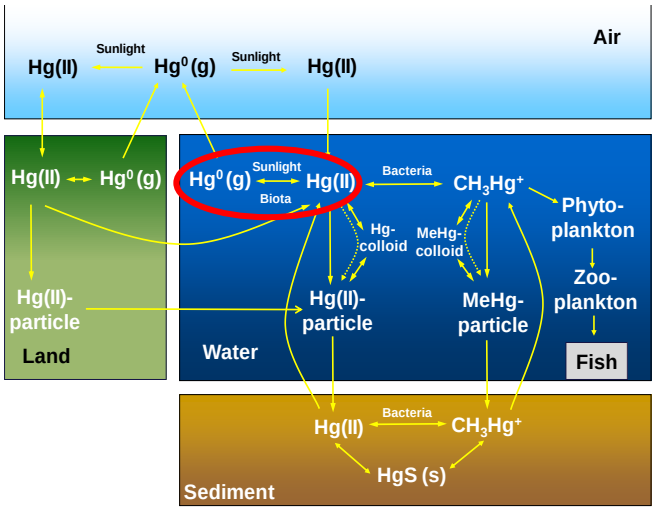


Figure 1.2: A general scheme of the biogeochemical cycle of Hg in the environment (with a focus on the aquatic environment).

After being released into the environment through either anthropogenic or natural sources, Hg is redistributed globally via a complex combination of chemical, physical, and biological processes. Physical mechanisms such as wind flux, runoff, and dry and wet deposition transport elemental and oxidized mercury species from one place to another. Most of Hg released into the atmosphere (about 99%) is in elemental form which undergoes oxidation processes and converts into Hg(II). The process is reversible. The chemical species that act as primary oxidants remain unknown. However, the process is thought to be driven and controlled by oxidants such as Br and OH radicals (Marley et al., 2014). Hg(II) is water soluble and has a shorter lifetime in the atmosphere than Hg(0). Once oxidized, 60 % of atmospheric mercury is deposited on land and 40 % in water (Morel et al., 1998).

Wet and dry deposition brings Hg to the terrestrial surface (UNEP, 2013). Hg(II) formed in the atmosphere can be deposited to the water surfaces by dry and wet deposition and Hg(0) only by dry deposition. Upon deposition, a portion of the oxidized mercury can rapidly re-volatilize to the atmosphere. The reductants of Hg in soil can be species such as Fe^{2+} and humic and fulvic compounds (Gabriel & Williamson, 2004). Reduction and volatilization processes can be enhanced by temperature (Kim et al., 1995, Lindberg et al., 1995) and solar radiation (Gustin et al., 2002).

Hg(II) already deposited can be reduced to Hg(0) which is re-emitted back into the atmosphere where it adsorbs onto particles and is deposited back in land. Reduction of Hg(II) to Hg(0) in the aqueous media can be either biologically and/or photo-chemically mediated. Hg(II) in the aquatic environment can undergo methylation/demethylation processes which are mostly biologically mediated. MeHg is bio-accumulated in aquatic organisms.

On the other hand, Hg(II) deposited in aquatic sediments can either be converted by microbes into MeHg or can be biologically reduced to Hg(0) which is further released into

the water body. A very important factor affecting increased amounts of Hg(0) in deep layer waters is tectonic activity. This is particularly observed in the Mediterranean Sea and described in detail in (Horvat et al., 2003). Despite considerable amounts of literature related to this topic, the behaviour of mercury and the processes of its conversion and distribution in natural aquatic environments are poorly understood and recognized. The literature on Hg biogeochemistry is very extensive; however, the intention of this introduction is not to review the available literature. More information regarding Hg chemistry in aqueous media will be provided in the following chapter.

1.2.1 Mercury in natural waters

Mercury exists in two oxidation states: +1 (the mercurous ion with a chemical formula Hg_2^{2+}, abbreviated Hg(I)) and +2 (the mercuric ion with the formula Hg^{2+}, abbreviated Hg(II)). Hg(I) is naturally stable only within very limited environmental conditions. It is only stable as a dimer (Hg_2^{2+}) in aqueous solution. Given that it rapidly and reversibly disproportionates to give Hg(0) and Hg(II), analytical methods used to determine it in water media are rarely reported and difficult to be applied due to instability of the species.

$$Hg_2^{2+} \leftrightarrow Hg^0 + Hg^{2+} \qquad (1)$$

Oxidation of Hg(0) into Hg_2^{2+} does not occur naturally, because the oxidizing agent which can enable this reaction should have potentials in the range from –0.80 V to –0.85 V and there are no natural oxidizing agents in this range. As a result, oxidation of Hg(0) will only form Hg(II).

There are many parameters (e.g pH, redox potential, organic matter) that influence Hg chemistry in aquatic environments. There is a constant interchange between Hg species, especially between Hg(0), Hg(II) and MeHg. Hg(II) in surface waters is present as complexed to hydroxide ($Hg(OH)^+$, $Hg(OH)^{3-}$) and to chloride ($HgCl^+$, HgClOH, $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$) ions depending on the pH and the chloride concentrations. In the water of oxidative properties the dominant compounds are $HgCl_4^{2-}$ and $HgOH^+$, while in reductive environments, CH_3HgS^- and HgS_2^- are the dominant species.

Hg(II) can also form organometallic compounds. The most common environmental forms are MeHg (CH_3Hg^+) and DMeHg (CH_3HgCH_3). The oxidation of Hg(0) into Hg(II) is an essential step leading to the methylation of Hg(II), as Hg(0) will not convert directly to MeHg in natural environments. The back conversion is also possible. However, methylation and demethylation processes highly depend on the redox potential.

In waters with low pH the most common Hg compounds are soluble ones such as $HgCl_2$ and CH_3Hg^{2+}, whereas in mildly alkaline conditions the dominant species are the dissolved gaseous species such as elemental Hg and $(CH_3)_2Hg$. Hg(0) is the dominant species in the surface waters while DMeHg is reported to be the dominant organic species in deeper oceanic waters (Fitzgerald et al., 2007, Mason et al., 2012, Horvat et al., 2003, Kotnik et al., 2007). Increased levels of DMeHg in deep waters suggest its formation in low-oxygen zones (Cossa and Sanjuan, 1997, Mason et al., 1990, Hammerschmidt et al., 2012). Mason et al. 1998 connects the production of DMeHg with heterotrophic conditions. Some papers (Mason et al., 1998, Cossa et al., 1994) indicate that DMeHg formation likely occurs in oxygenated environments. DMeHg has rarely been reported in surface waters except in the deep oceans (Kotnik et al., 2007, Bratkič et al., 2013, Cossa and Sanjuan, 1997b, Vandal et al., 1998), in slurry of salt marshes (Weber et al., 1998), and geothermal gases and waters (Hirner et al., 1998).

There is a high affinity between Hg and dissolved organic matter (DOM), which is attributed to the binding of Hg with sulphur– containing functional groups in organic matter (Ravichandran et al., 2004). In addition, DOM has the potential to promote MeHg formation by stimulating microbial growth or to inhibit methylation by reducing the amount of inorganic mercury available for methylation through complexation (Ullrich et al., 2001). Particularly strong associations are formed with humic matter, where the Hg atom is most likely bound to thiol (-RSH) groups. The proportion of Hg(II) bound to humic substances is lower in seawater than in freshwater environments due to chloride ion competition. In freshwaters more than 90% of Hg is complexed by organic matter (Mantoura et al., 1978). Methylmercury hydroxide (CH_3HgOH) is the most stable among MeHg species in the freshwater environment, whereas in seawater MeHg is present mainly as chloride (CH_3HgCl). As clarified in Figure 1.2, regardless of the complexity of the Hg species and compounds in water systems, our focus with be on the dissolved Hg(0) and Hg(II), the so-called RHg. Hg(0) is relatively unreactive but can be oxidized to Hg(II), particularly in the presence of chloride ions (Yamamoto et al., 1996). As will be further explained, the transformations between Hg(II) and Hg(0) are particularly affected by the presence of light. There are certain physical/chemical properties, which determine the properties of each form of Hg. Due to its vapour pressure, 0.261 Pa ($2.58 * 10^{-6}$ atm) at 25 °C (Huber et al., 2008), the Hg-Hg bond is very week; therefore, Hg(0) is more volatile than other metals. In water Hg(0) has a solubility of about 59 µg L^{-1} at 25 °C which increases by a factor of 1.3 for every 10 °C rise in temperature (Figure 1.3).

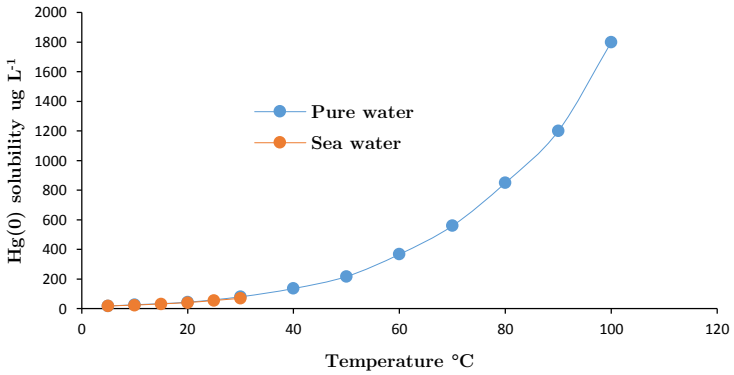


Figure 1.3: Solubility of Hg(0) in seawater and pure water (distilled) depending on temperature (Sanemasa et al., 1971).

The partitioning between dissolved gaseous phase in water and gas in atmosphere is described by Henry's law (Henry's coefficient). For DEM, Henry's coefficient is 0.32 at 25 °C (Andersson et al., 2008) and increases by a factor of 1.6 for every 10 °C of temperature rise. This constant is much higher compared to other Hg compounds ($HgCl_2$, HgC_2O_4, CH_3HgCl) resulting in gaseous species that will be sparingly dissolved and readily evaporate to the atmosphere from surface waters. This is a very important fact which determines the evasion rates of Hg(0) from water surfaces; therefore, accurate determination represents an important feature regarding the global Hg budget. In the framework of the assessment of the global mercury cycle, while estimating the evasion of Hg from oceanic waters, Henry's low constant is used for the calculations. Lately Henry's constant has been re-determination in MilliQ water (Andersson et al., 2008) (Eq. 1.1):

$$k_{H'} = \exp\left(\frac{-2404.3}{T} + 6.92\right) \qquad \text{Equation 1.1}$$

where $k_{H'}$ is the dimensionless Henry's constant and T is the temperature of the sample (K).

Since Henry's constant depends on the salinity of the sample, another equation was developed for seawater:

$$k_{H'} = \exp\left(\frac{-1871.6}{T} + 5.28\right) \qquad \text{Equation 1.2}$$

where $k_{H'}$ is the dimensionless Henry's constant and T is the temperature (K).

DEM is found at low levels in non-contaminated natural waters, ranging from a few pg L^{-1} to several hundred pg L^{-1}, representing a considerable fraction of THg (up to 50 %) (Table 1.1). The other quantifiable gaseous Hg species, DMeHg, is rarely reported and represents a small fraction in surface waters (almost 0%), while substantial proportion is reported for deeper oceanic waters (about 5% of THg), which connects the production of DMeHg with heterotrophic conditions. Since DMeHg is not stable in the presence of light and higher temperatures, the chances that it can be found in high quantities in surface waters are very low (Mason & Sullivan, 1999).

Table 1.1. Data reported for THg (ng L^{-1}), DEM (pg L^{-1}), DMeHg (pg L^{-1}) measurements and the % of DEM in relation to THg.

Geographical area	THg ng L^{-1}	DGM	DEM pg L^{-1}	DMeHg pg L^{-1}	% DGM	Reference
Mediterranean sea	0.162-0.466	4−104		<0.023	2.5−24.5	Horvat et al., 2003
Mediterranean Sea (offshore surface water)	2.0−10.1	11.9−20		Nd(not mentioned)	1.98-5.95	Enrica et al., 2002)
Mediterranean Sea	0.082−0.53	12−110		0.04−1.93	14.7-21.1	Kotnik et al., 2007
Eastern Mediterranean	0.30−4.99 (18.7)	16−38 (114)		nd	0.61−8.33	Fantozzi et al.,2013
Tyrrhenian sea	nd	13.8−26.5		nd		(Gårdfeldt et al., 2003)
Strait of Otranto		38−60				[47]
Minamata bay	0.80−1.67	19−442		nd	5.6−16.1	(Marumoto & Imai, 2015)
Baltic sea	0.70−1.2	17.4−17.6		nd	1.5−2.5	(Wängberg et al., 2001)
Yellow Sea	1.34−5.50	60−130		nd		(Z. J. Ci et al., 2011)
Western Bleak sea	0.32−2.37		41.2−232.2	<0.81−9.52	10-13	(Carl H. Lamborg et al., 2008)
North Sea	0.18−3.28	20−122		No evidence	3.72-11	(Coquery & Cossa, 1995)
Hudson Bay, surface			29.6	1.6		(Kirk et al., 2008)
Hudson Bay, water column	0.42		26.5	34.6	14.5	(Kirk et al., 2008)
Hudson Bay, bottom				61.3		(Kirk et al., 2008)
North Atlantic Ocean	0.48		96	18.6	24	(R. P. Mason et al., 1998)
North Atlantic Ocean	0.018-0.38		2-168	<0.046-149.5	45	(Bowman, Hammerschmidt, Lamborg, & Swarr, 2014)
South and equatorial Atlantic,surface	0.58		240	<2.3	<41.8	(R. P. Mason & Sullivan, 1999)

Atlantic coastal water at the Irish west coast	nd	13.4−40.3		nd		(Gårdfeldt et al., 2003)
North Pacific ocean	0.03−1.38				10−50	(Laurier, Mason, Gill, & Whalin, 2004)
Subtropical North Pacific Ocean	0.05		nd	2.99		(Hammerschmidt & Bowman, 2012)
Ranger Lake	nd	3.8−71.8		nd		(Marl Amyot, Mierle, Lean, & Mc Queen, 1997)
Arctic Alaskian Lakes		8−86				(Tseng, Lamborg, Fitzgerald, & Engstrom, 2004)
Reseirvor lake, USA	<0.2	12−68			<6-34	(Zhang, 2006)
Lake St. Louis (Frozen fluvial lake)	nd	27.6		nd		(N. J. O' Driscoll, Poissant, Canário, & Lean, 2008)
Ice melt		73.6		nd		(N. J. O' Driscoll et al., 2008)
Snow melt		368.2		nd		(N. J. O' Driscoll et al., 2008)
Fresh waters, Canadian Arctic	0.10−19.8	15−124		nd	0.63−15	(Chételat et al., 2014)
Bay of Biscay, Adour river estuary	0.5−1.04	40−52		<0.23	5.02−8.05	(Sharif et al., 2014)
Soyang Lake (artificial reseirvor)	0.13−2.25	3.6−160		nd	0.7−18.9	(Ahn, Kim, Holsen, Yi, & Han, 2010)
Bjejajka Cave, Surface water	2.00−31.0	80−2300		nd	4.0−7.42	(Kwokal, Cukrov, & Cuculić, 2014)
Bjejajka Cave, Sub Surface water	7.00−3700	70−1000			1−1.12	
Lenga Pit, Surface water	1.70−5.80	20−210		nd	1.18−3.62	(Kwokal et al., 2014)
Lenga Pit, Sub−surface water	3.00−15.1	20−360			0.67−2.38	

The presence of DEM in natural waters is due to several factors. A simplified scheme of the main mechanisms of production/losses of DEM in natural waters is depicted in Figure 1.4.

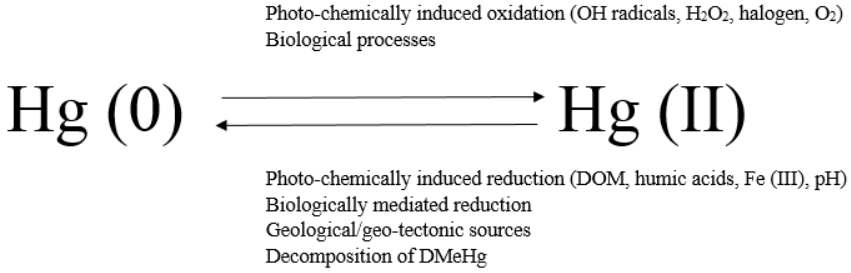


Figure 1.4: A simplified scheme of the main production/loss mechanisms of DEM in natural waters.

UV radiation induces primary and secondary photochemical reactions in water. Solar radiation has a significant effect on both the oxidation of Hg(0) and reduction of Hg(II). Hg(0) oxidation prevails over reduction in non-intense radiation, while reduction of Hg(II) is prevalent under intense radiation (Amyot et al., 1997). Regarding UV_A (320–400 nm) and UV_B (280−320 nm) radiation, Amyot et al., (1994) proved that UV_A light is primarily

responsible for the reduction of oxidized mercury forms. In contrast, Qureshi et al., (Qureshi et al., 2009) reported that UV_B radiation is the main effective driver of reduction in the surface ocean water. Table 1.2 demonstrates recent studies on seasonal changes of DEM concentrations in natural waters.

Table 1.2. DEM concentrations in pg L^{-1} during different seasons in different water compartments.

Geographical area	Winter	Spring	Summer	Autumn	
		DEM pg L^{-1}			Reference
Baltic sea	1.0−1.7	15−20			(Kuss & Schneider, 2007)
Mediterranean Sea		24	38	3.8	(Andersson et al., 2007)
Yellow sea, coastal seawater	16	23	69	27	(Z. J. Ci et al., 2011)
Fresh waters southern China	1.5− 2.1			22− 26	(Fu, Feng, Yin, & Zhang, 2013)
Estuary of Soča/Isonzo River		40−380	340−860	180−530	(Bratkič et al., 2013)
South China Sea	12	14	32	24	(Tseng et al., 2013)
Minamata Bay, open sea sites	54	68	170	82	(Marumoto & Imai, 2015)
Minamata Bay, coastal sites	101	105	263	92	(Marumoto & Imai, 2015)
Yellow Sea		27		28.2	(Marumoto & Imai, 2015)

There is a 61.6 to 76.8 % difference between Hg(0) concentrations in winter and summer.

Production of Hg(0) has been proved to occur in water also in the dark (Amyot et al., 1997, Fantozzi et al., 2009), in frozen waters, snow and snowpacks (O'Concubhair et al., 2012). The process is affected by bacteria, Cl/Br ions, particles, colloids, and presence of the reducing capacity of humic acids and organic matter (Andersson et al., 2011, Matthiessen et al., 1998, Rocha et al., 2003). Zhang et al. 2001 (Zhang & Lindberg, 2001) suggested that oxidation in dark occurs by hydroxyl radicals produced via Fenton reaction from the photochemically produced hydrogen peroxide (H_2O_2). A laboratory study on the mechanism of the oxidation of Hg(0) by OH radical is described by (Hines et al., 2004). The presence of oxygen also accelerates the oxidation rates of Hg(0). In frozen water samples, Hg(0) will quickly oxidize due to the presence of H_2O_2 in acidic conditions. This reaction is slow in unfrozen waters (O'Driscoll et al., 2008). The presence of chloride in water enhances the oxidation of Hg(0). It has been suggested that chloride is related to the inhibition of the reduction rates of Hg(II) due to the ability to compete with other ions or organic compounds present in the system (Allard and Arseni, 1991), therefore oxidation can be more important in seawater than freshwater (Yamamoto et al., 1996).

Other mechanisms responsible for the production of Hg(0) are microbial activity (Hines et al., 2006, Mason et al., 1995), abiotic mechanisms in the presence of humic acids (Allard and Arsenie, 1991), and possible decomposition of organo- mercury compounds (Mason & Sullivan, 1999). A relationship between the production of Hg(0) and phytoplankton biomass and algal cell densities has been reported (Poulain et al., 2004). Masson et al., (1995) concluded that microorganisms smaller than 3 μm play a primary role in reducing Hg(II) and the process is driven by cyanobacteria *Synecococcus sp.* (Mason et al., 1995). Moreover, algae such as *Anaeba cylindrical*, *Chlorella vulgaris* and *Nitzschia hantzschiana*, Fe(III) ions, humic acids and pH play an important role in the photochemical reduction of Hg(II) (Deng et al., 2008, Deng et al., 2009, Deng et al., 2010). Up to 380 times higher levels of Hg(0) were found in samples spiked with Fe(III) and exposed to sunlight for one hour (Zhang and Lindberg, 2001, Deng et al., 2009).

In complexes between Hg(II) and dissolved organic matter (DOM), Hg(II) is bound to specific DOM functional groups such as carboxylic groups (Qureshi et al., 2009, Si and Ariya, 2008). Significant reduction of Hg(II) was found to occur in the presence of oxalate as a result of direct photolysis of oxalate producing HO_2^{2+} radicals, which then reduce Hg(II) (Zhang et al., 2006). The organic acids, humic acids and semiquinones in the humic acids have also been proven to increase Hg(II) photoreduction rates (Lin and Pehkonen, 1998, Matthiessen et al., 1996, Matthiessen et al., 1998, Jardim et al., 2010). Intensive tectonic activity and other geological anomalies are an important source of Hg(0) in water. This was confirmed in the Mediterranean Sea which is tectonically very active (Horvat et al., 2003, Kotnik et al., 2007), where the estimated annual input of Hg(0) from geological sources is about 16 t (Rajar et al., 2007). Oxidation and reduction processes of Hg(0)/Hg(II) are occurring in water systems simultaneously. Several studies of kinetics were performed to evaluate rates of reduction and oxidation reactions (O'Driscoll et al., 2006, Poulain et al., 2007, Whalin & Mason, 2006). These reactions are pseudo first order and are highly dependent on the sample matrix and available reducible/oxidative mercury forms (O' Driscoll et al., 2006). Therefore the variability of reported values is large and different in freshwaters and marine waters. Table 1.3 demonstrates the reduction rates of Hg(II) and Table 1.4 the oxidation rates of Hg(0).

Table 1.3. Reduction reactions of Hg(II) in aqueous media.

Reduction of Hg(II)				
Reference	**Sample matrix**	**Exposure to light**	**Reaction type**	**Reaction rate**
Amyot 1994, 1997	Lake water	Light		
		UVA		UVA=7.76*10^{-5} s^{-1}
O'Driscoll et al 2006	River water	UVB	$Hg^{2+} + h\upsilon \rightarrow Hg^0$	UVB= 8.91*10 $^{-5}$ s^{-1}
				UVA=1.78*10 $^{-4}$ s^{-1}
				UVB=1.81*10 $^{-4}$ s^{-1}
Lalonde 2004	Sea water	UV		1.6 – 1.9*10 $^{-4}$ s^{-1}
Zhang 2006 Lin and Pehkonen 1998			$Hg^{2+} + H_2O + h\upsilon \rightarrow Hg(OH)_2 + Hg^0 + HOCl + H^+ \rightarrow Hg^{2+} + Cl^- + 2OH^-$	
Poulain et al., 2007	Freshwater	UV		0.3 – 3.9*10 $^{-4}$ s^{-1}
				1 .2 – 4.4*10 $^{-4}$ s^{-1}
(Zhang & Lindberg, 2001) (L. M. Whalin & Mason, 2006)			$Hg^{2+} + Fe(III) + h\upsilon \rightarrow Hg^0$	0 .6 – 0.8*10^{-4} s^{-1}
Philippidis et al., 1991, Barkay 1991			Hg^{2+} + MerA bacteria $\rightarrow Hg^0$	
Schroeder et al. 1992			$Hg^{2+} + H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + Hg^0$	

Table 1.4. Oxidation reactions of Hg(0) in aqueous media.

Oxidation of Hg(0)				
Author	**Sample matrix**		**Reaction type**	**Reaction rate**
Yamamoto, 1996	sea water		$Hg^0 + Cl^- \rightarrow Hg^{2+} + Cl^-$	$0.28 - 1.1*10^{-4}$ s^{-1}
Lalonde et al., 2001	Spiked pure water		$Hg^0 + Cl^- + h\upsilon_{UV} + benzoquinone \rightarrow Hg^{2+}$	$0.7*10^{-4}$ s^{-1}
Poulain et al., 2007	Spiked water	dark	$Hg^0 + bacteria + Cl \rightarrow Hg^{2+}$	
(L. M. Whalin & Mason, 2006)	Coastal water	dark	$Hg^0 \rightarrow Hg^{2+}$	$2.6 - 5.3*10^{-4}$ s^{-1}
	Fresh water			$8 - 15*10^{-4}$ s^{-1} $10 - 20*10^{-4}$ s^{-1} $0.28*10^{-4}$ s^{-1} $0.17*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Artificial water		$Hg^0 + fulvic\ acid \rightarrow Hg^{2+}$	$1.4–1.6*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Artificial water		$Hg^0 + semiquinones + Cl^- \rightarrow Hg^{2+}$	$0.7*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Saline water	dark	$Hg^0 + saline\ water \rightarrow Hg^{2+}$	$1.6*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Saline water	UV	$Hg^0 + h\upsilon \rightarrow Hg^{2+}$	
	Freshwater	Vis		
	Freshwater	UV		$0.25*10^{-4}$ s^{-1}
Lalonde 2004	Sea water	UV		$1.6–1.9*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Lake water	Light	$Hg^0 + NO^{3-} + h\upsilon \rightarrow Hg^{2+}$	$15.3*10^{-4}$ s^{-1}
(L. M. Whalin & Mason, 2006)	Lake water	Light	$Hg^0 + Cl^- + h\upsilon \rightarrow Hg^{2+}$	$0.006*10^{-4}$ s^{-1}
Mason et al., 2001	Pure water	Light	$Hg^0 + Cl^- + NO^{3-} + h\upsilon \rightarrow Hg^{2+}$	$6*10^{-4}$ s^{-1}
	Freshwater	Dark	$Hg^0 + Fe(III) \rightarrow Hg^{2+}$	
Schroeder et al., 1992			$Hg^0 + H_2O_2 + 2H^- \rightarrow 2H_2O + Hg^{2+}$	

Being a gas and mostly found on the water surface, volatilization of Hg(0) represents an important Hg flux in many aquatic systems. The evasion of Hg(0) from natural waters displays a diurnal and seasonal cycle that strongly depends on a number of physical and chemical factors such as temperature, UV irradiation, wind speed (Tseng et al., 2013), water mixing, chemical properties of water, salinity, the presence of organic matter, and the presence of microorganisms (Ci et al., 2015, Ci et al., 2011, Fantozzi et al., 2007, Feng et al., 2004). Rates of evasion can be very high in shallow warm waters such as the Mediterranean Sea, where the amount of Hg(0) evaporating from water system is estimated to be 49.8 t y^{-1} in 2005 and predicted to be about 43.8 t y^{-1} in 2020 (Rajar et al., 2007). Rolfhus and Fitzgerald (Rolfhus & Fitzgerald, 2001) showed that mercury volatilization from Long Island Sound, New York, was equivalent to 35 % of total annual mercury inputs to the system. Similar study from Great Lakes showed 50 % evaporation of the total mercury inputs. Large amount of elemental mercury (about 2000 t y^{-1} (Mason et al., 2012, Selin et al., 2009, Andersson et al., 2011, Garcia et al., 2005) is reported to be introduced into the atmosphere from marine and freshwater surface waters yearly (Strode et al., 2007, Garcia et al., 2005, Vandal et al., 1991).

Based on these facts and state of the art, the intention of this PhD was to accurately measure these Hg forms in water matrixes and carefully track the oxidation/reduction process in time. By this, we would be able to better explain the chemistry of Hg in water

systems and to accurately predict the evasion rates of Hg into the atmosphere, as one of the biggest natural sources of Hg into the atmosphere. Despite evasion from the natural water surfaces, another relevant source of Hg into the environment are TPPs that emit tons of Hg(0). Although almost all are equipped with wet FGD system for SO_2 and Hg removal, the performance regarding Hg retention will highly depend on the behaviour of Hg in the scrubber solution of these systems. The principal physical characteristics of wastewater include solids content, colour, odour and temperature.
Mercury chemistry in the scrubber will depend on the presence of other metals, ions, pH, redox potential, radicals etc and it is very complex (Stergaršek et al., 2008, Stergaršek et al., 2010, Stergaršek et al., 2013). The transformations between Hg(0) and Hg(II) are of primary concern also in these systems because they determine the retention efficiency for Hg (Meij et al., 2002, Lu et al., 2011, Omine et al., 2012, Stergaršek et al., 2013,).

1.3 Mercury in Wet Desulfurization Slurry

Due to the toxicity of the element, a strict control of Hg emissions in the atmosphere from industrial settings is required. According to the updated inventory of Hg emissions, coal burning is confirmed to be among the most important anthropogenic sources (UNEP, 2013). Accurate measurement of mercury emissions from combustion sources is important for our understanding of the global mercury budget. More importantly, quantification of individual mercury species from combustion sources will be critical when addressing questions concerning mercury control, toxicity, and fate and transport, as each species has dramatically different chemical and biological properties. While there are a number of possible technical approaches to control mercury emissions, there is no single best technology that can be applied broadly.

Hg is present in coal and its compounds are is not stable at elevated temperatures. When combusted, nearly all Hg forms are released in the flue gas, mainly composed of Hg(0). A clear fundamental understanding of mercury flue gas chemistry is needed to develop effective mercury control technologies. Air pollution control and prevention techniques are continuously under development and improvement. The most commonly used include: Electrostatic precipitators (ESP), Fabric filters (FF or bag house), Selective catalytic reduction (SCR), Activated carbon injection (ACI), Sorbents and Flue gas desulfurization (FGD).

FGDs are a branch of technologies used to remove sulphur dioxide (SO_2) from flue gases of thermal power plants. They are based on the reaction using an alkaline reagent (lime or limestone) to produce a solid compound (Stivastava et al., 2000). Depending on the type of FGD process, the salt by-product is calcium sulphite (anhydrite) and/or calcium sulphate (gypsum). When gypsum is formed, the reaction is as follows:

$$\mathbf{CaSO_3\ (solid) + ½\ O_2\ (gas) + 2H_2O\ (liquid) \rightarrow CaSO_4 \cdot 2H_2O\ (solid)}$$

When using aqueous slurry as sorbent *(wet scrubber)*, the FGD system is referred to as wet FGD (WFGD). When using a dry, powdered sorbent (*dry scrubber*), the system is referred to as a dry FGD system. Mercury released from coal burning enters the flue gas cleaning devices as a mixture of Hg_p, Hg(II), and Hg(0):

1. Hg_p is easily captured by conventional ESP.
2. Hg(II) due to its high solubility in the aqueous phase, passes easily from the gas phase into the scrubber liquor and is subsequently removed from the WFGD.

3. Hg(0) due to its high volatility and low solubility escapes the system and goes into the atmosphere.

The success of Hg removal consists in either modifying the chemistry of the solution by enhancing the oxidation of Hg(0) in flue gas to Hg(II), which is soluble in water, or in adsorbing Hg(0) onto appropriate adsorbers (activated carbon is the most commonly used). Current commercially available FGD technologies can achieve 70 % to 98 % of Hg(0) capture.

Given that the chemical species of Hg emitted vary from plant to plant, there is no single control technology which removes all forms of Hg. A general scheme of the Hg species across the TPP of a WFGD is given in Figure 1.5.

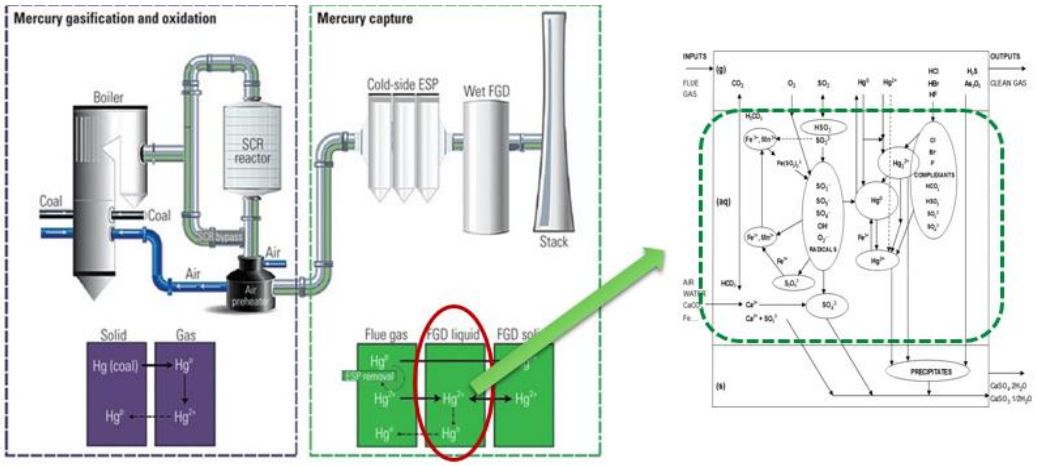


Figure 1.5: Left: A general scheme of the main Hg transformation processes in different parts of the TPP (http://www.powermag.com/determining-aqcs-mercury-removal-co-benefits/) and Right: Possible transformation processes in the scrubber solution of the WFGD plant with forced oxidation with air (Stergaršek et al., 2013).

One of the most investigated options of achieving high removal efficiency of Hg is based on the modification of the chemistry in the scrubber solution (Stergaršek et al., 2013, Córdoba et al., 2015, Stergaršek et al., 2010, Pudasainee et al., 2012, Krzyzynska et al., 2012). In the scrubber solution, a number of oxidants are able to oxidize Hg(0) under the chemical conditions at which WFGD operates. Such solutions contain numerous anions such as Cl^-, Br^-, OH^-, SO_4^{2-} , CO_3^{2-}, $S_4O_6^{2-}$ that tend to form strong complexes with Hg(II). An essential condition for good removal of Hg(0) is a relatively high redox potential in the acidic solution.

Latest data demonstrated that oxidation with air assures high Hg removal efficiency e.g the WFGD installed in the thermal power plant in Šoštanj, Slovenia. This TPP is equipped with two WFGD units installed for removing sulphur oxides. Both WFGD systems use the wet limestone process with forced oxidation with air (Stergaršek et al., 2008). Previews work has demonstrated a retention efficiency for Hg of more than 88% on average for all Hg species previously mentioned. Interesting and specific for this TPP is the property of the finer layer of the formed gypsum to retain Hg. This is shown to be caused due to the transition metals present within it (especially Fe^{2+} and Mn^{2+}) (Stergaršek et al., 2010, Stergaršek et al., 2013) which serve as catalysts. The scrubber solution contained in WFGD is characterized also by high particle density (which in most of the

cases is calcium sulphate ($CaSO_4$)), a pH of about 7±2, access to oxygen; different chemical species of oxygen, sulphur, halogens, carbon, hydrogen and trace metals are also contained in this water. THg concentrations in the scrubber solutions range from 100 ng L^{-1} to 2 mg L^{-1} (Omine et al., 2012, Wo et al., 2009, Córdoba et al., 2013, Lu et al., 2011, Meij et al., 2002), while DEM is reported to be between 22 and 44 ng L^{-1} (Stergaršek et al., 2010). However, values vary significantly depending on the working parameters of the WFGD, and the quality and type of coal used.

One of the biggest problems related to Hg(0) retention is the so called "re-emission" of Hg(0). Many researchers have confirmed that Hg(II) in the scrubber solution of the WFGD can be reduced back to Hg(0) (Wo et al., 2009, Chengli et al, 2010, Tang et al., 2010, Omine et al., 2012, Ochoa-González et al., 2013). One of the biggest challenges is therefore to increase the capability of the system to prevent the reduction of Hg(II) in the scrubber solution (Omine et al., 2012, Ochoa-González et al., 2013, Cheng et al., 2013, Cheng et al., 2013, Sun et al., 2014) and this can be achieved by correcting the chemistry of the scrubber solution.

The most common approach to measure Hg in TPPs is by conducting Hg measurements in the flue gas, inlet and outlet. In this way the removal efficiency of the installed WFGD system is calculated. The problem here is that such measurements are very expensive. Therefore, measurements of DEM in the scrubber solution can substitute Hg(0) measurements in the flue gas, reducing the cost of the analysis. Moreover, the same principle can also be applied for the measurements of oxidized Hg.

1.4 Mercury Analysis and Speciation, General Aspects

Mercury and its compounds occur at low concentration and some forms are not stable (DEM, RHg). Therefore, the analytic methods used to conduct measurements should be accurate enough to allow detection of low levels and on the spot measurements are suggested to be performed. A simplified scheme with the main steps undertaken for Hg determination in water samples and Hg speciation is given in Figure 1.6.

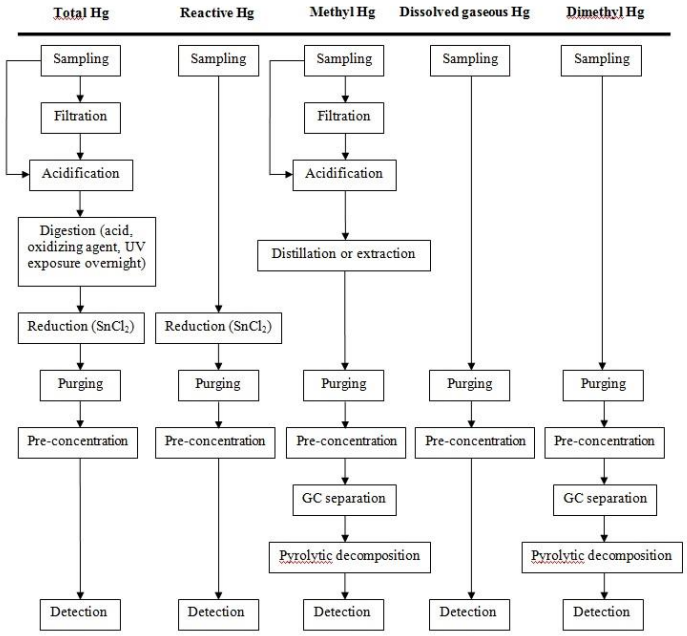


Figure 1.6: A simplified scheme with the main steps undertaken for Hg speciation (DEM is calculated from the difference between DGM and DMeHg, if measured).

Collection and handling of aqueous samples for Hg determination involves factors such as whether or not the sample is representative, possible inter-conversion processes, contamination, loss of Hg from the sample, preservation and storage of the matrix before analysis.

Sampling can contribute significant uncertainty to the results and is therefore one of the most important steps in the analytical procedure. For sampling, standardized and agreed protocols are needed that guarantee a representative sample. The work done in this PhD is focused on water samples.

Measurement of "dissolved" mercury compounds requires the removal of particulate materials from the sample by either filtration or centrifugation. Various types of filters can be employed: 0.45 μm membrane filters (precipitation, sea water), disposable polystyrene units (Nalgen) with nitrocellulose membrane filters, and pre-treated glass fibre filters.

Due to the fact that it is not always possible to conduct measurements in field, the samples need to be stored. The biggest problem when storing samples for Hg determination is the stability of the species over time. The stability of Hg and its species in solution is affected by factors such as (Parker et al., 2005, Yu et al., 2003):

a) The concentration of Hg and its compounds in the sample
b) The type of water matrix
c) The type of containers used for collection and storage of samples and the cleaning procedures applied to them
d) The agent added to the water samples for the storage of Hg

Containers and other sampling equipment which come into contact with water samples should be Hg-free. The biggest problem related to the storage is the instability of the element and its species. Scenarios such as volatilization of Hg from the sample, adsorption into the walls of the container, interchange between Hg species and diffusion of Hg(0) through the walls of the container from the surrounding atmosphere into the sample, have to be carefully considered.

The cleaning procedures applied to containers (Hammerschmidt et al., 2011) and preservation protocols used (Lamborg, 2012), highly effect the results obtained. It has been previously suggested that the best materials for sample storage are Pyrex, glass, Teflon (PTFE or FEP) (Horvat et al., 1996, U.S. EPA 2002) and Polyethylene terephthalate (PET) bottles. Plastics such as polypropylene (PP) are not recommended since these materials can contribute to either contamination or losses of Hg. Another material commonly used recently is fluorinated high density polyethylene (FLPE) bottles. FLPE is cheaper than Teflon and has lower permeability than HDPE (Braaten et al., 2014). The use of FLPE bottles is well documented in recent years (Naftz et al., 2014, Braaten et al., 2014, Hammerschmidt et al., 2011).

It is generally agreed that lowering the pH of the sample stabilizes Hg(II) (Benes et al., 1969, Lo et al., 1975) by preventing adsorption on the container walls. This way of preserving the samples is applied when THg needs to be determined but not in the case of volatile species and RHg due to unpredictable results this might introduce. The addition of acids such as nitric acid (HNO_3), hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) to the sample is generally practiced. Apart from acids, oxidizing agents have also been used to stabilize the sample and keep the Hg concentration unchanged with time. Among the most used in the past (but not lately) were dichromate, hydrogen peroxide and permanganate. Lately, the addition of Au(III) and HNO_3 has also been shown to stabilize Hg species in aqueous solutions (EPA, 2003). However, in choosing a preservative, we have to consider also the level of impurities we may introduce. Therefore, small amounts are strongly recommended. A table with the results of several studies is given below (Table 1.5):

Table 1.5. The effect of the preservative added to the sample.

Reference	Sample matrix	Bottle type	Conc. µg L^{-1}	Preservative added to the sample	Stability of THg
Rosain et al., 1973	Natural, DW	PE polyvinyl chloride	25	pH 2-7 HNO_3	Severe loss Stable for 17 days
Feldman et al., 1974	DW	glass PE	0.1-10 0.1-10	5% HNO_3 + 0.01 % $K_2Cr_2O_7$	Stable for 5 months Stable for 10 days
Lo & Wail, 1975		PE		No preservative added HNO_3 , pH = 0.5 $K_2Cr_2O_7$ 0.05 % $K_2Cr_2O_7$ 0.05 % + HNO_3 pH = 0.5 $HAuCl_4$ x $3H_2O$ 0.2 ppm $HAuCl_4$ x $3H_2O$ 0.2 ppm + HNO_3 , pH = 0.5 H_2O_2 0.1 %	95 % lost in 21 days 16 % lost in 21 days 25 % lost in 21 days 2 % lost in 21 days 90 % lost in 21 days 2 % lost in 21 days 87 % lost in 21 days
State, 1976) Christman and Ingle et a., 1976	DW	Pyrex glass	0.1	1 % HNO_3 + 16 ppb Au(III)	Stable for 1 week
Stoeppler and Matthes et al., 1978	Seawater	Glass	2.5	HCl pH=2.5	2.5 months
Piccolino et al., 1983	Tap water	PE, glass	1-7	0.15 % HNO_3 0.5 % HNO_3 0.05 % $K_2Cr_2O_7$ + 0.15 % HNO_3 0.05 % $K_2Cr_2O_7$ + 0.5 % HNO_3 0.05 % $KMnO_4$ + 0.5 % HNO_3	10% lost in 14 days 7% lost in 21 days 7% lost in 28 days 0% lost in 45 days 0% lost in 45 days
Freimann, et al., 2000	Seawater	Teflon		HNO_3 pH=0.9	Stable for 6 months
Krivan and Haas, 1988	DW	PE, PP, glass, quartz	30-1000	2% HCl + 2%H_2O_2	4% loss in 2 months
Leermakers et al., 1990	DW	PE Pyrex glass PTFE	4	0.05% (v/v) H_2SO_4 + 0.02% (w/v) $KMnO_4$ pH 1 with HNO_3	Problem the formation of MnO_2 At least 1 month
	Seawater	PE Pyrex glass	0.05	pH 1 with HNO_3	At least 1 month
Caroli et al., 1996	Deionized water	HDPE	1-10 ng g^{-1}	0.01% $K_2Cr_2O_7$ + 1% HNO_3	Stable for 1 month
Fadini et al., 2000)	River water	PET	1–9 ng L^{-1}	by freezing at −18 °C	Stable up to 40 days
Hall et al., 2002	River water	FEP HDPE PET PP		BrCl solution 0.5 % BrCl 2 % HCl 0.04% $K_2Cr_2O_7$ + 1% HNO_3	14 days 28 days stable when BrCl is used, 20% los with the other preservation methods
EPA, 2003	Natural waters			2 ppm Au(III) + 2% HNO_3	More than 2 years
Parker et al., 2005)	Freshwater, Seawater	Teflon glass		0.5 % HCl	At least 120 days stable
Hammerschmidt et al., 2011	Seawater	Teflon FLPE LDPE PC	0.002	0.4 - 0.5 % HCl	Significantly higher after 15 weeks Significantly higher after 3 weeks 5 times higher after 5 weeks Stable for more than 8 months

Polyethylene, PE; Polypropylene, PP; Polycarbonate, PC; Teflon, FEP and PTFE; High density polyethylene, HDPE; Low density polyethylene, LDPE; Fluorinated high density polyethylene, FLPE; Polyethylene terephthalate (copolyester), PET; Distilled water, DW. LODs are highly affected by the procedural and reagent blanks.

Due to low concentrations, most analytical methods for measuring Hg in natural waters are based on pre-concentration, using gold or other precious metals for inorganic Hg species and other suitable adsorbent materials, and cryo-trapping for organo-mercury species (Amouroux et al., 1998). Since THg analysis alone cannot accurately describe Hg chemistry in a sample, all current research recommend Hg speciation analysis instead. Speciation of Hg will give us information about its mobility and toxicity, but it is still a challenge, as the determination of individual species at low concentrations is often a subject of analytical errors/artefacts.

Extracting Hg species from the water matrix requires attention because it might lead to significant losses/contamination if it is not performed carefully. The separation of Hg species is especially critical when MeHg has to be determined due to interferences stemming mostly from the high levels of Hg(0) and Hg(II) present in the sample or formed during the analytical steps. The volatile species (e.g DEM and DMeHg) are simply separated by purging the sample with an Hg-free gas. The separation of RHg is done the same way as for volatile species with the difference that $SnCl_2$ is added prior to purging.

The detection of Hg and its species is the last step in the analytical procedure. Cold vapour techniques are the most commonly used. They involve the absorbance and fluorescence spectrometry. Many instrumental analytical methods can be used among which the most frequently employed are: CV AAS; CV AFS; ICP-MS; electrochemical methods and neutron activation analyses (NAA). The relative detection limits of some techniques are presented in Table 1.6. It should be noted, however, that the detection limits reported are dependent on the overall analytical procedure including sample preparation prior to the final quantification step (Horvat 1995).

Table 1.6. Most frequently used methods for quantification of mercury and their relative detection limits (Horvat et al., 1996, Horvat et al., 2005).

Method		Detection limit
AAS	Colorimetric methods	0.01– 0.1 μg g^{-1}
	Graphite furnace (GF AAS)	1 ng g^{-1}
	Cold vapour (CV AAS)	0.01–1 ng g^{-1}
AFS	Cold vapour (CV AFS)	0.001 – 0.01 ng g^{-1}
NAA	Instrumental (INNA)	1–10 ng g^{-1}
	Radiochemical (RNAA)	0.01 – 1 ng g^{-1}
GC	Electron capture detector	0.01 – 0.05 ng g^{-1}
	Atomic emission detector	0.05 ng g^{-1}
	Mass spectrometer	0.1 ng g^{-1}
	CV AAS, CV AFS	0.01 – 0.05 ng g^{-1}
HPLC	UV	1 ng mL^{-1}
	CV AAS	0.5 ng mL^{-1}
	CV AFS	0.08 ng mL^{-1}
	Electrochemical detectors	0.1 – 1 ng mL^{-1}
ICP MS		0.01 ng mL^{-1}
ICP AES		2 ng mL^{-1}
Photo-acoustic spectroscopy		0.05 ng
X ray fluorescence		5 ng g^{-1} – 1 ng g^{-1}
Gold-fil analyser		0.05 μg g^{-1}

CV AAS is a very widely used analytical technique which assures a limit of detection down to about 10 ng g^{-1}. Depending on weather the determination is done directly or following pre-concentration on a gold surface before being thermally desorbed, the limit of detection changes. There are many interferences that can occur and this is related to the

presence of water vapour, NO_2, SO_2, ozone and other organic and inorganic compounds. Some of these interferences can be successfully removed by the Zeeman background correction. All mercury forms should be converted into Hg(0), as the AAS can only detects mercury in its elemental form.

The development of commercial, relatively inexpensive, extremely sensitive, selective cold vapour atomic fluorescence spectrometry (CV AFS) instrumentation in the late 1980s and 1990s made this the most popular detector for the laboratories working on the biogeochemical cycling of Hg. The basis of AFS determination of mercury is detection of the radiant energy emitted, perpendicular to the incident light beam. In this way the signal is measured relative to "zero" rather than as a small difference in a large signal (as in the case of AAS). Therefore, AFS achieves much better sensitivities and linearity over a wider concentration range. Care is needed to avoid quenching of the fluorescence signal by gaseous substances such as CO/CO_2, O_2, or N_2. Apart from spectral interferences, there are a number of interferences dependent on the composition of the sample. They may cause non-specific absorption (volatile organic compounds), interfere with reduction (bind ionic mercury in complexes or amalgamate Hg(0)), and interfere with the pre-concentration of Hg on the adsorption trap (volatile halides and hydrides).

In recent years, the use of inductively coupled plasma mass spectrometry (ICP-MS) in speciation analysis has increased tremendously (Hintelmann et al., 1997, Heumann et al., 1998, Monperrus et al., 2003, Rodriguez-Gonzalez & Garcia Alonso, 2010). Besides its high sensitivity and selectivity, ICP-MS offers the opportunity to perform speciated isotope dilution mass spectrometry (SID-MS). Introducing mercury in the form of gaseous species into a dry plasma greatly reduced occurrence of memory effects, which was one of the major problems for the effective use of ICP-MS initially. Alternatively, many other methods can be used, as listed in Table 1.6. Their use is limited due to either the costs or the complexity of the analytical procedure. Since CV AFS detectors are simple, very sensitive, and inexpensive, they are the most commonly used.

1.5 A Review of the Analytical Methods for the Determination of DEM

The existing methods for DEM determination in aqueous media can be grouped as discrete/manual methods, and continuous/semi-continuous ones.

1.5.1 Manual methods for DEM determination in water

The manual methods have been used to conduct DEM measurements in water samples and have been applied to different sample matrixes. Although different designs are used by different research groups (some examples are given in Figure 1.7), all are based on quantitative removal of dissolved Hg(0) from the water matrix. A known volume of water is purged with an inert Hg-free gas (or air) for a certain time by applying an appropriate gas flow. Nitrogen is used in most cases. The Hg(0) stripped from the sample is pre- concentrated on an Au trap and then thermally desorbed and quantified by a suitable detector (CV AFS, CV AAS, ICP MS). Since these are quantitatively based methods, the stripping efficiency of DEM is important; therefore, the optimisation of the method should be done carefully. It is generally dependant on the sample volume taken for

analysis, purging gas flow, purging time, sample matrix, sample temperature and the concentration of DEM. However, under optimised conditions, such factors should have minimal effect.

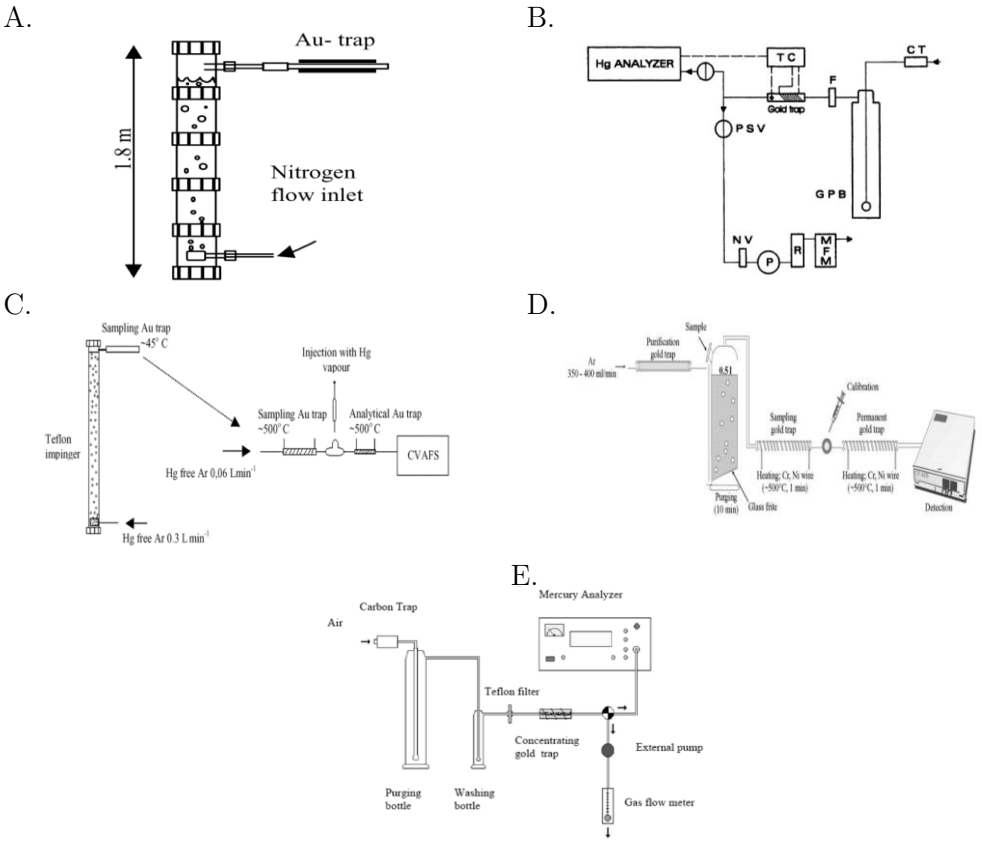


Figure 1.7: The most common systems for manual DEM measurement, (A) Wangeberg et al., 2001 (B) Lanzillota and Ferrara 2001 (C) Gårdfeldt et al., 2002 (D) Horvat et al., 2003 (E) Ferrara et al., 2003.

High stripping efficiencies of DEM from the sample are achieved by adjusting the ratio between the sample volume and the purging gas flow, a ratio which determines the purging time of the sample. Due to an absence of an agreed protocol, different researchers have optimized these parameters based on their own purging systems designs. As a consequence, there is a variety of values for purging flow, sample volume, and purging time (Table 1.7).

Table 1.7. Analytical parameters used for the determination of DGM in water samples.

Sample matrix	**Geographical position**	**Sample volume (L)**	**Purging time (min)**	**Purging gas**	**Purging flow ($Lmin^{-1}$)**	**LOD**	**Precision/ Reproducibility/ Repeatability**
(Marc Amyot et al., 1997)	Seawater (Gulf of Mexico)	2	45	N_2	1	nd	nd
(Wängberg et al., 2001)	Seawater (Baltic Sea)	2	90	N_2	0.3	1.1 pg L^{-1}	± 6 % [a]
(E. Lanzillotta & Ferrara, 2001)	Seawater (Mediterranean Sea)	1	10	air	0.3	0.5 pg	*nd*
(Horvat et al., 2003)	Seawater (Mediterranean Sea)	0.5	10	N_2	0.3	5 pg L^{-1}	4 %[b]
(Gårdfeldt et al., 2002)	Seawater (Mediterranean Sea)	2	90	N_2	0.3	2.7 pg L^{-1}	± 6 % [a]
(Ferrara et al., 2003)	Seawater (Mediterranean Sea)	1	10	air	0.2	0.6 pg L^{-1}	2 % [c]
(Fantozzi et al., 2013)	Seawater (Eastern Mediterranean)	1	10	air	0.2	0.5 pg	2%[c]
(Ci et al., 2015)	Seawater (Yellow sea, China)	1	30	air	0.5	3.0 pg L^{-1}	nd
(Marumoto & Imai, 2015)	Seawater (Minamata Bay)	0.8	30	N_2	0.75	2.7 pg L^{-1}	nd
(Rahman et al., 2013)	Coastal groundwater and seawater (Hampyeong Bay, Yellow Sea)	0.5	30	N_2	0.04	nd	nd
(Amyot et al., 2001a)	Freshwater (Bay of lake St. Pierre, a widening of the St. Lawrence river)	0.06	8		1	nd	nd
(Tseng et al., 2003)	Freshwater (Arctic Alaskian lakes)	2	30	N_2	1	nd	< 5 % [c]
(O' Driscoll et al., 2003)	Freshwater (Two lakes in Kejimkujik, Nova Scotia)	1	30	air		nd	nd
(Garcia et al., 2005)	Freshwater (Canadian Shield lake, Lake Croche)	0.5	15	air	-	nd	nd
(Mason et al., 2001)	Oceanic (Atlantic Ocean)	2	30	Ar	0.5	10 pg L^{-1}	*nd*

a, precision
b, repeatability
c, reproducibily
nd – no data

The sample volumes taken for analysis vary from 0.06 L to 2 L while purging times range from 8 (Amyot et al., 2001a) to 90 minutes (Wängberg et al., 2001, Gårdfeldt et al., 2002). High sample volumes would require longer purging time. In addition, due to the gaseous nature of DEM (and DMeHg), the temperature of the samples should be carefully considered during measurements. Since Henry's constant decreases with decreasing temperature, theoretically longer purging times are required for water samples at low temperatures. However, prolonged purging time may result in analytical artefacts due to possible transformation processes that cannot be controlled and detected. In addition, a long analysis time leads to preclusion of the method to be used when quick changes of DEM in aqueous systems are expected and need to be tracked. Therefore by decreasing the sample volume and applying high enough purging gas flows, a higher resolution time can be achieved (Amyot et al., 2001a, Horvat et al., 2003). However, a very high purging flow can lead to breakthrough phenomena resulting in under-estimation of the concentrations.

The LOD values for the reported methods (Table 1.7) are calculated as 3 times standard deviation of repeated blanks but no values for Limit of Quantification (LOQ) are provided. The LOD is not reported in all cases (Amyot et al., 1997, Amyot et al., 2001a, O'Driscoll et al., 2003, Garcia et al., 2005, Rahman et al., 2013). The precision is either reported as the relative standard deviation of replicate measurements of the sample (O'Driscoll et al., 2003), or as the relative standard deviations of the standards (which consist of known amounts of Hg vapour introduced into the system (Lindberg et al., 2000).

1.5.2 Continuous methods for DEM determination in aqueous samples

As suggested by O'Driscoll et al. (2003) the use of in-field continuous DEM measurements when combined with flux measurements would give detailed information regarding the kinetics of DEM formation and Hg fluxes. Some methods which enable continuous/semi-continuous measurements of DEM in surface waters have already been developed, optimised and applied in different field expeditions in both surface freshwaters (Lindberg et al., 2000, O'Driscoll et al., 2003, O'Driscoll et al., 2003) and seawater (Gårdfeldt et al., 2002, Marks et al., 2002, Andersson et al., 2008). Several different designs with two major working principles are used (Figure 1.8 and Table 1.8).

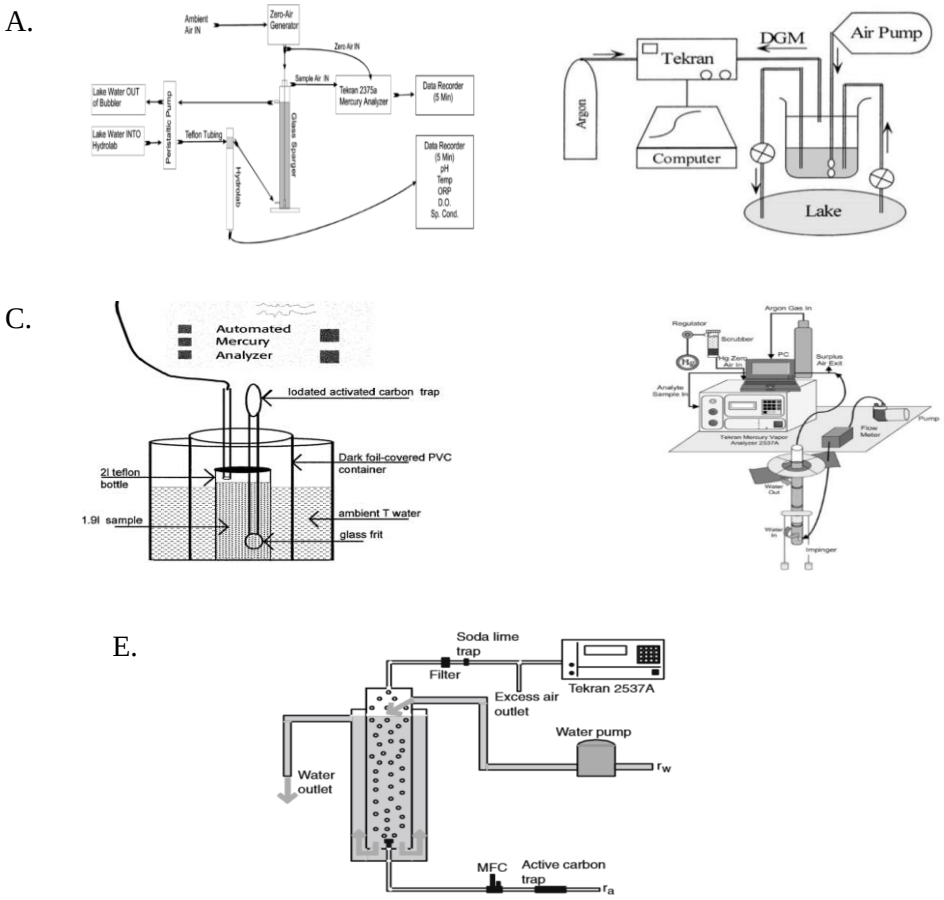


Figure 1.8: Different design of the continuous methods in use for DEM determination in surface natural waters: (A) O'Driscoll et al., 2003, (B) Amyot et al., 2001a, (C) Lindberg et al., 2000, (D) Gårdfeldt et al., 2002, (E) Andersson et al., 2008.

They are either based on quantitative removal or on the equilibrium between gaseous and water phases. Nevertheless, the effect of water temperature, dissolved organic carbon (DOC) and pH on the overall performance of the systems is significant and should be carefully considered. The main working parameters of the most commonly used methods are presented in Table 1.8. In all cases, the results obtained by continuous methods are evaluated by comparing with the discrete methods.

Table 1.8. The main parameters of continuous methods for DGM [a] measurements.

Sample matrix		**Working principle**	**Sample flow ($Lmin^{-1}$)**	**Purging gas**	**Purging gas flow ($Lmin^{-1}$)**	**LOD**	**Calibration**
(Marks et al., 2002)	Seawater (Baltic Sea)	Equilibrium	1	air	1.5	3 pg L^{-1}	
(Gårdfeldt et al., 2002)	Seawater (Gota alv estuary, Sweden)	Equilibrium	-	air	2	3 pg L^{-1}	internal mercury permeation calibration source
(Andersson et al., 2008)	Seawater (North Atlantic and Arctic Oceans)	Equilibrium	16	air	1.2	< 1.4 pg L^{-1}	
(Lindberg et al., 2000)	Freshwater (North American lakes)	Quantitative removal	2	N_2/air	1.5	Nd	internal mercury permeation calibration source
(Amyot et al., 2001a)	Freshwater (Bay of lake St. Pierre, a widening of the St. Lawrence river)	Quantitative removal	0.055	air		8.5 pg L^{-1}	solution of aqueous Hg(0) of known concentration
(O'Driscoll et al., 2003)	Freshwater (two lakes in Kejimkujik Park, Nova Scotia)	Quantitative removal	0.05	air	1	4.48 pg L^{-1}	internal mercury permeation calibration source

[a] we have used the term DEM as in the original papers, in which it is stressed that what is measured is probably Hg(0) but none of the authors specifies that the measured species is only dissolved Hg(0).

In the methods based on the equilibrium between phases, the time in which the equilibrium is reached is important to assure the reliability of the results (Andersson et al., 2008). The equilibrium depends on purging gas flow, inlet water flow and the temperature of the sample. A change in the gas/water ratio and sample temperature alters the equilibrium and the results obtained are not a trustable indicator of the real concentration. In addition to temperature, salinity also influences the measurements and therefore several analytical biases are expected when sample temperature and salinity change, which can lead to deviations from the real DGM concentration (O'Driscoll et al., 2003, Andersson et al., 2008).

The detector to which these systems are connected measures the gaseous Hg(0). Most automated methods use CV AFS detection developed for continuous measurements of gaseous elemental Hg (GEM) in air with or without gold amalgamation, which have an internal permeation source for calibration. In order to calculate the DGM concentrations in water samples for different continuous models, several different mathematical models are applied.

The most common biases introduced by using continuous methods are related to the exposure of the system to light (Amyot et al., 2001a), the effect of temperature (O'Driscoll et al., 2003) and the calculation of the final concentration of DEM (Lindberg et al., 2000). In addition, interferences by other unknown volatile Hg species might be a problem (O'Driscoll et al., 2003). Another limitation of the available continuous methods is their inability to measure DEM in deep waters. Although the biggest interest is to measure DEM in surface waters due to the interchange with the atmosphere, its determination in the mixed or bottom water layer might reveal important information related to the Hg chemistry and the overall Hg cycle in water systems. Nevertheless, when using these methods, the contact of the sample with the surrounding environment is reduced to minimum due to hermetic designs and thus the potential for Hg transformations is smaller (O'Driscoll et al., 2003). For the determination of LOD, either 3 times standard deviation of blanks (O'Driscoll et al., 2003) or 3 times standard deviation of the samples with the lowest concentrations have been used (Amyot et al., 2001a).

The theoretical background of the described methods has substantially contributed to the development of the semi-continuous method during this PhD. By comparing both groups of methods (quantitative removal-equilibrium), we decided to follow the logics of the equilibrium ones. Many parameters were carefully considered, such as the hermetic nature of the system, the ratio between the gaseous and liquid phases, calibration issues and resolution time of the measurements. After careful consideration and complexity that they represented in many cases, we did not develop a mathematic model to calculate the results, as will be shown in the Results and Discussion section. Such models most likely introduce large errors to the final result.

Due to the fact that not much effort was put in discussing the issues related to the calibration of the existing and the newly developed techniques and based to the latest debates on the calibration with Hg(0) vapour, we performed a comparison of different calibration techniques that might be used for DEM and RHg measurements.

1.5.3 Calibration in Hg analysis

The calibration of instruments for Hg measurements is important in order to establish a metrological traceability to the international system of units (SI). Calibration is done by means of certified reference standard solutions.

For THg measurements this is not a problem since the method for THg determination in water samples is well established. There are many available certified reference standard solutions (e.g SRM 3133). The stock standard solution is diluted to an intermediate concentration and the latter is further used to prepare a series of solutions with different Hg(II) concentrations. Any working standard solution with a concentration below 10 ng mL^{-1} should be prepared on a daily basis (Horvat, 1995).

In contrast, for the determination of Hg species, e.g DEM and RHg, there are no available certified standards. In many studies using the double amalgamation method for the determination of the mentioned species, the calibration of the analytical instrument is performed using the mercury-saturated air calibration method (Dumarey et al., 1985). The Hg(0) vapours are generated from liquid elemental Hg in thermally controlled vessels called calibration units (Figure 1.9). There are commercially available calibration units with precise temperature control.

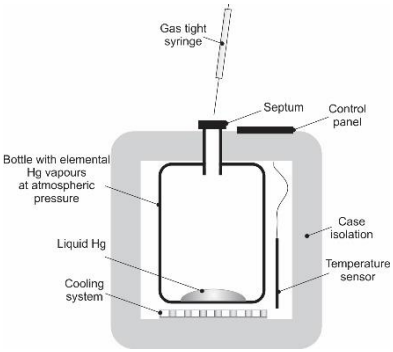


Figure 1.9: Schematic view of a mercury calibration unit.

The basic principle of this form of calibration consists in introducing known and precise volumes of saturated Hg(0) vapours into the analytical instrument (detector) by making multiple injections manually or automatically. Manual injections are done via a gastight syringe which requires careful and skilful handling. When automated calibration is performed (e.g Tekran 2537A for air measurements), an internal permeation Hg source is used which automatically supplies known quantities of Hg(0) vapours to the measurement line. The calculation of the mass of saturated Hg(0) vapours contained in the calibration unit is usually made by using the Eq. 1.3. The equation was firstly introduced by Dumarey et al. (1985) and is named after the author. The Dumarey equation is plotted between 288 and 298 K and has been further developed by Brown et al., (Brown, 2008):

$$\gamma_{Hg}^{0} = \delta \frac{D}{T} 10^{-\left(A+\left[\frac{B}{T}\right]\right)} \qquad \text{Equation 1.3}$$

where γ^{0}_{Hg} is the mass concentration of mercury vapour in the taken volume (in ng mL^{-1}), T is the temperature of saturated vapour inside the calibration device (in K), A (− 8.1344), B (3240.9 K) and D (3216522 K ng mL^{-1}) are constants and δ is the deviation of the theoretical saturated vapour mass concentration of mercury in the calibration unit from the real one.

It was experimentally shown that a change in temperature of only 1 °C leads to 8 % change in mass concentration of Hg in the closed calibration device (Brown et al., 2008). The equation is currently validated and its uncertainty was estimated to be 2 % (Dumarey et al., 2010). Several papers (Huber et al., 2006, Zampella et al., 2014, Ent et al., 2014,

Brown et al., 2008a, Brown, et al., 2008b, Brown et al., 2008c) have addressed biases by using Dumarey's equation when describing the dependence between Hg saturated vapours and temperature. Unfortunately, most measurements of DEM are traceable to empirical relationships. Consequently, the result of a measurement will depend on which equation is chosen to represent the vapour pressure of mercury, and its accuracy. There are several empirical equations to describe the vapour pressure of Hg at a given temperature and the agreement between equations differs by 5% or more. The differences are due to different methodologies used when the vapour pressure is measured.

Huber et al. (2006) have developed a new equation, the results of which differ from Dumarey's equation by about 7 % at relevant temperature (Figure 1.10).

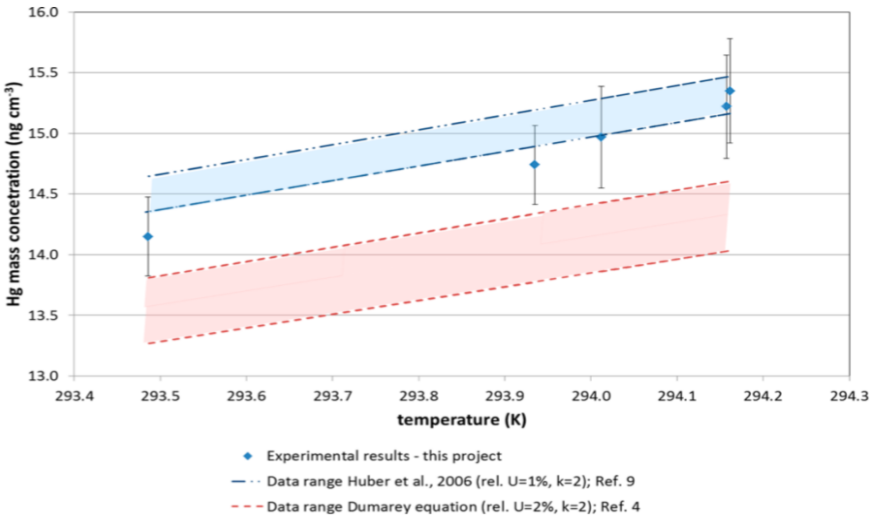


Figure 1.10: Hg mass concentration results (in ng cm^{-3}) obtained under room temperature conditions in this project. They correspond to five replicates produced on different days over 2 weeks. Vertical bars are expanded combined uncertainty estimations (k = 2). For comparison purposes, data corresponding to the Dumarey equation and values of mass concentrations in air calculated assuming that the ideal gas law applies, from results of mercury vapour pressure measurements in the presence of only liquid mercury are also shown (Quetel et al., 2014).

This issue is the focus of current debates about accurate Hg measurements. There is an immediate need to minimize the dependence of Hg vapour measurement on these empirical equations. The calibration of the detectors for RHg measurements is conducted in the same way.

Chapter 2

Aims and Hypothesis

2.1 Argumentation of the Scientific Relevance

This dissertation aims to stress the importance of accurate and reliable dissolved elemental mercury (DEM) and reactive mercury (RHg) measurements to support studies to better understand the chemistry of Hg in the natural and industrial environments. In natural waters high frequency and precise measurements of DEM and RHg would lead to better understanding of the transformation processes, including the formation and degradation of MeHg. In industrial systems, increased knowledge of Hg chemistry can be used to control the removal efficiencies of Hg in the FGD system. Our research was designed to address gaps and challenges in current knowledge of analytical methods for DEM and RHg measurements. Some issues have been previously investigated, but there are still unanswered questions regarding existing methodologies, e.g calibration. Other issues (e.g. stability of DEM and RHg; pre-concentration techniques) were also addressed in this work.

2.2 Aims

- To investigate the stability of DEM and RHg in natural waters and in the scrubber solution of a WFGD with respect to storage conditions, temperature, exposure to light and time.
- To prepare and check the performance of the gold traps using different substrates (SiO_2 and Al_2O_3) for Hg pre-concertation to reduce passivation problems.
- To verify the suitability of different calibration procedures for manual and semi-continuous methods.
- To develop and optimize the analytical procedures for determination of dissolved gaseous mercury (DEM) and reactive Hg (Hg(II) in surface waters using continuous and discontinuous methods.
- To develop and optimize a robust method for continuous determination of DEM and RHg in wet FGD slurry solution.
- To test the developed semi-continuous method in natural waters and in a pilot WFGD system.

2.3 Hypotheses

- Stability of Hg compounds in aqueous samples depends on storage time, temperature, container materials and preservation method.
- Passivation of the gold traps depends on gold coating of the silica powder.
- Calibration of the manual discontinuous method can be performed by gaseous Hg calibration, while the semi-continuous method must apply conversion factors determined by the manual method.
- Continuous on-line measurement of DEM in the wet FGD slurry provides information on oxidation/reduction processes in the slurry solution.
- Continuous measurements of DEM in the FGD slurry solution is a good predictor of Hg(0) measurements in the flue gas and as such can be used as a diagnostic tool for monitoring the efficiency of Hg removal technology.

Chapter 3

Experimental

3.1 Reagents and Other Materials

SRM 3133 (9.954 mg g^{-1} ± 0.053 mg g^{-1}) Hg(II) standard solution obtained from NIST was used to prepare the working standard solutions.

Hg(II) standard solution of 1 ng mL^{-1} was prepared fresh every day. 95 mL MilliQ water + 5 mL HNO_3 were spiked with 20 µL of Hg(II) standard solution of 5 µg mL^{-1}.

Hg(II) standard solution of 10 ng mL^{-1} was prepared by spiking 94.8 mL MilliQ water + 5 mL HNO_3 with 200 µL of Hg(II) standard solution of 5 µg mL^{-1}.

Monobromine chloride (BrCl) used for sample digestion for THg determination was prepared by dissolving 0.55 g KBr and 0.75 g $KBrO_3$ in 10 mL of MilliQ water and 40 mL of HCl. Both salts were previously heated for 12 hours at 180 °C.

Tin chloride ($SnCl_2$), 3 %, was prepared freshly every time the analysis had to be performed. The solution was prepared by dissolving 30 g of $SnCl_2$ ($SnCl_2$*$2H_2O$ (MERCK, Emsure)) in 1000 mL of MilliQ water, acidified to 1 % HCl (fuming, MERCK, Emsure, 37%) and purged with nitrogen for two hours.

Hydroxilamonium hydrochlorid (NH_2OH*HCl 30%) was prepared by dissolving 75g of $NH_2OH \cdot HCl$ in 250 mL of MilliQ water and 0.125 mL of 3% $SnCl_2$ was added to it prior to purging for 2 hours.

Hg(0) (DEM) stock solution was prepared by adding few grams of liquid Hg in a 5 L glass bottle (Duran, acid pre-cleaned) filled with MilliQ water. The concentration of DEM in this solution at room temperature ranged from 40 to 50 µg L^{-1} (average 46 µg L^{-1}).

MilliQ water was produced by Milli-RO Plus 10 (Millipore) from MERCK QPAK® 1.

Distilled water: The distilled water was prepared by condensing large amounts of tap water by appropriate instrumental units, using a single distillation step.

WFGD aqueous samples used for the validation of the flow injection semi-continuous method were taken from the TPP in Šoštanj, Slovenia. Visually they are similar to a

suspension solution where the water phase and the solid phase are homogenously mixed. It was characterised by a brownish colour and particle density of about 10 %.

Perma pure trap: It is made from a Nafion membrane and is considered a moisture exchanger wherein the functioning drying system additionally requires a drying gas flow (in our case N_2). The drying process is based on a water-specific chemical process. Nafion is a copolymer of perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid and tetrafluoroethylene. It spontaneously absorbs water from the entering gaseous phase. Each sulfonic group can be surrounded by a maximum of 13 water molecules. Water is transported to the wall side. This transport is carried out quickly, and always in the direction of the lower water vapour concentration. The amount of residual water in the Nafion wall is temperature-dependent. At higher temperatures, water is more strongly restrained by the wall and cannot be delivered to the dry gas.

3.2 Instrumentation

3.2.1 Hg measurements

- ***Atomic absorption spectrophotometry***

UT 3000 mercury analyser: Semi-continuous measurements of DEM were conducted by UT 3000 mercury analyser, which utilizes a single amalgamation step and a CVAAS mercury detector. The Hg(0) is stripped from the water sample using nitrogen, pumped onto the Au trap where it amalgamates, desorbed by heating and finally detected in the absorption cell (at 253.7 nm). The absorbance is displayed on the screen of the detector. The whole measurement cycle requires at least 3 minutes. For samples with low DEM concentrations longer amalgamation periods (up to 0.5 hours) can be applied.

RA-915$^+$ Mercury Analyser (Lumex), is a portable multifunctional atomic absorption spectrometer with Zeeman background correction, which eliminates the effect of interfering impurities. The operating principle is based on the differential variant of the Zeeman atomic absorption spectrometry using high-frequency modulation of light polarisation. The mercury lamp is placed in a magnetic field and the resonance Hg line (254 nm) is split into tree polarized Zeeman components, the radiation of which is depended on Hg amount in the environment (Multifunctional Mercury Analyser RA-915$^+$, Operating manual)

- ***Atomic florescence spectrophotometry***

Tekran 2500: The detector is connected to a double amalgamation system. DEM stripped from the solution is collected and amalgamated onto a sampling Au trap, desorbed and amalgamated onto an analytical Au trap and subsequently introduced in the detector by a stream of argon. The flow of argon ranged between 50-60 mL min $^{-1}$. The light produced by the Hg lamp in the detector excites the Hg atoms, which emit light. The amount of light emitted is proportional to the amount of Hg present in the sample. The signal is converted into electrical signal and displayed in the mini screen of Tekran 2500.

A recorder, connected to the detector, enables the conversion of the electrical signal into a peak.

Tekran 2600: is based on the same principle as Tekran 2500, with the exception that it is equipped with an auto-sampler for automated sample introduction.

3.2.2 Two saturated gaseous mercury sources (calibration units)

- *UT 3000 Mercury Analyser Calibration Unit* consists of a specially designed Hg vessel (chamber) surrounded by an aluminium jacket that is cooled by a thermoelectric cooler. The mercury chamber contains liquid Hg of high purity and the temperature is ambient-depended, measured with a high precision temperature sensor. Based on the temperature the concentration of saturated vapours in the vessel is automatically calculated and displayed on the UT3000 monitor (Manual, 2012).

- *Tekran 2505 calibration unit* is based on the same principle but the temperature of the Hg chamber is thermoelectrically controlled to provide a capability to control the temperature (0 to 30 °C). Both Hg vapour calibration units calculate Hg concentration on the basis of Dumarey equation providing comparable results.

Peristaltic pump: A Masterflex L/S precision peristatic pump (Modular Drive w/, Remote I/O; 600 rpm) and Masterflex standard pump head for L/S 16 tubing (PC housing/SS rotor). Peroxide-cured silicone tubing (L/S 16) was used only in the part of the pump head.

3.2.3 Instrumentation for Au trap characterisation

- ***Coating of the materials.***

BALZERS SCD 050 sputter coater is generally used for the deposition of conductive films onto surfaces, either by Ar-sputtering of a noble metal target or evaporation of carbon filaments. Sputtering is a vacuum evaporation process.

- ***Characterisation of the surfaces***

Scanning Electron Microscope (SEM) was used for the characterization of the surfaces of the materials.

X-ray diffractometer used for the characterisation of the phase composition of the samples was the D4 ENDEAVOR.

3.3 Preparation of Au Traps

Hg can form weak bonds with other metals, forming amalgams. This fact is utilized when developing analytical methods for Hg determination in samples with low Hg content. Given that pre-concentration of Hg in a solid phase is widely used, improvement and high quality materials are needed to assure accurate results and low detection limits. In addition, pre-concentration can be used during sampling as a technique for sample storage (Fatemian et al., 1999). Pre-concentration of Hg has been commonly achieved by amalgamation on a noble metal. The most widely used material is gold-coated silica (Au traps) (Leopold et al., 2009, Vikesland et al., 2015). Although the high affinity of gold surfaces for mercury is well-known, gold-based materials have been used almost exclusively for enrichment of Hg(0) vapour in connection with CV techniques.

As already stated, the levels of Hg species, in particular of DEM, are very low; therefore, high quality of pre-concentration materials is of crucial importance. In addition, a less expensive method of preparing the Au traps in order to reduce the costs of the analysis was tested. In this work, two nano-gold supported metal oxides materials (Au/SiO_2 and Au/Al_2O_3) were used for the sampling, pre-concentration, and determination of gaseous Hg and their performances were compared to those of commercially available gold-coated sand traps.

We initially increased the amount of Au on the surface of the commercially available Au traps. This was achieved by sputtering Au on the surface.

Later, we coated with Au the oxides of silica and aluminium, SiO_2 and Al_2O_3, not coated before. The coating was done by aqueous solution of hydrogen tetrachloroaurate dihydrate ($HAuCl_4*2H_2O$). The sample preparation involved the following steps (
Figure 3.1):

- Preparation of the Au(III) solution was done by weighing 0.3 g of the Au salt and dissolving it in 100 mL of MilliQ water.
- Addition of the particles and mixing for about 20 min-30 min in a magnetic stirrer.
- Drying the excess of water from the samples (oven, at 80 °C).
- After obtaining a dry yellowish samples, portions were put in a ceramic container and further in the oven in inert atmosphere.
- The final product was packed in quartz tubes and used for Hg analyses.



Figure 3.1: Preparation steps for Au coating of Al_2O_3 (the same was done also for SiO_2). (A) The alumina was exposed to the Au solution. (B) The ceramic plate in which the particles were placed in the oven. (C) The oven used to reduce Au on the alumina surface and (D) The final product.

XRD measurements were performed in the X-ray diffractometer BRUKER AXS D4 ENDEAVOR. The sample was carefully packed in the sample holder (specimen holder)

made of plastic. XRD is an analytical technique looking at X-ray scattering from crystalline materials (Klug et al., 1954). Every material produces a unique X-ray "fingerprint" of X-ray intensity versus scattering angle, a characteristic of its crystalline atomic structure. Therefore a diffraction pattern is obtained. The diffraction pattern is a product of the unique crystal structure. Qualitative analysis is possible by comparing the XRD pattern of an unknown material to a library of known patterns. SEM measurements were performed with the JSM 5800 electron microscope (Jožef Stefan Institute, Ljubljana) and with the ZEIZZ electron microscope (Faculty of Chemistry, University of Ljubljana). SEM is a near-surface sensitive technique. It uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure. For the identification of elemental composition of the material surfaces, the Energy Dispersive X-ray Spectroscopy (EDS) technique was used. Prior to the analysis on SEM, the samples were sprinkled onto adhesive carbon tapes which were supported on an aluminium sample holder.

3.4 Testing the Impact of Moisture on Performance of Au Traps

Along with the pre-concentration materials, another very important parameter which highly affects the results during Hg measurements is the interference primarily caused by water vapour. Therefore, a study was conducted which compared the performances of three different candidates to be used as drying materials for Hg measurements. The compared drying agents included: Silicagel, Sodalime and Perma Pure trap.

3.5 Method for Total Mercury (THg) Determination in Water Samples

EPA 1631 E revision method

For the determination of THg in water samples, a validated method was used, namely EPA 1631 E revision. This method is based on double amalgamation of Hg on Au traps. Based on this method, 39.4 mL of a sample was weighed directly in a 125 mL Teflon bottle. After addition of 0.4 mL HCl (30 %, suprapur) and 0.2 mL BrCl, the Teflon bottles were closed and left to react at room temperature under UV light overnight. Before measurement, 40 µL of NH_2OH*HCl were added. An aliquot was then introduced to the instrument. Hg(II) in the sample was reduced to Hg(0) with 3 % $SnCl_2$. Hg(0) was stripped from the aqueous sample by Argon gas via phase separator, and detected by CVAFS, Tekran 2600.

3.6 Manual/(Discontinuous) Method for DEM and RHg Determination

A schematic presentation of the system used for manual determination of DEM is shown in Figure 3.2. It is composed by two main parts, the bubbling system where DEM is striped from the sample matrix and the double amalgamation system, where DEM is quantified (CV AFS). In the purging step, 100 mL of sample were transferred to a glass bubbler. The purging gas (Hg-free nitrogen) entered the glass bubbler (500 mL Pyrex glass) through a glass frit sealed at the bottom of the bubbler 'cup'.

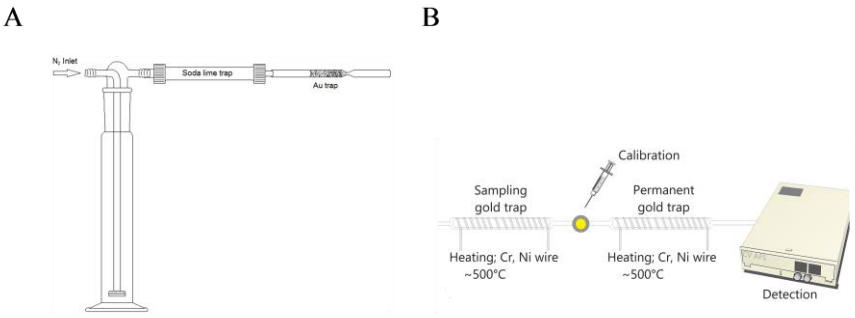


Figure 3.2: Schematic presentation of the setup for manual determination of DEM in water, (A) the bubbling system, (B) the double amalgamation system (Kotnik et al., 2003).

The sample was purged for 10 min under N_2 flow of about 800 mL min^{-1}. This guaranteed the most efficient recovery and allowed for quantitative removal of volatile Hg species in a short period of time. Volatile mercury species (primarily DEM) were collected (amalgamated) onto a sampling gold-coated silica trap (a quartz tube with a length of 120 cm in the middle of which 0.5 g of Au-coated silica is packed; Teflon tubes and connectors are used on both sides of the quartz tube). In order to remove water vapour, a soda lime trap was installed before the Au trap. In the measurement step, the Au sampling trap was transferred to the double amalgamation system for desorption. CV AFS analyser (Tekran 2500) was used for quantitative detection of Hg. The flow of argon used ranged at about 50-60 mL min^{-1}. For calibration purposes, Tekran 2505 and the calibration unit from the UT 3000 detector were used. Aliquots of Hg(0) vapour (ranging from 5–25 μL), corresponding to 25 to 140 pg of Hg were transferred into the double amalgamation system with a gas-tight syringe through a Teflon septum. When the calibration unit from the UT is used, the range of concentrations is wider due to higher temperature of the Hg vapour (about 2 °C below room temperature). When samples with higher concentrations had to be measured, higher amounts of Hg(0) were used for calibration (100-600 pg). For the determination of RHg, the same method as for DEM was applied. The only difference was that a reducing agent, $SnCl_2$, was added to the sample prior to purging. Therefore, a total amount of Hg(0) was measured: DEM + (Hg(II) reduced to Hg(0)). When calculating the final result for RHg, the results of DEM measurements from the same sample were subtracted.

3.7 Semi-Continuous Method for DEM Determination

Besides the manual methods for DEM and RHg determination, we also developed and used semi-continuous methods. Their resolution time depends on the type of the detector used to conduct the measurements. Two different system designs were tested:

- Continuous equilibrium system based on the opposite phase stripping of DEM

This method was previously developed by Anderson et al., 2008 and was applied to conduct measurements in natural surface waters. The system was developed in order to measure DEM continuously, with high time resolution, in surface waters. Such measurements are important for capturing the dynamic behaviour of DEM in surface waters. In this system a continuous high water flow enters the systems while a gas flow purges the sample and enters in the opposite direction of the sample flow. It is based on the opposite flow extraction principle which enables a longer contact time between aqueous and gaseous phases and thereby facilitates the exchange of mercury between phases.

Automated method uses an opposite flow bubbler (gas/liquid separator or extractor). The system consists of a smaller Plexiglas cylinder attached inside a larger one. A constant flow of water sample is entering the top of the inner cylinder and leaving at the top of the outer one. Through the glass frit in the bottom of the inner cylinder, a constant flow of Hg-free air is pumped into the system and purges the sample in the opposite direction (Andersson et al., 2008).

A simplified scheme of the automated system is given in Figure 3.3.

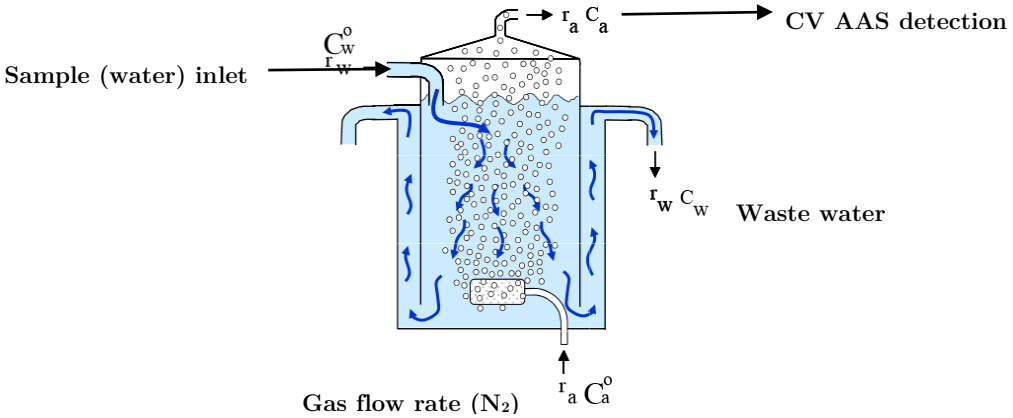


Figure 3.3: A scheme of the continuous system developed for DEM measurements (Andersson et al., 2008). The bubbles indicate the air flow while the arrows indicate the water flow.

The results are given in Results and Discussion. An equilibrium concentration of Hg(0) in the outgoing sample water is established and is represented as the Hg(0) equilibrium concentration in the outgoing air in the top of the inner cylinder according to Henry's law equilibrium (Andersson et al., 2008). The contact time between the air and the water is important in order to establish the air-water equilibrium. The contact time can be adjusted by regulating the flow rate of water and the air flow rate.

A soda lime trap was used between the bubbler system and the inlet of the detector. For the measurements of gaseous Hg(0) in the outlet of the system, two different types of detectors were tested: Lumex, which is based on an atomic absorption (AAS) principle with a Zeeman background correction, and UT 3000, based on a single gold amalgamation of Hg followed by AAS detection. A mathematical model was developed and applied to link the DEM concentration in the gaseous phase and the DEM concentration in the aqueous phase. The DEM concentration is calculated using Eq. 3.1 (Andersson et al., 2008):

$$C_w^0 = \frac{C_a}{H'} + (C_a - C_a^0)\frac{r_a}{r_w} \qquad \text{Equation 3.1}$$

where C_w^0 is the concentration of the Hg(0) in the outgoing water; C_a is the concentration in the outgoing air in the top of the inner cylinder; r_a is the flow of air and r_w is the flow of water.

In this work we tested two different dimensions of the bubbling system (bubblers): one with the capacity of 12 L of water and the other with a maximum capacity of 500 mL (small bubbler). The second was made of glass.

- Flow injection system for DEM and RHg determination

The system based on a flow injection analysis is schematically presented in Figure 3.4. In this system, the same as in the first one, an equilibrium is reached between phases (liquid and gaseous). It is made of several glass units (components) such as sample and gas introduction lines, mixing reaction coil and phase separator. The sample is introduced continuously by a peristaltic pump and is carried through the system by an inert Hg-free gas flow (nitrogen, N_2), ranging flow from 75 to 80 mL min $^{-1}$.

The sample was introduced into the continuous system by a Teflon tube (about 20 cm long, external diameter of 3 mm) which enters the bottle in a way that does not allow Hg(0) loses. After carrier gas and the sample are mixed, the sample enters the mixing reaction coil (with a length of 180 mm, packed in 15 rings) in which the sample and the gas are equilibrated. The length of the mixing reaction coil was chosen in accordance with the sample concentration. Initially a mixing reaction coil of 90 mm packed in 7 rings was used.

In order to lower the limit of detection (LOD), we tested a double-sized column which assured a significant analytical signal. In the outlet of the mixing reaction coil, a gas-liquid phase separator is installed to separate the phases. It consists of two parts: the U shape (diameter of 9 mm), which is constantly filled with sample and the upper part (headspace, with a diameter of 17 mm) where Hg(0) vapour is collected.

No drying material was used between the outlet of gas-liquid separator and the inlet of the detector as no improvements were noticed regarding the repeatability and sensitivity of the method. Therefore, to avoid water to enter the gas line which goes to the detector, a glass tube (with a diameter of 4 mm), through which the gaseous Hg(0) leaves the system, enters the headspace of the phase separator and hangs about 5 mm below the outlet of the mixing reaction coil. Hg(0) vapour stripped from the sample leaves the system from this tube and is further transported to the detector via a Teflon tube (about 80 cm long and external diameter of 3 mm).

In order to assure the optimal flow for UT 3000 detector at 0.3 L min^{-1}, a make-up gas (pure air) was connected before the detector. Quantification of gaseous Hg(0) was performed by CV AAS (UT 3000 detector). The resolution time (amalgamation time) of

the measurements was set most of the time at 3 min but when the limit of detection (LOD) needs to be lower, it can be increased, depending on the concentration of the sample (especially for natural water samples).

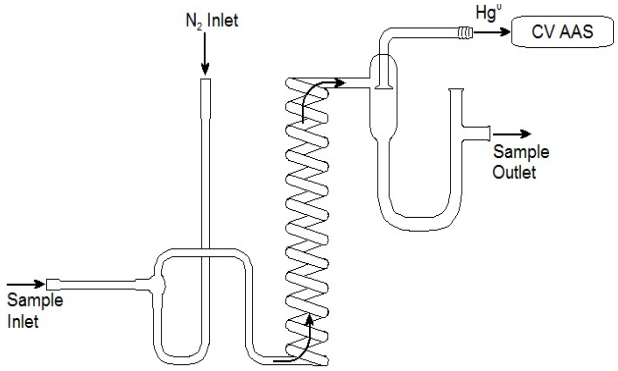


Figure 3.4: Schematic presentation of the setup of the semi-continuous system for determining DEM in water.

The absorbance is measured and its values in the UT3000 detector correspond to the intensity of light absorbed by Hg(0) in the gaseous phase, which depends on the concentration (Lambert-Beer law). The concentration of Hg(0) in the gaseous phase is proportionally correlated with the concentration of DEM in the water sample. However, as the partitioning of DEM between gaseous and liquid phases is largely affected by the composition of the aqueous solution, the conversion factor to obtain DEM needs to be determined for each sample matrix. This is done by the use of manual method, which is used as a reference method as it measures total concentration of DEM in liquid samples. Moreover, the calibration of the continuous method has to be performed by manual method.

The flow injection semi-continuous method was adopted also for RHg measurements. The system is the same as the one described for DEM with the exception that a new line for $SnCl_2$ is added, as shown in Figure 3.5.

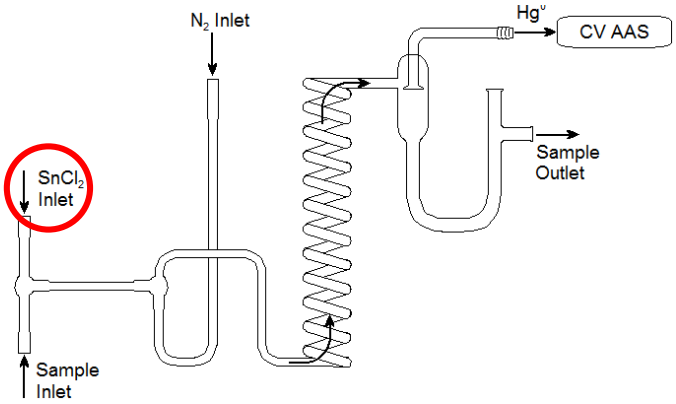


Figure 3.5: Schematic presentation of the setup of the semi-continuous system for determining DEM in water.

RHg using the continuous method was only applied to conduct measurements in the scrubber solution of the WFGD solution.

3.8 The Stability of DEM and RHg in Natural Water Samples and in the Scrubber Solution of the WFGD

The preparation and storage of the samples for DEM determination

The experiments of the stability of DEM in water samples were conducted in freshwater and seawater samples with no storing agent added to the sample (freshwater sample from river Sava, Ljubljana, Slovenia) and with the addition of a storing agent. The samples were stored at room temperature and in the fridge at 4 °C.

Freshwater samples for DEM determination without addition of a storing agent: 1 L glass bottles were filled to the top with freshwater sample from Sava River, Ljubljana, Slovenia and Potocnikov Graben River, Podljubelj, Slovenia. These two rivers were chosen as the most representative water bodies with low and high DEM concentration, respectively. The samples were stored in the fridge at 4 °C.

Seawater samples spiked with DEM stock solution and Hg(II) standard solution with $AuCl_3$ x HNO_3 solution used as a storing agent:

a) Seawater spiked with 10 ng L^{-1} Hg(II) and 5 ng L^{-1} Hg(0)
b) Seawater spiked with 10 ng L^{-1} Hg(II) and 5 ng L^{-1} Hg(0) and 1 mg L^{-1} $AuCl_3$
c) Seawater spiked with 10 ng L^{-1} Hg(II) and 5 ng L^{-1} Hg(0) with 2% HNO_3 and 1 mg L^{-1} $AuCl_3$

Chapter 4

Results and Discussion

4.1 DEM and RHg Stability

DEM and Hg(II) are not stable in water and it is therefore advisable to measure them on the sampling site. Since this is not always possible, storage and transportation of the sample to the laboratory may lead to serious analytical errors. Therefore, volatilization of Hg from the sample, adsorption to the walls of the container, interchange between Hg species, and diffusion of Hg(0) through the walls of the container from the surrounding atmosphere into the sample, have to be carefully considered. As a result, accurate determination may also depend on the use of appropriate containers and storage conditions. Hence, the goal of the experiment was to test the storage conditions under which the losses of the Hg species of interest (DEM and RHg) in natural water systems and in the scrubber solution of the WFGD systems, are minimal.

4.1.1 Stability of DEM and RHg in freshwater samples

The stability of DEM and RHg was initially checked in freshwater samples. Samples were collected manually by submerging pre-cleaned glass bottles in the water stream (about 10 cm deep). We choose two rivers with different Hg content. River 1 represents a sample with low Hg content and it was collected in the Sava River in Ljubljana, only few meters away from the analytical laboratory. River 2 represents a contaminated site. The samples in this case were collected in the Potočnikov Graben, North-West part of Slovenia affected by former mercury mine at Podljubelj. Samples were kept in dark and at low temperatures upon arrival in the laboratory. During the experimental time, one of the parallel samples was kept at room temperature and exposed to light, while the other was stored in the fridge at 4 °C in the dark.

The results obtained for DEM measurements for the Sava River, River 1, are presented graphically in the Figure 4.1.

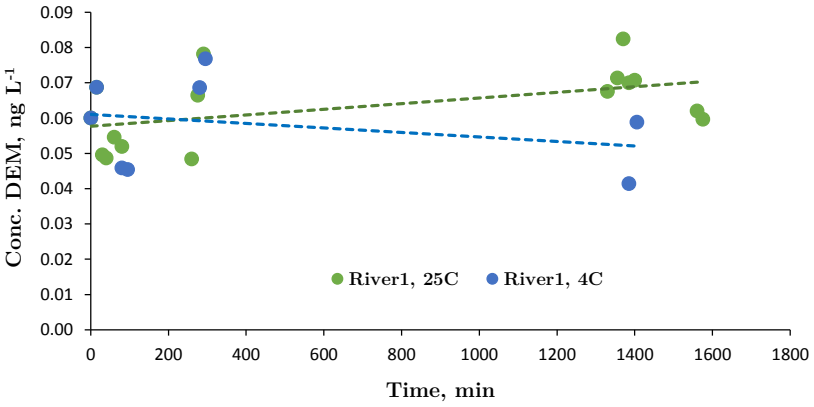


Figure 4.1: The stability of DEM in freshwater samples collected in River 1 stored at room temperature (20-23°C) and in the refrigerator (4 °C).

Evidently, storage of the river water at 4 °C protects concentrations of DEM over a 24 hour storage period. Interestingly, when samples were stored at room temperature, the concentrations of DEM decreased after about 4 hours of storage from 0.06 ng L^{-1} to about 0.05 ng L^{-1} and subsequently increased (after 23 hours) to about 0.07 ng L^{-1}. After 26 hours they were back to the initial concentration. This indicates that some elemental mercury is oxidized to inorganic mercury and later reduced back to Hg(0), which can be explained by enhanced reduction potential occurring at room temperature.

RHg was also measured in the samples from Sava River (Figure 4.2).

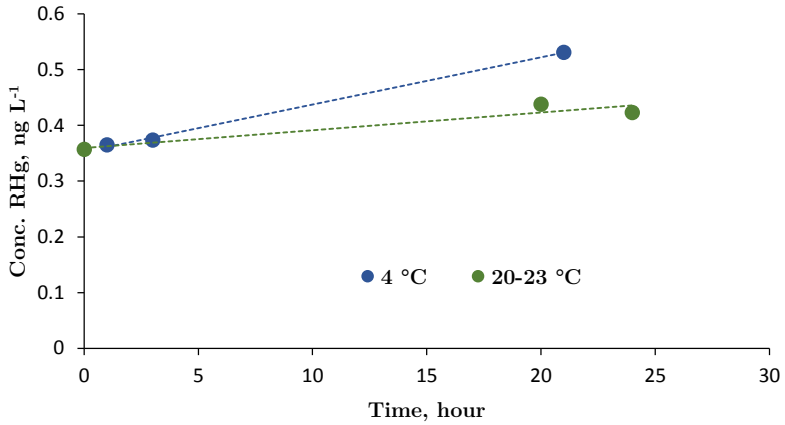


Figure 4.2: The stability of RHg in the River 1 (Sava River).

An increase of RHg was observed when the sample was stored in dark in the refrigerator. A possible explanation for this is either the diffusion of additional Hg(0) from the bottle walls into the sample or oxidation of Hg(0), which is known to occur also in the dark at low temperatures (Fantozzi et al., 2009). No significant changes of RHg stored at room temperature were observed.

As stated in the beginning of this section, the stability of DEM was also checked in the river with higher Hg content. The storage of the samples was the same as for River 1 and the obtained results are given in Figure 4.3.

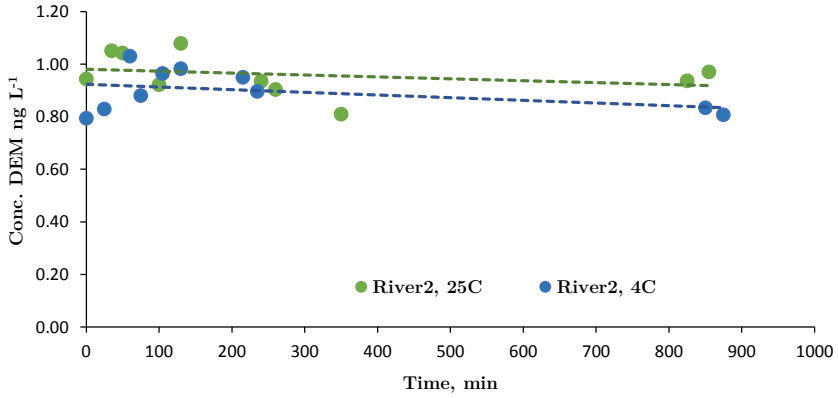


Figure 4.3: The stability of DEM in freshwater samples collected in River 2 stored at room temperature (20-23 °C) and in the refrigerator (4 °C).

In case of stream water sample obtained from a former mercury mining region (Fig. 4.3), the concentrations were much higher than in river Sava. A slight change in the concentration of DEM was observed after 5 hours for samples stored at room temperature (0.94 to 0.81 ng L^{-1}) and after 15 hours the measured concentrations increased up to 0.97 ng L^{-1}, comparable with the initial level. In the samples in the fridge, a slight increase was observed after one hour of storage (0.80 to 1.03 ng L^{-1}) and after 15 hours, the concentrations were more or less stable. Lindberg et al. (2000) showed that fresh water samples collected over short periods are not necessarily stable due to volatilisation and/or oxidation. Overall, measurements made within 4–6 h are not critical for DEM losses.

4.1.2 Stability of DEM in seawater samples

The stability of DEM in seawater was checked during a research cruise in the Adriatic Sea. The samples were collected and stored in glass bottles (acid pre-cleaned) for about 6 hours and measured in time intervals: immediately after sampling, after about 1 and 6 hours. The results obtained for two samples are demonstrated in Figure 4.4.

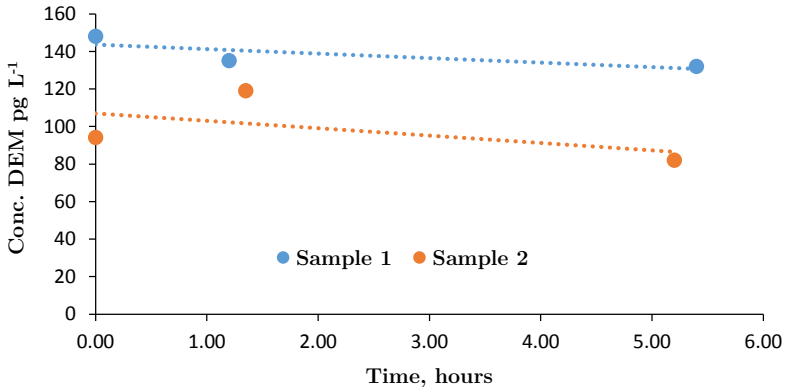


Figure 4.4: The stability of DEM in seawater samples.

Surprisingly, DEM in seawater did not show a drastic decrease after 6 hours of storage. The results obtained for Sample 1 were 10% lower. Concentration in sample 2 increased by

about 20% after 90 min of storage and after about 6 hours, the results were approximately 12% lower when compared with the first measurement. The differences, however, are within the measurement uncertainty of the manual method used to conduct the measurements. A similar study conducted by Rolfhus & Fitzgerald 2001 in coastal marine water showed no statistical differences in concentration after two days of storage in refrigerator in the dark. Independently from storage conditions, it was clear that the safest time period to measure DEM in seawater was within 1-3 hours after sampling. The results obtained after few hours (5-6 or more) might be related to changes in Hg chemistry occurring in the water sample, volatilisation of the species from the water samples or additional Hg(0) diffusing into the bottle.

It is generally agreed that lowering the pH of the sample would stabilize Hg in the sample. On the other hand, it is also known that acidification might cause unpredictable behaviour of DEM and RHg in the water sample. The need to preserve the sample for DEM and RHg is highly important; therefore, we conducted experiments by testing the stability of the mentioned species in water samples with $AuCl_3$ and acidified with HNO_3. Due to low natural concentrations, the samples were spiked with additional amounts of Hg(II) standard solution and Hg(0) stock solution. The stability was checked over a period of several hours and days. As reported by Environment Protection Agency (EPA, 2003) the gold stabilization method was thought to directly prevent deposition by keeping all Hg in solution in environmental water samples. The suggested procedure from EPA was applied first. We added 1ppm (mg L^{-1}) $AuCl_3$ in 2% HNO_3 to the samples. We observed Au precipitation on the glass filter of the bubbler for RHg measurements.

$$AuCl_3 + SnCl_2 \rightarrow SnCl_4 + Au^0\downarrow$$

The presence of Au particles might lead to adsorption of Hg(0). For this reason, we 're-optimized' the ratio $AuCl_3 : HNO_3$. The best ratio where no Au precipitation was observed was when 0.5 mg L^{-1} $AuCl_3$ and 0.5% HNO_3 were added to the sample. Interestingly, in simple water matrixes such as distilled water or tap water, the levels of Hg(II) and Hg(0) were decreased by about 80% when the agents were added to the sample. A different effect was observed for seawater samples. Mercury losses are generally greater from distilled water than from natural water due to the lack of complexing and chelating agents in distilled water (Hamlin et al., 1989). In order to have elevated Hg concentrations, the samples were spiked with additional Hg(0) and Hg(II). Measurements before and after the addition of the agents were performed, and the results are given in Figure 4.5. The results for DEM were subtracted from the total RHg measured.

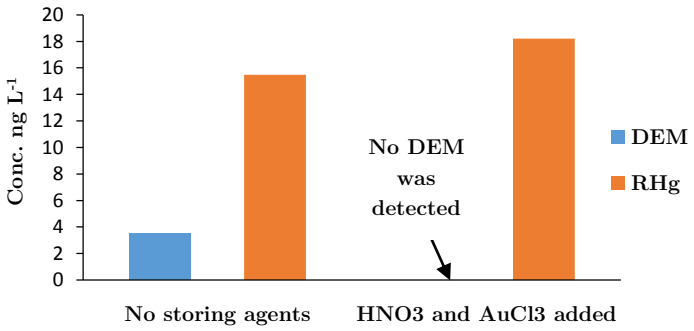


Figure 4.5: Stability of DEM and RHg in seawater as a result of HNO_3 and $AuCl_3$ addition.

In repeated tests, independently from the DEM and RHg concentration in the seawater samples, $AuCl_3$ when combined with HNO_3 caused oxidation of Hg(0) into Hg(II). The stability of the formed Hg(II) in a parallel sample with final RHg concentration of about 5 ng L^{-1} was checked for more than 48 hours. The obtained results are given in Figure 4.6.

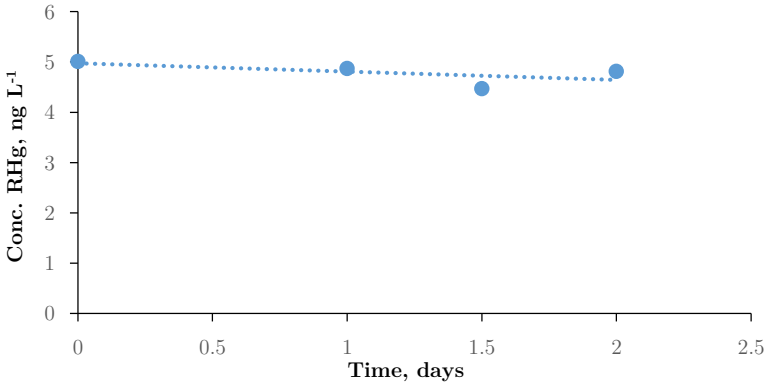


Figure 4.6: The stability of RHg in a seawater sample with time in the presence of $AuCl_3$ and HNO_3.

The differences in the concentration of RHg in two consecutive days did not exceed 8 %. This is a good indicator that $AuCl_3$ and HNO_3 can be used to preserve samples for RHg measurements when DEM is already measured at the sampling site. In this case, the results for only RHg can be calculated by subtracting the DEM results from the total results.

Besides natural water samples, the stability of RHg and DEM was also checked in the scrubber solutions of the WFGD without and with the presence of $AuCl_3$ and HNO_3. The stability of these species in such sample matrix is very important in order to determine the time allowed for these samples to be stored before being measured. It is known that scrubber solution samples are very reactive and therefore the stability of the Hg species is a problem. Moreover, the presence of particles affects this stability as a result of adsorption or other physical processes.

4.1.3 Stability of DEM and RHg in scrubber solutions

In order to conduct the experiment, five different scrubber samples were analysed during a time period of 24 hours. The samples were taken from two different sources: the thermal power plant in Šoštanj, Slovenia, and from the pilot plant in the laboratory. In all samples, DEM, RHg and THg were determined. Due to large differences in concentrations between them, we put all DEM measurements on one graph (Figure 4.7) and the RHg results on the other (Figure 4.8). The measurements were conducted using the manual method.

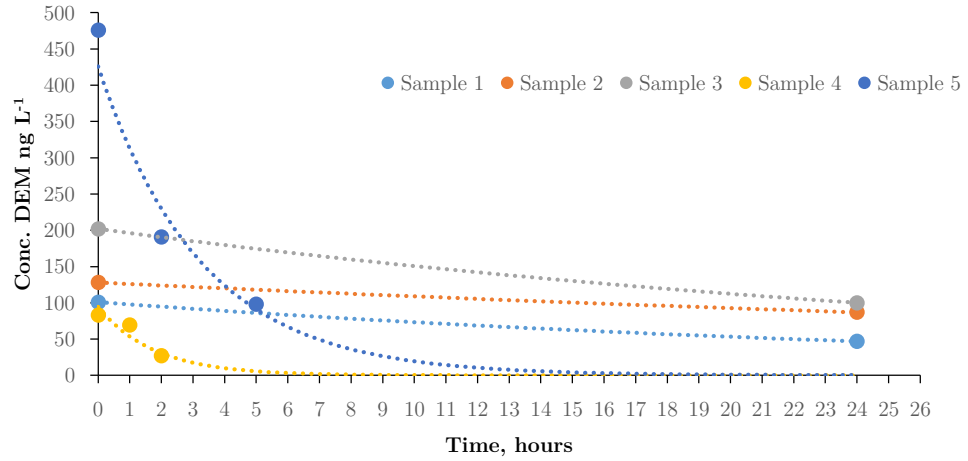


Figure 4.7: The stability of the DEM in the scrubber solution of the WFGD system.

DEM was shown to be very unstable in the scrubber solution. A decrease in the concentration was noticed immediately after the first hour of storage. After 2 hours there was a decrease of more than 50 %. This indicates the need for DEM measurements immediately after sampling. The results obtained after 24 hours of storage demonstrated significant losses.

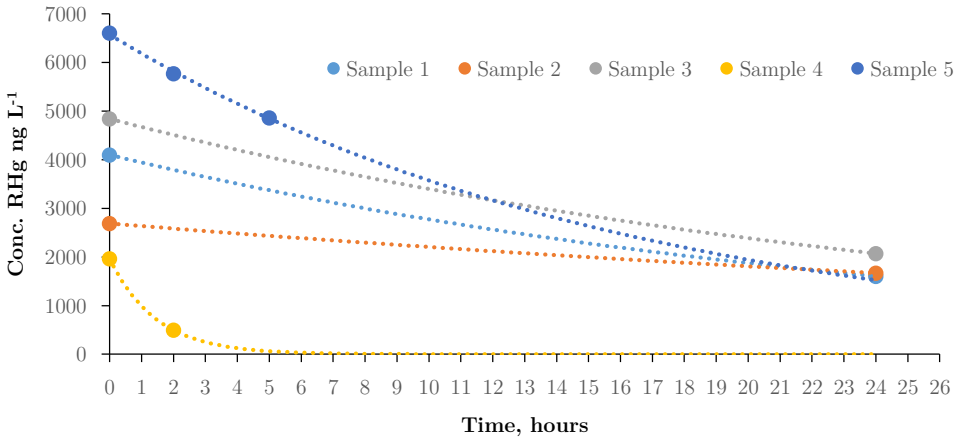


Figure 4.8: The stability of RHg in the scrubber solution of the WFGD system.

The results of RHg in the analysed samples had significantly decreased after 2-5 hours of storage. The degree of the decrease, expressed in %, was the same for both species (DEM and RHg) in the same sample (e.g the losses of DEM and RHg in Sample 1 were 54 and 61 %, respectively) and it ranged from 30 to 80 %.

Interestingly, THg results of the samples ranged from 187 to 202 μg L^{-1}. This is an indication that the losses did not occur as a result of adsorption on particles. Most probably the Hg(0) in the solution is escaping. Another scenario could be the reduction of Hg(II) into Hg(0) and its quick loss from the sample. However, possible interconversion/adsorption to particles might also occur but it is difficult to notice due to the enormous differences in concentration of these species and THg (few ng L^{-1} for DEM and RHg to a few hundred μg L^{-1} for THg).

Since the results for natural waters clearly demonstrated the oxidation of Hg(0) into Hg(II) in the presence of the $AuCl_3$ and HNO_3, the experiments were not repeated with the scrubber solutions of the WFGD.

4.2 Gold Trap Characterization and Development

A very important step in Hg analyses is the pre-concentration on gold traps. Most methodologies use gold traps consisting of a silica powder coated with thin layers of gold. The problem is that after prolonged use, these traps become passivated. This results in lower and irreproducible measurements of mercury. The passivation is often observed when seawater samples are measured.

One of the objectives of this work was to find the reasons for passivation and to prepare Au traps that are resistant to passivation. In this work we were using as a reference material the commercially available gold-coated silica powder produced by Brooks Rand. The material is very expensive and therefore a cheaper way to produce home-made gold traps would greatly reduce the costs of the analysis.

The first hypothesis regarding the possible causes of passivation was related to the formation of additional compounds on the surface of the Au-coated material. We therefore first performed XRD measurements of the passivated and the new commercially available Au-coated silica. The obtained results are given in Figure 4.9, in which the red line belongs to the passivated sample and the black to the commercially available Au-coated silica.

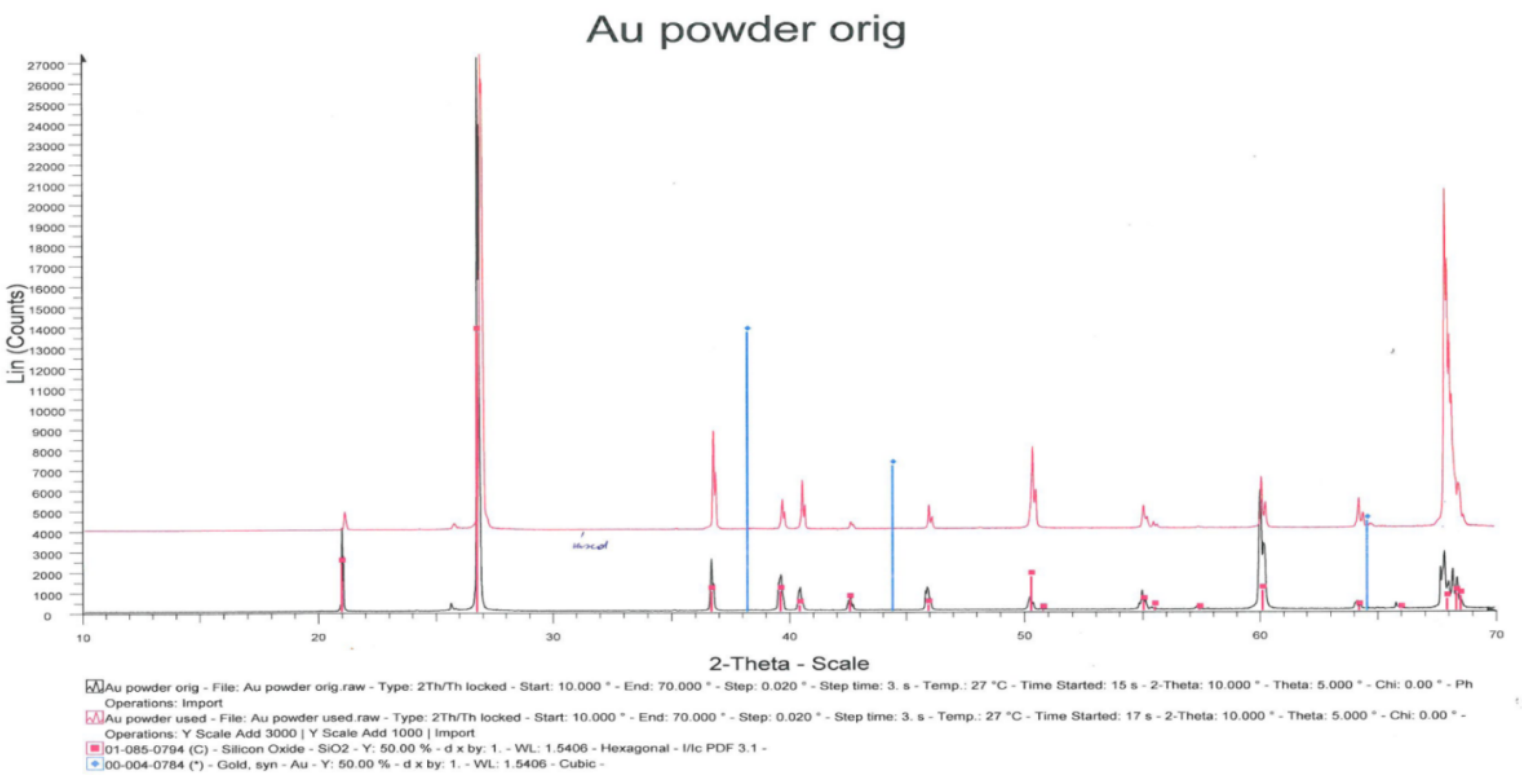
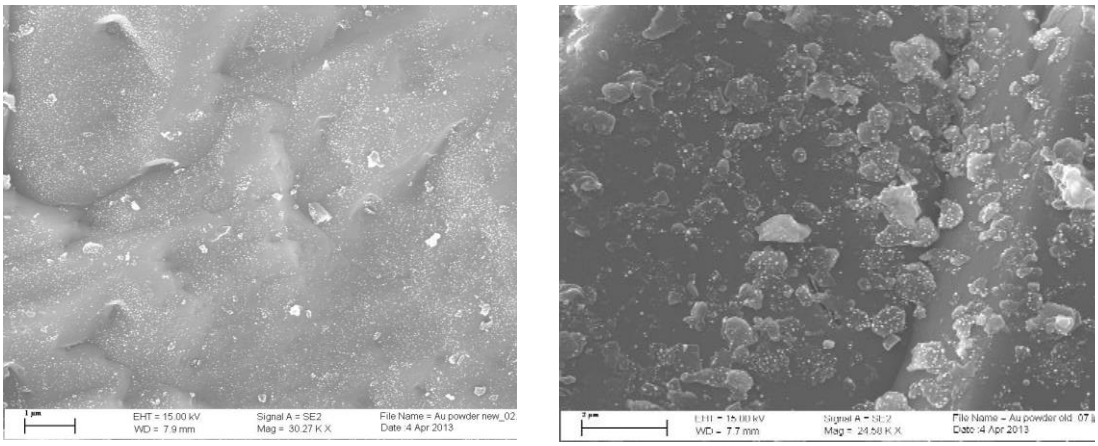


Figure 4.9: Au-coated powder. Red line: Passivated sample; black line: fresh sample.

No differences were noticed when the two patterns were compared, except for the last peak which is due to the instrument performance. Qualitative analysis showed that all peaks belong to silicon oxide. No traces of the presence of Au or any other element/compound were distinguished on the surface of the Au-coated silica. Although this position is usually where the heavy metals come up, repeated measurements of the same samples excluded this opportunity.

SEM measurements were further conducted for the same samples and a comparison is demonstrated in Figure 4.10.



Commercial new Au trap | Au passivated trap

Figure 4.10: Comparison of surfaces between new and passivated Au -coated silica.

We could clearly distinguish the presence of Au (white points) on the surface of the silica oxide. In a new trap, Au was homogeneously distributed on the surface of the silica. The opposite was observed for the passivated sample, where large uncovered silica surfaces were observed. Clearly, agglomeration of Au particles occurred. The latter is highly related to the exposure of the trap to high temperatures during Hg measurements.

This is supported by the fact that the size of the particles and the thickness of the Au layer are small enough to allow the agglomeration process to take place. Therefore, in order to improve the precision and sensitivity of the measurements, a better coating of the surface with Au would be helpful. We therefore added one more Au nano layer to the existing commercial materials and SEM measurements were conducted in order to check the quality of the coating. Figure 4.11 shows the obtained SEM image of the sample with an additional Au layer.

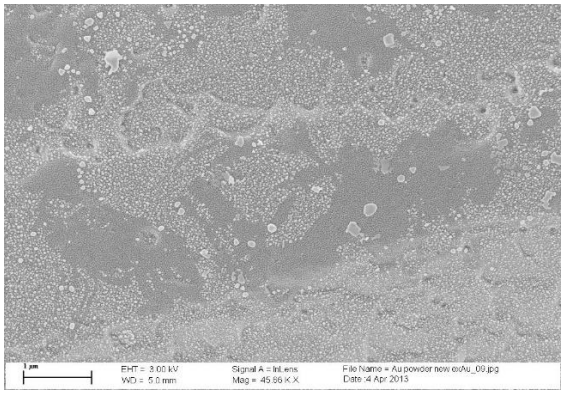


Figure 4.11: SEM image of the Au silica with an additional Au layer on the surface.

SEM images confirmed the addition of the new Au layer on the SiO_2 surface. The thickness of the Au nano-layer varied from 30 nm to 70 nm and the shape of the particles is not round but elliptic, due to the instrument we used for coating. The increased amount of Au on the surface was proven quantitatively by EDS analysis showing about 2.24 % Au when compared with about 1% present in the original sample.

In order to test the performance of the coated silica sample in Hg measurements, the sample was packed in quartz tubes and 27.8 pg Hg(0) was injected into the double amalgamation system and detected on CV AFS detector. A commercially available trap was used for reference. A comparison of the results is given in Figure 4.12.

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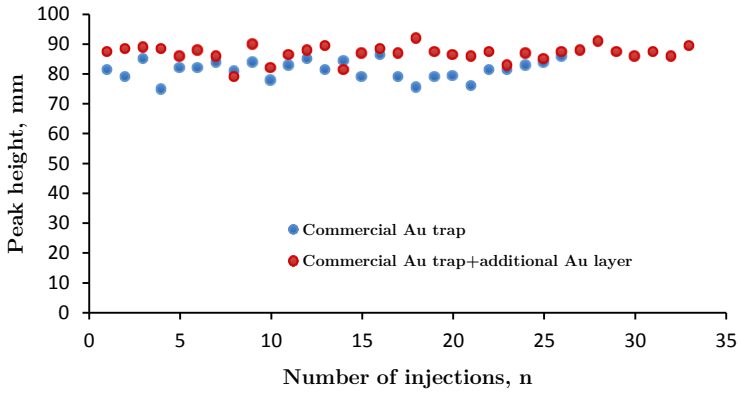


Figure 4.12: Hg(0) measurements; comparison between a commercially available Au trap and a trap with an additional Au layer.

Repeated tests during several days showed on average about 7 % higher results for the trap with an additional Au layer. The reproducibility of the measurements varied from 1 to 4% for the trap with the new Au layer and up to 9% for the commercial one. No other differences were noticed between the performances of the traps regarding desorption temperature, retention time or peak shape. In order to reduce the costs of the analyses using Au traps, we took silica oxide powder and coated it with Au as demonstrated in the experimental section. Heating at 500 °C for 1 hour under hydrogen atmosphere did not give good results. SEM images showed large uncovered surfaces. In addition, Au seemed not to be properly attached to the silica surface. We therefore increased the heating time and the SEM measurements are demonstrated in Figure 4.13.

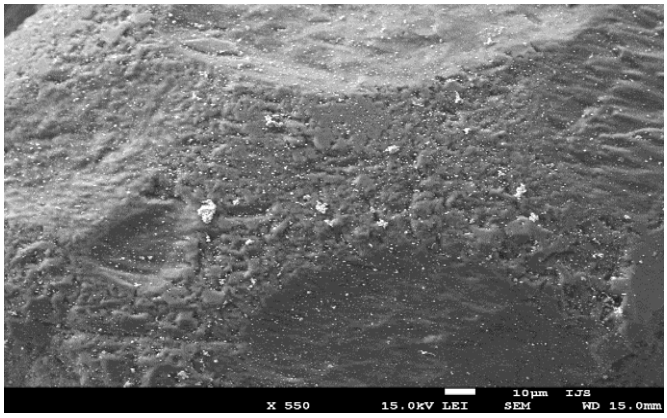


Figure 4.13: SEM image of the Au-coated silica oxide.

The surface was not fully covered but it was not possible to improve this. Coating by using sputtering on the surface is an expensive method, allows only very small amounts of sample to be prepared at once (about 1 gram) and the coating is done on only one side of the particle.

Hg measurements were again performed by introducing Hg(0) vapour into the double amalgamation system (Figure 4.14).

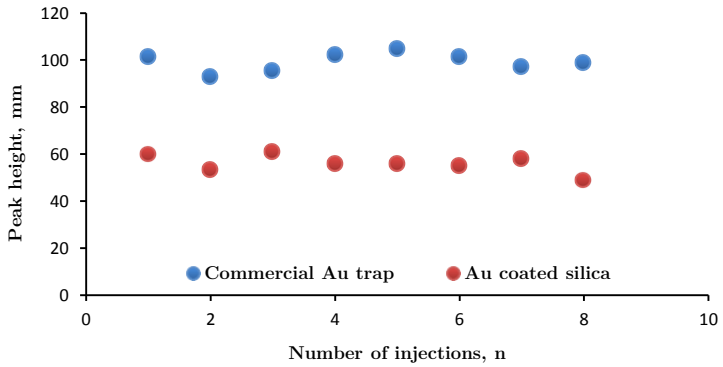
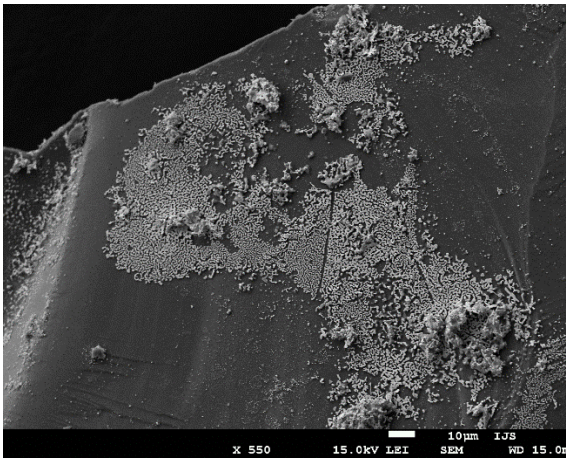


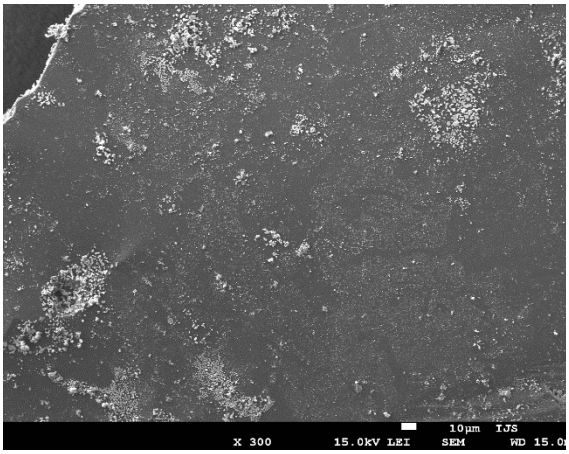
Figure 4.14: Hg(0) measurements; comparison between the commercially available Au trap and SiO_2 covered with Au.

When the results were compared with the reference Au trap, they differed by about 40%. Numerous repeated tests showed the same behaviour. The repeatability of the measurements was good (with an average of about 8%) but the sensitivity was poor. For this reason we chose a more inert material to coat with gold, namely aluminium oxide (alumina). The same as for silica oxide, optimisation of temperature and the time needed for Au to be reduced on the alumina surface was needed. SEM images are shown in Figure 4.15.

500 °C, 1 hour



500 °C,2 hours



600 °C, 3 hours

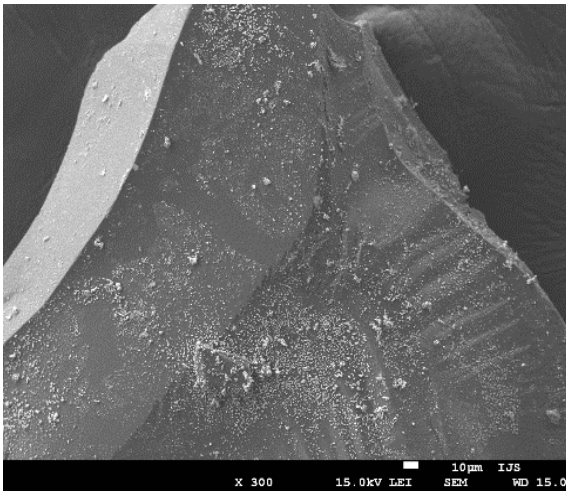


Figure 4.15: SEM images of Al_2O_3 samples coated with Au and exposed to three different temperatures and for different times of reducing Au on the surface.

The obtained results were better when compared with SiO_2 in terms of homogeneity and Hg measurements. When Au was reduced on the sample surface at 500 °C for 1 hour, the surface was not homogeneously coated. On the other hand, a 2 hour reduction period at the same temperature resulted in a significant improvement of the coating. No differences in the temperature for Hg desorption were needed for the new coated material.

Therefore, we increased the temperature and the time of reduction for the third sample and the SEM images showed the best results. This material was chosen to further continue the experiment. Three experiments were performed:

a) Measurements of pure Hg(0) vapour
b) Measurements of MilliQ water spiked with Hg(0) stock solution
c) Measurements of seawater spiked with Hg(0) stock solution
d) Measurements of the scrubber solution of a WFGD system

The first test of the alumina trap included the injection of known amounts of pure Hg(0) vapour via a gas-tight syringe into the double amalgamation system where alumina trap was installed (Figure 4.16). The obtained results were compared with a new commercially available Au silica trap.

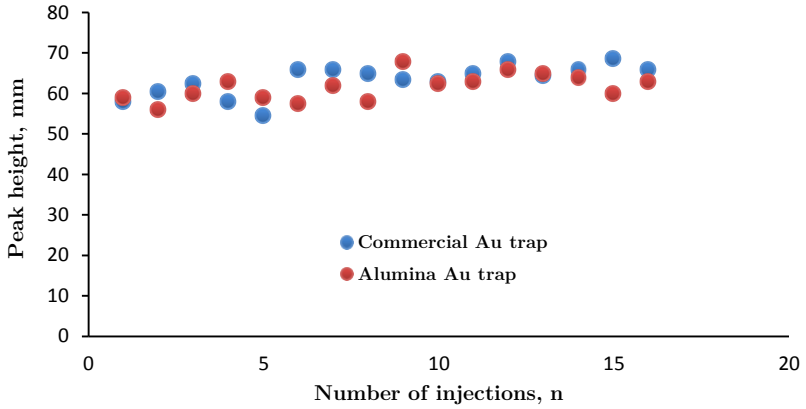


Figure 4.16: Measurement comparison of Hg(0) results between Au silica commercial trap and alumina Au-coated trap.

The comparability of results between traps was good and no significant differences between them were observed. When the calibration curve was made by injecting different amounts of Hg(0) vapours (20 pg to 200 pg), a linear response was obtained (Figure 4.17).

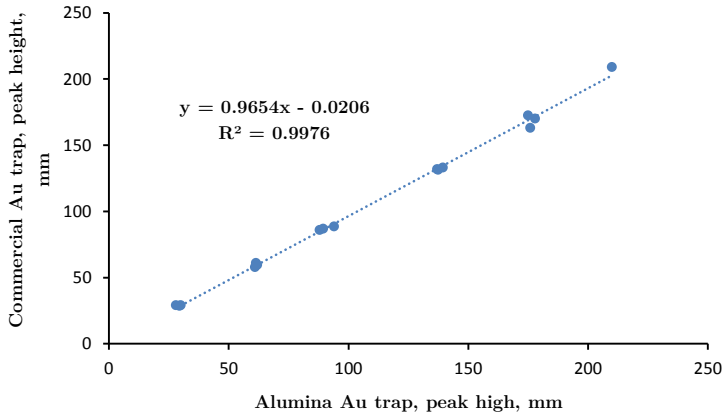


Figure 4.17: Correlation between results obtained with the Au coated alumina and the commercial Au traps.

The linearity of the obtained results was very good. Furthermore, the comparability of the results obtained with the coated Al_2O_3 and the reference trap was excellent. We therefore continued the testing by measuring Hg(0) dissolved in water matrixes.

We continued the test of trap performance by measuring DEM in distilled water. A series of solutions with DEM concentrations varying from 0.5 to 1 ng L^{-1} were prepared by spiking DEM stock solution in distilled water, and measured on the double amalgamation system. The obtained results are given in Figure 4.18.

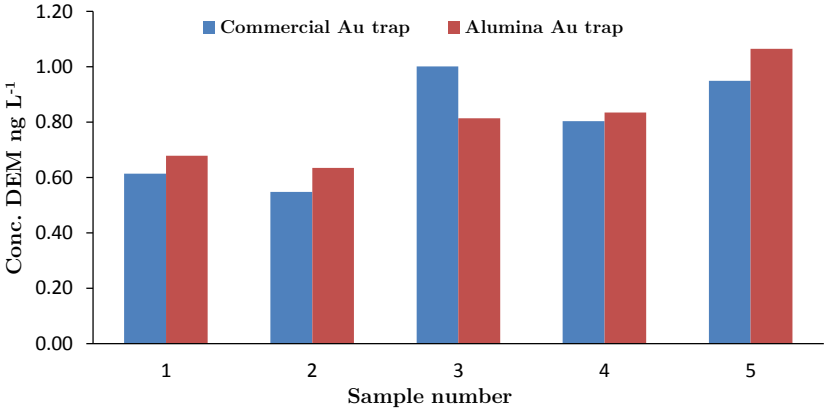


Figure 4.18: Comparison of the results when distilled water is spiked with DEM stock solution and measured with the commercially available Au trap and alumina Au-coated trap.

The comparability of the results ranged between 5-15 % expressed as relative standard deviation.

In addition, the calibration curve using a wider range of concentrations (0.1-2 ng L^{-1}) was also made. The concentrations were measured at the same time by the alumina and the commercially available Au trap (silica trap). The linear regression line comparing the results obtained from both is given in Figure 4.19.

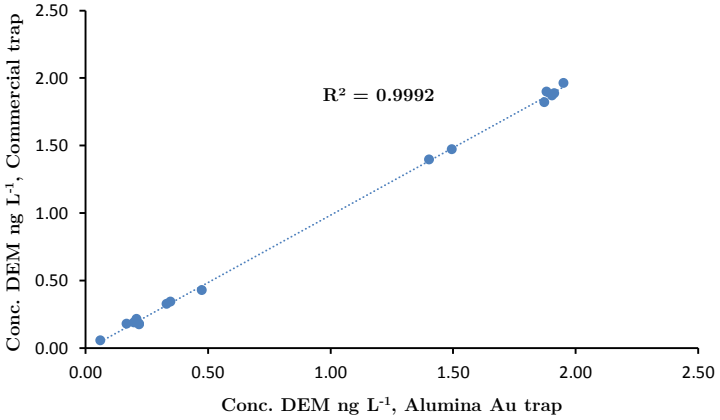


Figure 4.19: Calibration curve of alumina oxide Au-coated trap when different Hg(0) amounts were spiked in the distilled water.

As expected, the correlation factor of the results was almost one, demonstrating the linearity and the high comparability of the results obtained. As a result, further tests were conducted by measuring DEM in seawater samples. Seawater was chosen because it is the most widely measured matrix for Hg measurements in our laboratory. Given that the natural DEM concentrations in seawater are very low, we spiked it with DEM stock solution and a comparison of the results obtained with the coated alumina material and the reference material is demonstrated in Figure 4.20.

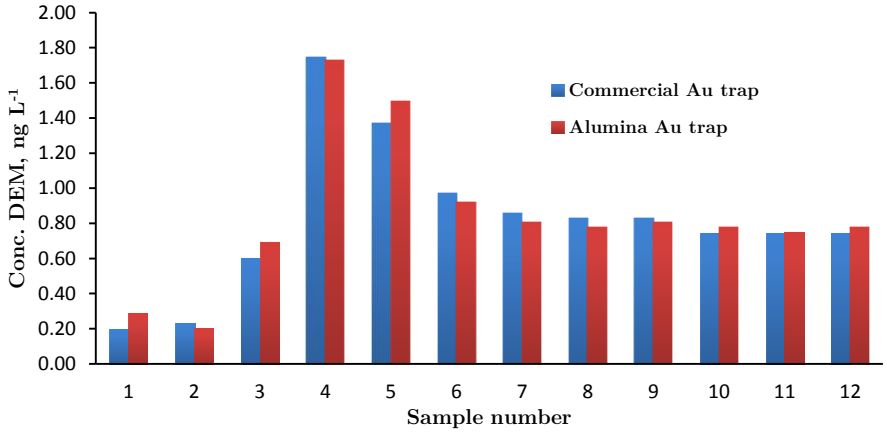


Figure 4.20: Comparison of the results when seawater is spiked with Hg(0) stock solution and measured with the commercially available Au trap and alumina Au-coated trap.

The differences between traps expressed as relative standard deviation did not exceed 7 %, which was not statistically significant.

Repeated tests performed about one month later using the same water matrix spiked with higher concentrations of DEM stock solution (0-30 ng L^{-1}) confirmed the linear response for the tested concentration range for both traps (Figure 4.21).

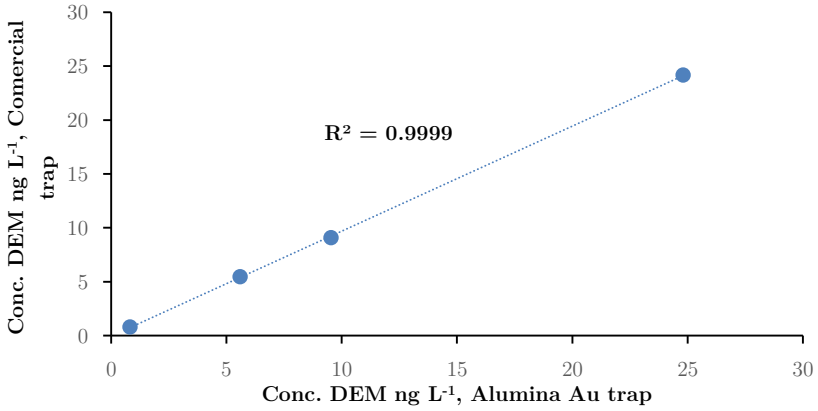


Figure 4.21: Calibration curve of Alumina Au-coated trap when different Hg(0) amounts were spiked in seawater.

The linearity was confirmed also for higher concentrations. Measurements of DEM in the scrubber solutions were also performed and the comparison of the results obtained with both traps (commercially available Au-coated silica and Au-coated alumina) is given in Figure 4.22.

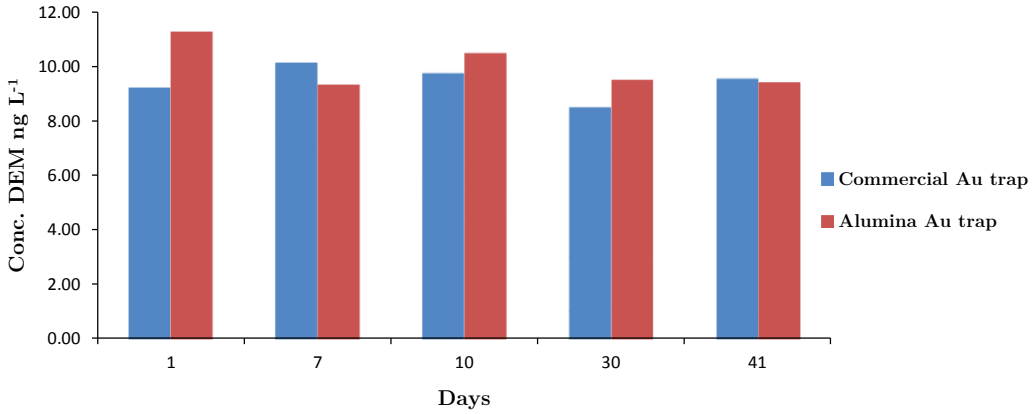


Figure 4.22: Comparison of the results for DEM in the scrubber solution measured with the commercially available Au silica trap and alumina Au-coated trap.

Besides the pre-concentration materials, one of the most important and significant interferences in Hg measurements is water vapour. Thus, it is of crucial importance to find an appropriate drying material that would reduce to minimum the water vapour reaching the gold trap. Generally a drying trap is installed between the bubbling system and the Au trap. The quality of such materials should be checked before use in order to determine possible losses of Hg on it. The drying material influences not only the blanks of the system, but also the reading of the results. Therefore, extreme care should be taken to assure that the drying material does not affect the quantitative pre-concentration of Hg on the Au trap. For these reasons, we compared three different approaches of removing water vapour. We tested silica gel powder, soda lime and the Perma Pure trap. The first two were heated to approximately 120 °C to remove water vapour possible traces of Hg. The Perma Pure trap (made from a Nafion membrane) is considered a moisture exchanger wherein the functioning drying system additionally requires a drying gas flow (we used N_2). Nafion is a copolymer of perfluoro-3,6-dioxa-4-methyl-7-octene-sulfonic acid and tetrafluoroethylene.

It spontaneously absorbs water from the gaseous phase. Each sulfonic acid is surrounded by a maximum of 13 water molecules. The water is transported to the wall side. This transport is carried out quickly. The water transport is always in the direction of the lower water vapour concentration. The amount of residual water in the Nafion wall is temperature-dependent. At higher temperatures, more water is retained by the wall and cannot be delivered to the dry gas accordingly.

The testing included blank measurements with and without the presence of the drying material and also measurements of Hg(II) standard solution after reduction with $SnCl_2$. The measurement system installed for the purpose of this experiment was similar to the one used for DEM and RHg measurements in water samples. When no drying material was used, the Au trap was dried by a flow of nitrogen for 3 minutes before desorption in the double amalgamation system. This increased the analysis time for about 2 times. Figure 4.23 shows a typical example when silica gel was used to conduct Hg measurements in water systems, including blanks. The measurements were conducted for about 6 hours without changing the silica gel.

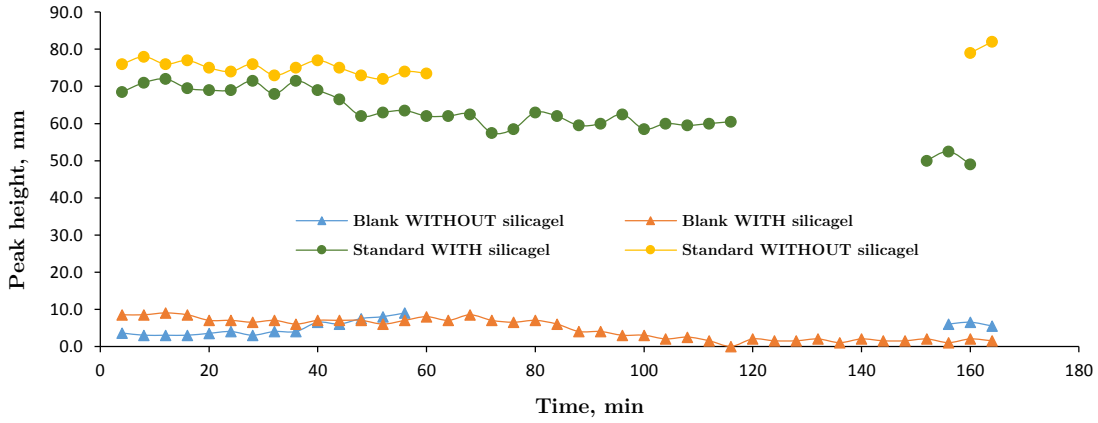


Figure 4.23: Blanks and standards measured with and without the presence of silica gel.

When no silica gel was used, the blanks increased after about 2 hours while the opposite would happen with the blanks when the drying material was used. When the silica gel was saturated with water vapour, the difference between the peak height of the standard and of the blank remained constant but the sensitivity of the measurements was lower. The results obtained when no silica gel was used were higher by about 10 % compared to the measurements using the silica gel. After 2 to 5 hours, depending on the level of humidity, the peak heights decrease.

The same experiments were repeated with soda lime and the obtained results are shown in Figure 4.24. We observed that the time needed for saturation of the soda lime with water vapours was about 3 times longer than for silica gel.

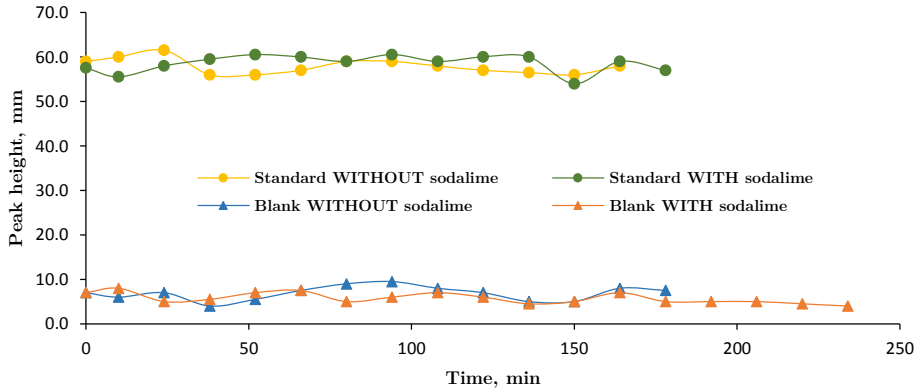


Figure 4.24: Results obtained for blanks and Hg measurements with and without soda lime.

There were no significant differences (about 3%) between the results with or without soda lime. Furthermore, the blanks were reduced by 20% on average when soda lime trap (SLT) was used, which is excellent for measuring low concentrations of Hg.

The third drying material tested was the Perma Pure trap and the results obtained for the standards and blanks are shown in Figure 4.25.

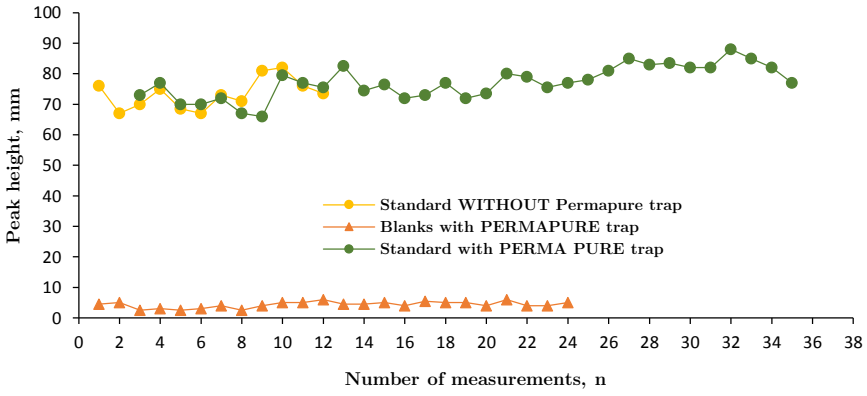


Figure 4.25: Results obtained for the Perma Pure trap test using blanks and standards.

We obtained about 5% higher results for the Hg(II) standard when the Perma Pure trap was used. In repeated tests, the comparability ranged ±2 %. The repeatability of the measurements was the same in both cases (6.8–6.9%).

Overall, the results with soda lime and Perma Pure trap were good and either of these drying materials can be used for Hg measurements. The Perma Pure trap is applicable in the lab and we have implemented its use in the automated method for THg measurements, but it is quite expensive since large amounts of N_2 are needed. Moreover, it is not practical to use in manual methods for DEM, RHg or THg and it should be avoided when Hg in samples with higher temperatures needs to be measured. An example of results obtained when measuring samples with temperatures ranging between 28–36 °C is given in Figure 4.26.

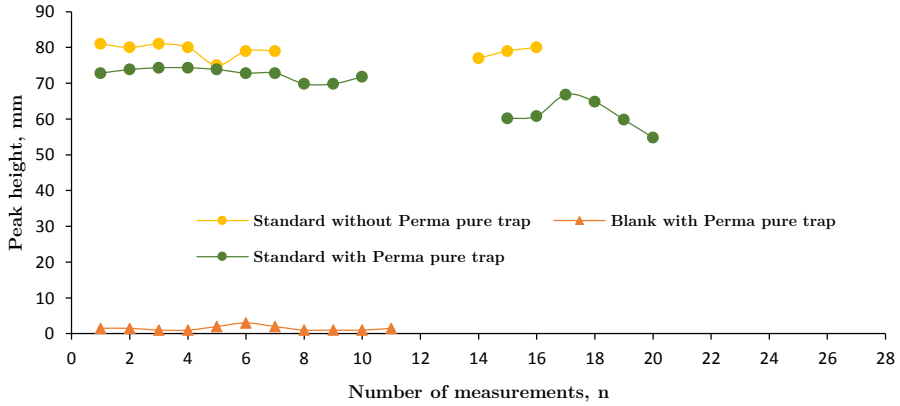


Figure 4.26: Results obtained when Perma Pure trap was applied for measuring water samples with higher temperatures.

After 2.5 hours of running the system, we observed a decrease in the performance of the Perma Pure trap as a result of increased levels of humidity. The Nafion membrane lost its initial shape due to large amounts of water (as predicted theoretically). We therefore used soda lime as a more practical and less expensive material.

4.3 Calibration of Methods for DEM Measurements

The calibration of the instruments for DEM measurements is the most critical step in ensuring reliability of the data obtained. We tested and compared three different ways of calibrating the manual setup system for DEM measurements in water samples.

The first is based on conventional instruments and the use of Dumarey equation describing the dependence between Hg concentration at saturation and temperature. Generally a known amount of mercury vapour is withdrawn with a gas-tight syringe from a calibrator and introduced into the measurement stream of the instrumental setup, normally based on pre-concentration of Hg on gold traps and subsequent detection by CV AFS. Several empirical equations are available to describe the vapour pressure of mercury at a given temperature, which is the basis for calibrating Hg instruments. The agreement between these equations differs by 5 % or more.

The second alternative is based on the reduction of known amounts of Hg(II) in aqueous solution and the pre-concentrated Hg(0) on Au traps is further desorbed and detected by CV AFS. The third approach was based on the reduction of known amounts of Hg(II) in closed vials. After equilibration of Hg(0) between aqueous and gas phases, a known volume was taken from the headspace of the vial using a gas-tight syringe and measured as described above.

4.3.1 Calibration with pure Hg(0) vapour

Calibration of the detector with Hg(0) pure vapour was performed by injecting known volumes of Hg(0) vapours into the double amalgamation system. The volumes were further converted into amount by applying the Dumarey equation. An example of a calibration curve for Hg amounts between 10 and 170 pg is shown in Figure 4.27.

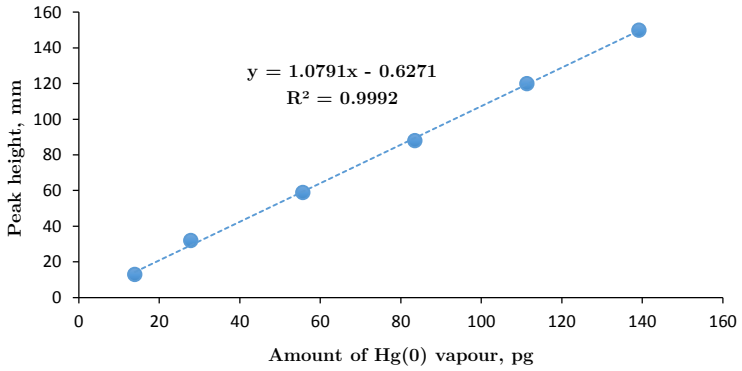


Figure 4.27: Example of a calibration curve with pure Hg(0) vapour from the calibration unit. Every point in the graph represents an average of at least 3 measurements.

In all repeated tests, the linearity of the results was excellent. The repeatability of the measurements was about 3 % on average, expressed as relative standard deviation of at least three measurements.

The calibration by using the Tekran 2505 calibration unit is only successful if sufficient care is taken when using the syringe and injecting the standard. However, there are dilemmas regarding the calculation of the amount of Hg(0) vapour standard and how much the potential differences affect the results when real samples are measured. Therefore, we tested the calibration of the instruments by using Hg(II) solutions and reduction with $SnCl_2$.

4.3.2 Calibration with Hg(II) reduced with $SnCl_2$

A certified reference standard (SRM 3133) was used to perform the calibration with Hg(II) reduction. Hg(II) standard solution of 1 ng mL^{-1} was prepared and a series of spiked solutions was prepared in MilliQ water. $SnCl_2$ was used as the reducing agent. The amounts of Hg reduced ranged between 14 pg and 140 pg.

The experiment was repeated for three different days, using three different Hg (II) standard solutions prepared fresh every day. The same amounts of Hg(0) were withdrawn from the calibration instrument and measured.

A typical example of comparison between these two calibration modes is given in Figure 4.28:

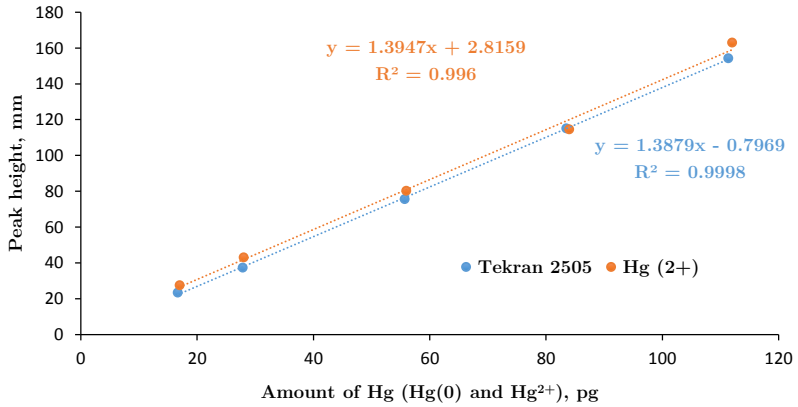


Figure 4.28: Comparison of calibration using Hg(0) and Hg(II) standard solution. Each point is the average of at least 3 consecutive measurements. The relative standard deviation varied from 1 to 5 %.

The repeatability of the results with both methods was very good (the relative standard deviation ranged between 0.41 to 3.22 % for three or more measurements). The same can be said of linearity and comparability. The last was re-confirmed in several other tests performed in different days. The difference between the calibration curves was between 2 and 5 %.

4.3.3 Calibration using Hg(0) vapour collected in the headspace of gas-tight vials

Besides the two conventional methods of instrument calibration, we tested an additional one. The method consists in producing Hg(0) vapour in gas-tight vials in which a certain amount of Hg(II) is reduced with $SnCl_2$. The experiment was conducted in different months, in different laboratories and using different calibration units (Tekran 2505 and UT 3000) as reference.

Gas-tight vials were used for the experiment. In each, 1 mL of $SnCl_2$ and a certain amount of Hg(II) was added. The vials were shaken for 3 minutes and from each, Hg(0) vapour was taken with a gas-tight syringe. When 14 to 84 pg of Hg(II) solution were reduced, there was a clear irreproducibility of the results obtained. Most of the vials exhibited the same trend, although the amounts of Hg(II) reduced in them were different. Additional problems were connected with the needle of the gas-tight syringe used to withdraw Hg(0) vapour. The experiment was repeated with higher amounts of Hg(II) reduced, namely 25, 50, 100, 150, 200 and 250 ng. Table 4.1 presents the obtained results.

Table 4.1: Amounts of Hg(II) reduced and the % of Hg(0) in the gaseous phase.

	After 5 min	**After 2 hours**	**After 24 hours**
ng Hg(II) aqueous	**% of Hg in the gaseous phase**	**% of Hg in the gaseous phase**	**% of Hg in the gaseous phase**
25	nd	nd	55
50	nd	68	50
100	68	57	61
150	56	47	54
200	50	45	54
250	42	45	52

nd not detected

Interestingly, the amount of reduced Hg(II) in the gaseous phase decreases with increasing Hg(II) amount. The maximum measured percentage of Hg(0) in the gaseous phase was about 68%. The higher amount of Hg(0) indicates a more saturated air in the vials with higher Hg(II) reduced. Since there was probably not enough time for Hg(II) saturation to occur, we measured the same standards after about 2 hours.

For lower amounts of Hg, it was not possible to distinguish between the reduction of 50 pg or 600 pg of Hg(II). All the peak heights obtained were the same. They were measured again a second time, but no improvement was observed.

Since the repeatability of the measurements is very poor, the sensitivity significantly decreased due to the limited amount of Hg going in the gaseous phase. Furthermore, the syringe was damaged by water vapour. Consequently, this way of calibration is not recommended for DEM determination in water samples. This part of the work was therefore not taken any further.

We continued using the calibration with Hg(0) vapour for the manual method due to its feasibility to be applied either in laboratory or in the field. For the calibration of semi-continuous methods, we used diluted solutions of DEM because calibration with Hg(0) vapour was not possible. However, when either DEM or RHg need to be measured and the calibration unit is not available, the calibration by reduction of Hg(II) standard solution can be successfully applied.

4.4 Semi-Continuous Methods

As pointed out through all this PhD, continuous measurements of DEM (and RHg) are of high importance, particularly in the scrubber solutions of WFGD. Therefore, one of our main goals was to develop a continuous method for measurements of these two Hg forms. To achieve this, two systems were validated and applied to measurements in surface non-contaminated marine waters and in scrubber solutions of the WFGD. Both systems were designed and used for the purpose of capturing the dynamic behaviour of DEM and RHg. The working principle for both is based on the water-gas equilibrium where DEM and RHg are eliminated from the water phase and measured on appropriate detectors. The following sections describe the optimisation procedure.

4.4.1 Continuous equilibrium system based on opposite flow principle

The first continuous method is based on the equilibrium between liquid and gaseous phases, achieved by opposite flow. In this method, the purging gas and the sample flow are in opposite directions. Regarding measurements in natural surface waters, one of the biggest advantages of this system is the ability to keep the water flow rate high (up to 12 L min^{-1}), allowing more DEM to be transported into the system (Andersson et al., 2008). In contrast, this would represent a disadvantage when applied in the scrubber solutions of the WFGD because such high flows would block the system because of the presence of particles.

The use of an appropriate detector determines the resolution time of the method. This is a critical parameter and is closely related to weather the method is continuous or semi-continuous. We compared two detectors: Lumex and UT 3000 mercury analyser. Initially, we used the Lumex detector to measure the concentration of Hg(0) in the outgoing gas with a frequency of once per second.

In order to optimise the method in laboratory conditions, we used tap water. The optimised parameters include the sample flow, purging gas flow, the stability of the system, linearity etc. In addition, the calibration of the method was carried out. For this purpose, appropriate dilutions of DEM stock solution in tap water were made and measured by both the manual and continuous method. The manual method was used as a reference method, since it is quantitative.

Before starting the measurements, the air/water ratio was set in order to determine the equilibrium between the phases. For this purpose, we prepared solutions of tap water spiked with DEM stock solution and measured them with both methods. The comparability of the results obtained is shown in Figure 4.29. Different air/water flow ratios (0.55; 0.26; 0.69; 0.33) were tested and the comparability of the results is also shown.

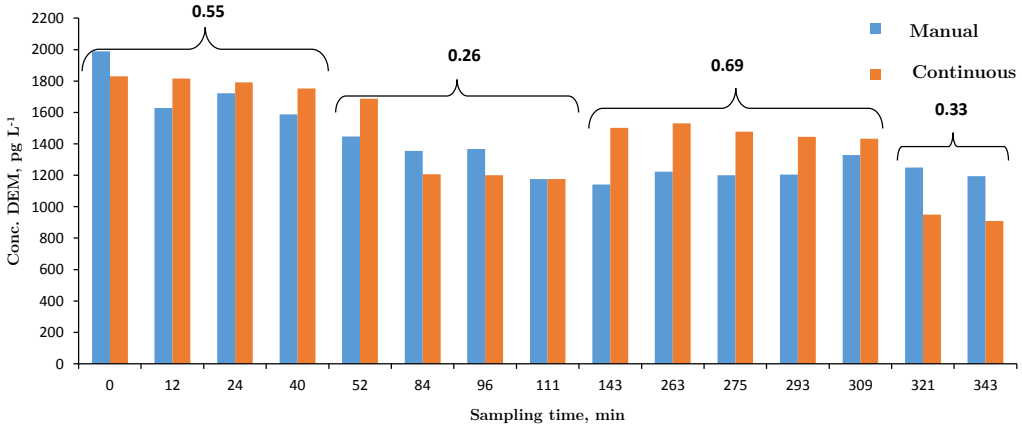


Figure 4.29: Optimizing the air/water ratio.

The best comparability of results was achieved at the ratio 0.55. It is very important to maintain this ratio unchanged. Changes during the analytical cycle lead to unpredictable results that so not reflect the real concentration of DEM in the aqueous sample. The importance of the time required to achieve equilibrium is also evident. The sample measured in minute 52 is significantly higher compared to the one measured 20 min later.

In addition to the air/water flow ratio, the calibration of the method is of great relevance. Andersson et al., 2008 reported only the calibration of the detector used to conduct the measurements and that was done by Hg(0) vapour taken from an independent calibration unit. Our intention was to calibrate the whole system and we did this by using aqueous standard solutions with known DEM concentrations. For this purpose, a series of standards with DEM concentrations ranging from 40 to 450 pg L^{-1} were prepared and measured (the concentrations were determined by the manual method). The obtained results are given in Figure 4.30 in the form a regression line.

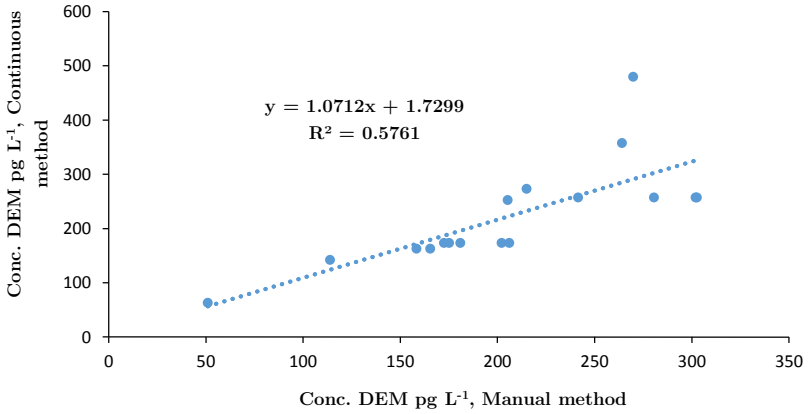


Figure 4.30: Linear regression of the results obtained by the manual and continuous methods using the Lumex detector.

In order to calculate the results of DEM in the aqueous phase measured by the continuous method, the equation developed by Andersson et al., 2008 (Eq. 3.1) is available and recommended for use when conducting measurements with this method. When we applied the equation to our data, we noticed a constant error in the final result. The reason for this is that the equation uses the Henry's coefficient, which is highly dependent on temperature. Therefore, significant changes were noticed in the obtained results which did not correspond to real changes in DEM concentration. In order to avoid the use of this equation, we calculated the results by taking in account the partitioning coefficient calculated as a ratio between DEM in the outlet gas, measured by the detector of the continuous method, and DEM in the aqueous phase measured by the manual method.

The comparison of the results shows that the methods are not linear. Repeated experiments demonstrated that for concentrations on the Lumex detector above 200 pg L^{-1}, the agreement between the results was poor and inconsistent.

Therefore, we changed the detector and used the UT 3000 mercury analyser instead. In contrast to Lumex, the UT 3000 detector enables a resolution time of the measurements ranging from 3 to 30 minutes. Given that the minimum resolution time for conducting measurements was 3 minutes, the method is automatically considered semi-continuous. As in the experiments with the Lumex detector, we prepared a series of solutions with DEM concentrations ranging from about 100 to 700 pg L^{-1}. The comparison of the results obtained by the manual and the semi-continuous method is given in Figure 4.31.

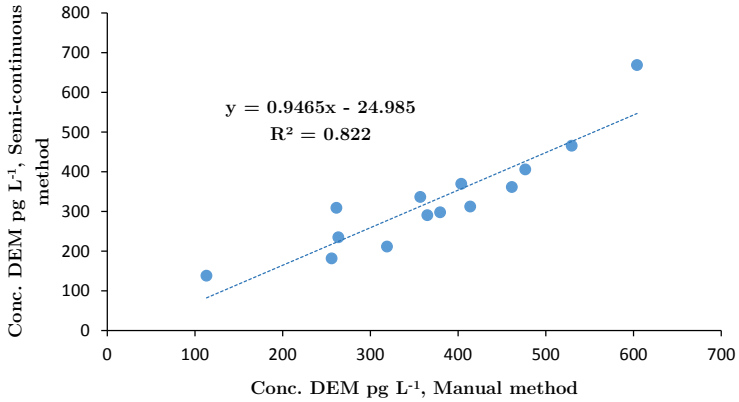


Figure 4.31: Linear regression of the results obtained by the manual and continuous methods using the UT 3000 detector.

From the regression line, it is clear that both methods demonstrated good linearity in the tested concentration range. The results obtained by the manual method were consistently higher compared to the semi-continuous method. Since the comparison between data and the linearity was better using the UT 3000 detector, we used only this detector in further experiments. The linearity for a wider concentration range (from 100 to about 1600 pg L^{-1}) was also demonstrated and is shown in Figure 4.32.

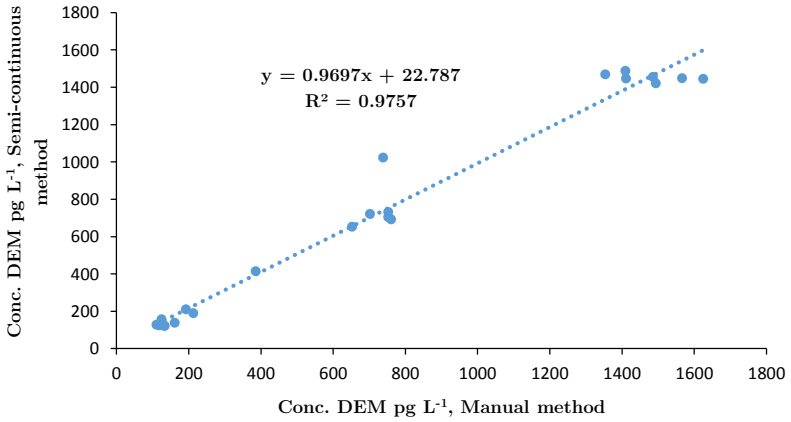


Figure 4.32: Comparison of the results calculated based on the partitioning coefficient.

The linearity of the results was very good. Moreover, the comparison of the results obtained by both methods was improved by about 20% when the partitioning coefficient was used to calculate the results instead of the equation reported by Anderson et al. (2008).

When solutions with lower DEM concentrations (40–200 pg L^{-1}) were measured, the method showed good ability to track the changes. The results are given in Figure 4.33.

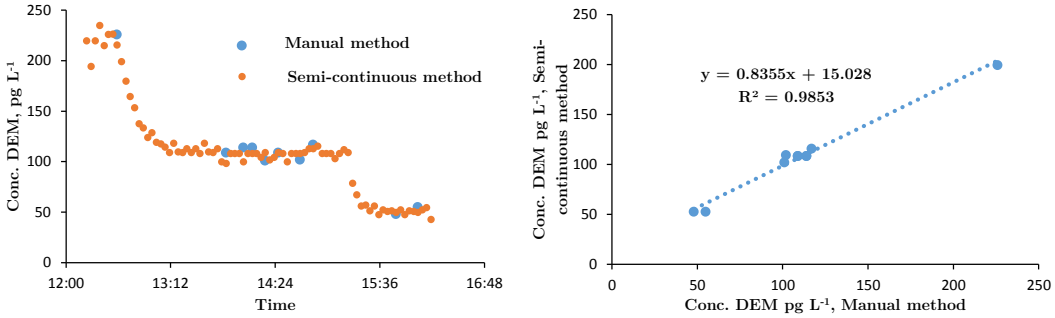


Figure 4.33: Comparison of the results between the manual and the continuous methods using the UT 3000 detector: left figure demonstrates the ability to track the changes and the right the regression line of the results.

Despite good linearity and repeatability of the methods (about 6% for the manual method and 4-5% for the continuous, expressed as relative standard deviation), the differences between the results obtained by both methods ranged between 5 and 20 %.

When the method was applied to surface waters of the Adriatic Sea, the results were not comparable. One of the main reasons was that the equilibrium between aqueous and liquid phases was difficult to maintain. Therefore the measured concentration is not related to the equilibrium concentration. As a result, the comparability of the results between manual and continuous methods was poor and unpredictable. This method was therefore not further used to conduct measurements. Due to the large amount of sample needed, this method would also require high dilution of the WFGD scrubber solution and detection would not be possible.

Therefore, we built and optimized a system of four times smaller dimensions. This system is identical to the bigger one but only made of glass instead of Plexi glass. As before, different sample flow rates were used ranging from 1.14 to 2.42 L min^{-1} and the air flow rate from 0.33 L min^{-1} to 1 L min^{-1}. The temperature of the sample in the outlet and inlet of the system was the same, 15 °C. The flows were limited by the dimensions of the bubbling system.

To verify and optimise the air/water flow ratio, tap water spiked with DEM was measured by applying different ratios; the most suitable ones (0.88; 0.49; 0.29) are given Figure 4.34.

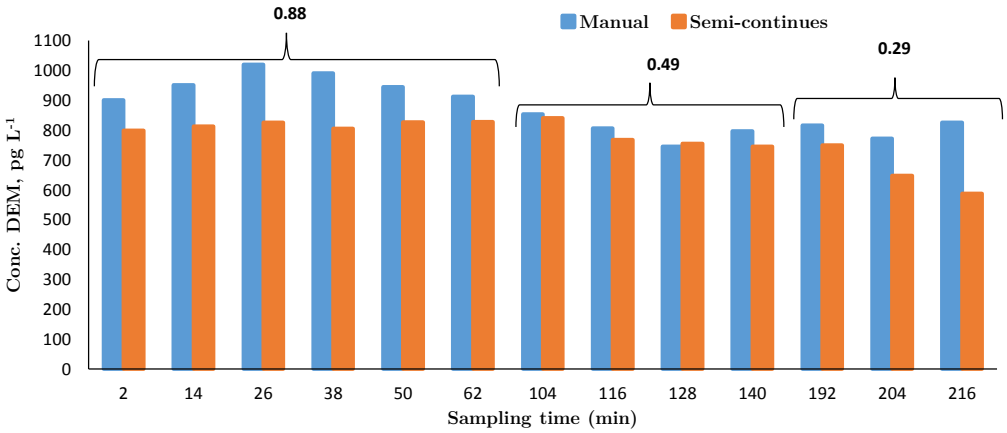


Figure 4.34: Comparison of results obtained with both methods when different air/sample flow ratios were used.

The comparability of the results was best at the ratio of 0.49. The calibration of the system was done as before: a series of solutions with different DEM concentrations (ranging from 50 to 800 pg L^{-1}) were prepared and measured with both methods. The regression line comparing the results, is shown in Figure 4.35.

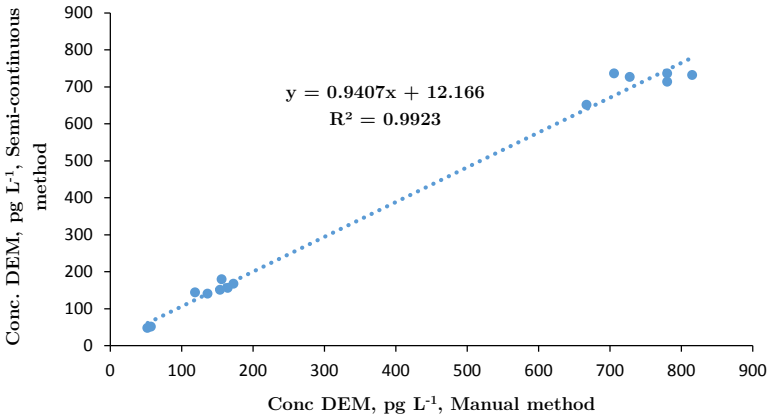


Figure 4.35: Comparison of results obtained with both methods during calibration with DEM solutions and the calculations based on the partitioning coefficient.

The comparison was better when the results were calculated based on the partitioning coefficient and the results were about 10 % higher with the manual method. However, the linearity of the methods was very good both at low DEM concentrations (<100 pg L^{-1}) as well as at higher concentrations (~800 pg L^{-1}).

In order to check the stripping efficiency of the method, we spiked tap water with different amounts of DEM and measured them with both methods. The obtained results showed a stripping efficiency of about 80 %.

The small bubbler setup was intended for DEM measurements in the scrubber solution of the WFGD. When the pilot plant was in operation, a stream of the WFGD scrubber solution was diluted about 20 times with tap water and the sample was measured using the continuous method with the UT 3000 detector. Parallel measurements with the manual method were also performed. The results were not comparable and DEM was often not detectable. The spiking of the scrubber with DEM did not give better results due to adsorption of Hg(0) to particles. Because of the large dilution factor, it was not possible to obtain a large enough analytical signal. The particle density strongly affected the performance of the glass filter installed in the bubbling system.

For this reason, we performed further tests in which only water without particles from the WFGD scrubber solution was measured. For this purpose, the scrubber was left to precipitate for about 3 days. Since the detection of such low levels was not possible (samples at 0 and 20 minutes), the sample was spiked with DEM. The comparison of the results obtained by both methods is given in the Figure 4.36.

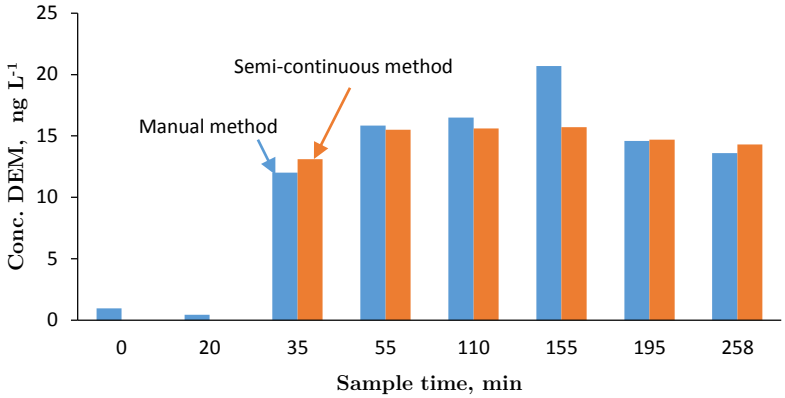


Figure 4.36: Filtrate solution of the WFGD scrubber diluted with tap water and measured with the continuous and manual methods.

The comparability of the results was very good. However, as shown by the first two samples, no signal was obtained initially. This led to the need of spiking the samples with DEM. Samples measured after 35 minutes and later showed good comparability and good DEM recovery from the sample matrix. The LOD of the continuous method was about 1 ng L^{-1}.

Despite the optimisation and calibration of the method, when applied to samples, no results were obtained. The reasons were related to physical difficulties due to the nature of the sample, the effectiveness of the purging etc. Based on the experience gained with the tested systems, we designed a completely different one which would enable DEM determination primarily in the scrubber solutions.

4.4.2 Optimization and validation of a semi-continuous method for DEM and RHg measurements based on the flow injection analysis

The developed and optimised semi-continuous method is based on the flow injection analysis and it also measures RHg. Parameters such as equilibration time, stripping efficiency, purging flow and sample flow were optimized in order to assure the quality, reliability and consistency of the results. The system was initially intended to perform DEM and RHg measurements only in WFGD scrubber solutions, where Hg concentrations are several times higher than in non-contaminated natural waters.

Sample volume and gas flow rate optimisation

The design of the system allowed sample flow rates of up to 15 mL min^{-1}. With samples of higher densities, such as WFGD scrubber solution, the optimal flow rate was 8 mL min^{-1} at which we also optimized the gas flow rate. The optimal flow of N_2 was about 75 mL min^{-1} (Figure 4.37).

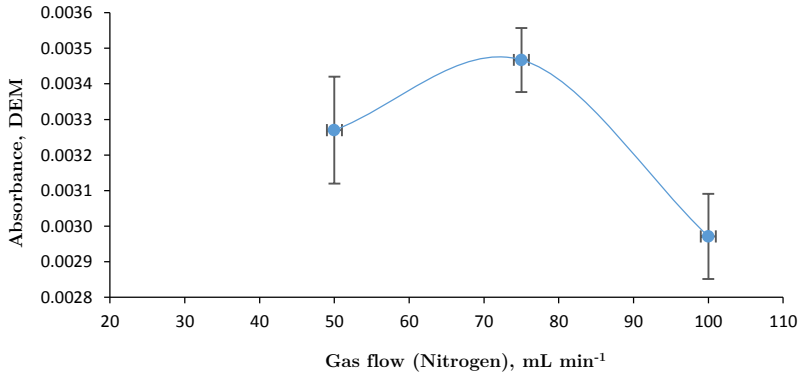


Figure 4.37: Optimisation of the nitrogen flow rate for the semi-continuous method.

Based on these results, a gas flow rate of 75 mL min^{-1} was selected as optimal. In repeated tests, it was noticed that increasing the N_2 flow rate to more than 85 mL min^{-1} led to about 20 % lower results.

Equilibration time

Since the semi − continuous method operates on the basis of partitioning of Hg(0) between the equilibrated liquid and gaseous phases, the concentration of Hg(0) in the gaseous phase is proportional to Hg(0) dissolved in the aqueous phase. In the semi-continuous method, the gaseous Hg(0) was removed through the gas−liquid separator and measured by the CV AAS detector. A stable signal was obtained after about 8 min of continuous sample flow for distilled water and more than 10 minutes for the WFGD scrubber solution. This indicates that the composition of the aqueous phase defines the time needed for equilibrium to be achieved.

All the experiments were conducted under room temperature and an example of results is given in Figure 4.38.

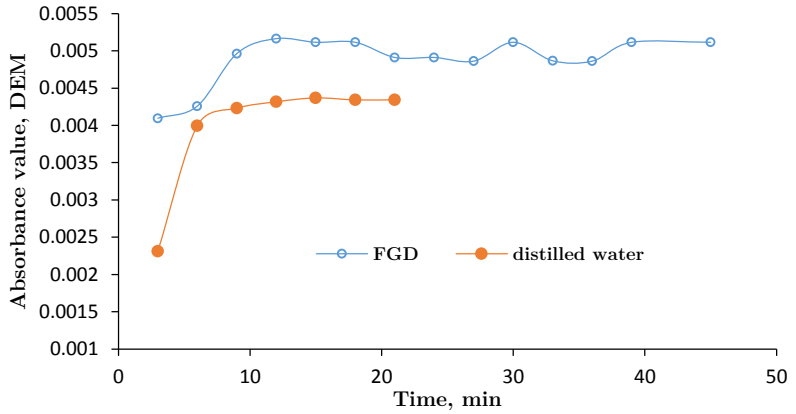


Figure 4.38: Comparison of times needed for stabilization of the output signal for distilled water and for WFGD aqueous samples when measured with the semi−continuous method.

The time needed for the system to achieve stability in the case of distilled water is slightly shorter than for the WFGD aqueous samples. This is mostly related to the sample matrix. The equilibration time for RHg was the same as for DEM.

Stripping efficiency of the semi-continuous system

In order to determine the effectiveness of stripping Hg(0) from a simple matrix such as distilled water, a series of samples with DEM concentrations in the range of 1.5 to 4 ng L^{-1} were prepared and measured by both methods (Figure 4.39).

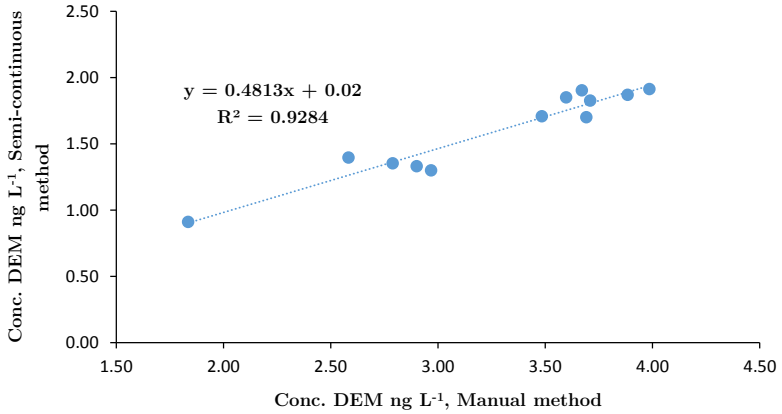


Figure 4.39: The effectiveness of stripping in the semi-continuous method for DEM determination in distilled water samples spiked with different amounts of DEM.

The response over the tested concentration range was linear. The proportion of Hg(0) stripped from the aqueous phase during mixing in the reaction coil ranged from 43 to 54 %, with an average of 48 %.

The experiment was repeated with three WFGD scrubber solutions with different concentrations of DEM (Figure 4.40).

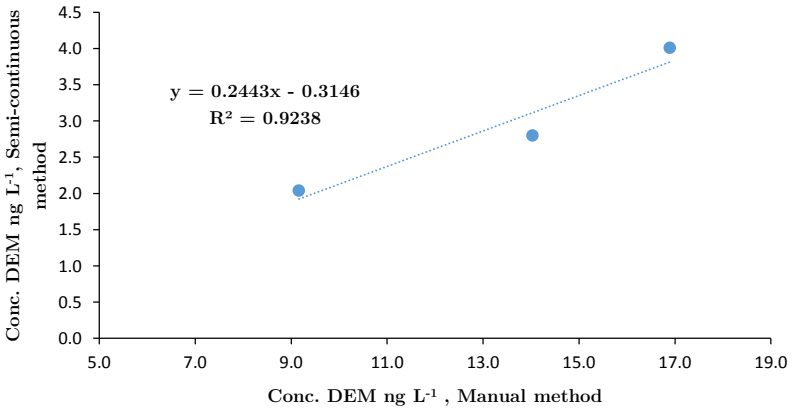


Figure 4.40: The stripping effectiveness of the semi-continuous method for DEM measurements in WFGD scrubber solution.

A linear response was obtained; however, the stripping effectiveness of the semi-continuous method was only 20 – 25 %. This clearly demonstrates that the water

composition is the main factor affecting the partitioning of Hg(0) in the semi-continuous method.

We further tested the effect of particle density on the effectiveness of stripping Hg(0) during mixing in the reaction coil. Three samples were prepared with different particle densities by diluting WFGD scrubber solution of particle density of 88 g L^{-1}. The percentage of Hg(0) stripped from the aqueous phase depended significantly on the concentration of the particles, ranging from 42 % to 22 % for particle concentrations of 17.6 g L^{-1} and 88 g L^{-1}, respectively. The obtained results are given in Figure 4.41.

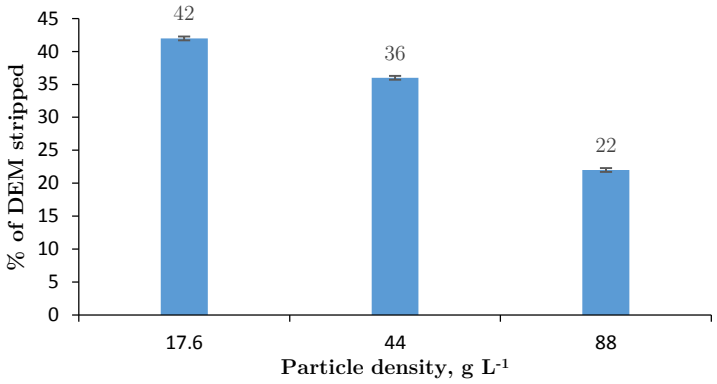


Figure 4.41: Effect of particles on the efficiency of stripping in the semi–continuous method.

Clearly the striping efficiency when the suspension sample was not diluted (particle density of 88 g L^{-1}), decreased by about 50 % when compared with the diluted sample (particle density of about 17.6 g L^{-1}). The error bars on the graph relate to the standard deviation of 2-3 measurements.

RHg was also measured in the same samples. The obtained results are demonstrated in Figure 4.42.

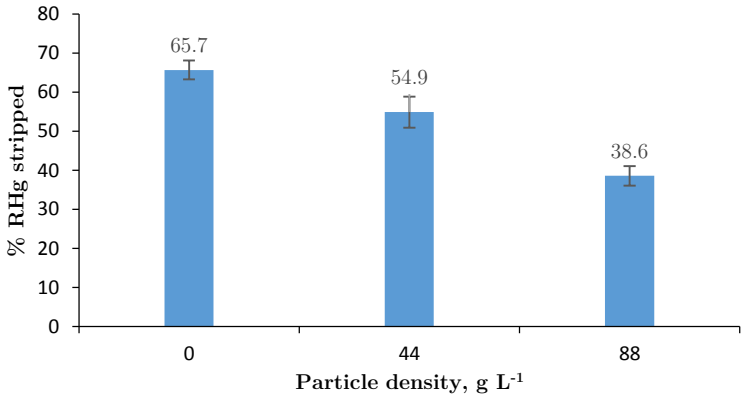


Figure 4.42: The stripping efficiency of RHg depending on particle density.

When no particles were present, the recovery of RHg was about 65 % and it decreased to 40 % when the density of the particles was 88 g L^{-1}. Therefore, the effect of the sample matrix is the drawback of the method.

Calibration

The main difference between the manual and the semi-continuous mode is that DEM in continuous mode is not removed from aqueous solution quantitatively, but partitioned between gaseous and liquid phases. The proportion of Hg in gaseous phase depends on several factors, in particular the gas and liquid flow rates and the composition of the liquid phase.

CV AAS and CV AFS were calibrated with gaseous calibration units, while the semi-continuous method was verified against the results obtained with the manual method which was used as a reference. Based on the fact that the partitioning of DEM between liquid and gaseous phases is matrix-dependent, we initially performed a series of standard addition experiments using spiking of test samples with solutions of known quantities of DEM.

A relationship between DEM concentration in water and Hg(0) absorbance results measured by the continuous system had to be established. A direct calibration of the continuous method with Hg(0) vapour is not feasible. Therefore, the method had to be calibrated through regular calibration using the manual method.

A series of liquid solutions (with a total volume of 500 mL distilled water) with different DEM concentrations was prepared from the stock Hg(0) solution. An aliquot of 100 mL was measured with the manual method and the rest of the solution was measured at the same time with the continuous method following the procedures described.

The concentration of DEM determined with the manual method ranged from 0 to 30 ng L^{-1}. The calibration curve was linear over the range of concentrations of interest. The absorbance results obtained from the UT 3000 detector are well correlated with the results obtained with the manual method. A typical example of the calibration curve is given in Figure 4.43.

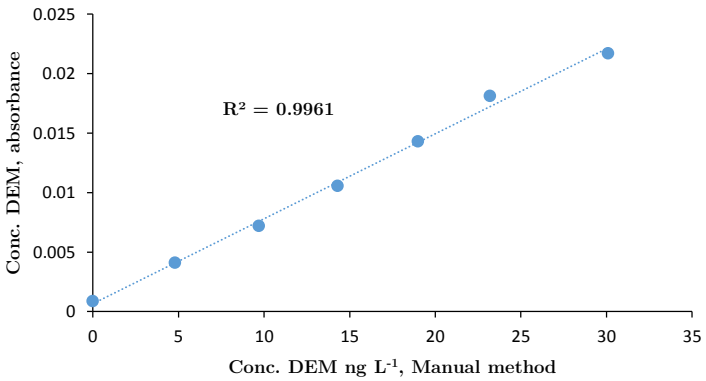


Figure 4.43: Correlation between the semi-continuous and manual methods for measuring DEM. Each point on the calibration curve is the average of 3 to 6 measurements. The relative standard deviation ranged from 0.33 to 1 %.

Every point in the calibration curve is an average of 3 to 6 absorbance readings from the semi-continuous method. The relative standard deviation ranged from 0.33 to 1 %. The equation of the curve was used to calculate the concentration of DEM in unknown samples. Calibration of the systems by liquid solutions is a known procedure (Amyot et al., 2001) but not widely used (O'Driscoll et al., 2003, Driscoll et al., 2007, Andersson et al., 2008). Amyot et al., 2001 prepared the stock solution by purging gaseous Hg(0) into MilliQ water and proceeding in the same way as described in this work.

The same experiment was repeated with the scrubber solution samples from the WFGD. Most of the spiked DEM was oxidised into Hg(II), which prevents the standard addition mode to be used for calibration. The curve obtained is given in Figure 4.44.

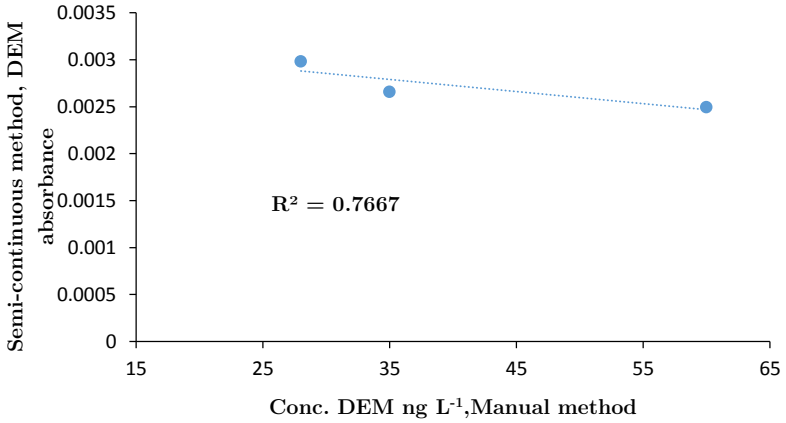


Figure 4.44: Calibration of the system with Hg(0)-spiked FGD sample.

Clearly the added DEM was not recovered from the sample matrix, but when THg was measured, a linear increase in concentration was observed. We believe that this may have been caused by the special nature of the sample matrix, primarily related to the presence of particles. When the same experiment was repeated the same day under the same conditions using distilled water, a linear calibration curve (correlation coefficient of 0.9966) was obtained.

In addition, experiments with natural seawater at much lower concentration resulted in the same conclusion. Therefore, to obtain the concentration of DEM by using the semi-continuous method, additional measurements by manual method were needed as a reference against which a partitioning coefficient was measured for each water matrix. The partitioning coefficient changed depending on particle density.

The calibration of the system was also done with Hg(II). A series of distilled water samples were spiked with Hg(II) certified standard solution and the calibration curve was made. The prepared standard solutions were measured with both methods and the results are given in Figure 4.45.

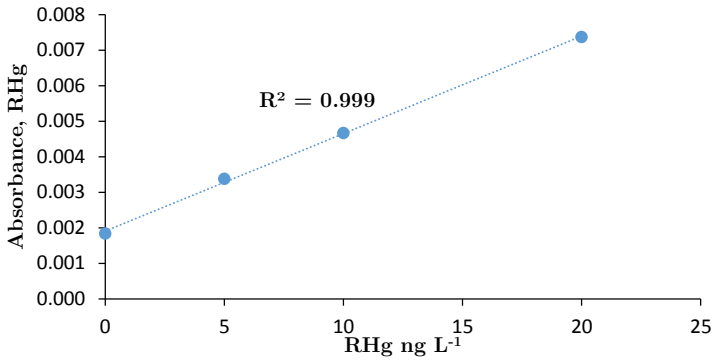


Figure 4.45: Calibration of the system with Hg(II)-spiked distilled water (0-20 ng L^{-1}). Every point is an average of 4-7 measurements of the absorbance: the relative standard deviation from 1 to 6 %.

When the experiment was repeated by spiking scrubber solutions, the spiked Hg(II) was adsorbed onto particles. This was further proven by measurements of DEM, RHg and THg in filtered and non-filtered samples.

Performance characteristics of the methods

The LOD was calculated as three times the standard deviation of the sample with the lowest DEM/RHg concentration. LOD for the continuous method ranged from 4 to 14 pg L^{-1}, while for the manual method it was about 11 pg L^{-1}.

The limit of detection for RHg measurements calculated in the same way was from 0.2 to 0.6 ng L^{-1} for the manual method, and 0.8–1 ng L^{-1} for the continuous method. It has to be mentioned, however, that LOD of both methods largely depends on the uncontaminated conditions in the laboratory air and glassware. For the precision of the methods under repeatable conditions, 3-4 spiked distilled water samples were measured the same day in both systems and the relative standard deviation of the measurements was calculated.

DEM determination varied from 1 to 9 % with the manual method and 0.5–8 % with the continuous method. For the precision of the methods and reproducibility of the systems, measurements were performed in consecutive days and the standard deviation calculated. For the manual method was 10 – 20 %, while for the continuous method, it was about 22 %. However, we want to draw attention to the fact that the high variability is mostly related to the instability of the solution. When the sample is freshly prepared in different days following the same procedure, the reproducibility for both methods did not exceed 7 %.

For RHg, the repeatability and reproducibility of the manual method expressed as relative standard deviation were about 10 and 14 %, respectively. For the same parameters in the continuous method, repeatability and reproducibility were about 3 % and <15 %, respectively.

The uncertainty represents *a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand'.*

Generally, the measurement uncertainty is comprised of several components. Some of them may be evaluated from the statistical distribution of the results of series of measurements and can be characterised by standard deviations. Other components, which

also can be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information. In estimating the overall uncertainty, it may be necessary to take each source of uncertainty and treat it separately to obtain the contribution from that source. Each of the separate contributions to uncertainty is referred to as an uncertainty component (EURACHEM 2012). In mercury measurements, the uncertainty is well estimated for methods such as the determination of Hg in particles (Singh et al., 2013) and mercury in air (Brown et al., 2008). However, so far there is no an uncertainty estimation for the methods for DEM and RHg determination in water. Despite the work done to improve the reporting of results by associating them with a proper uncertainty estimation, the later still remains a missing piece in the puzzle.

Mostly, this is related to the complexity of mercury species. Their determination is affected by many factors such as the temperature, cleanness of glassware, calibration etc. The best way to evaluate the uncertainty is the GUM approach, which considers all the parameters possibly affecting the result. In the case of DEM and RHg, the uncertainty of the measurements will be very similar due to the fact that they are determined in the same way, using the same way of calibrating the detectors and the same instruments. Generally, a mathematical model is applied to link the output signal from the detector and the DEM/RHg concentration, as shown in Equation 4.1:

$$C_{DEM/RHg)} = \left[\frac{(h_{sample} - h_{blank})}{(h_{standard} - h_{background})}\right] x \left[\frac{mass\ of\ Hg(0) injected}{volume_{sample}}\right] \qquad \text{Equation 4.1}$$

where $C_{DEM/RHg}$ is the calculated concentration of DEM or RHg in pg L^{-1}, h_{sample} is the peak height of the sample, h_{blank} is the peak height of the bubbler blank, $h_{background}$ is the peak height of the background signal of the detector and $h_{standard}$ is the peak height of the standard (Hg(0) vapour).

The best estimation would involve the drawing of a 'fish bonne' graph which has to include all the parameters that can influence the final result (Figure 4.46).

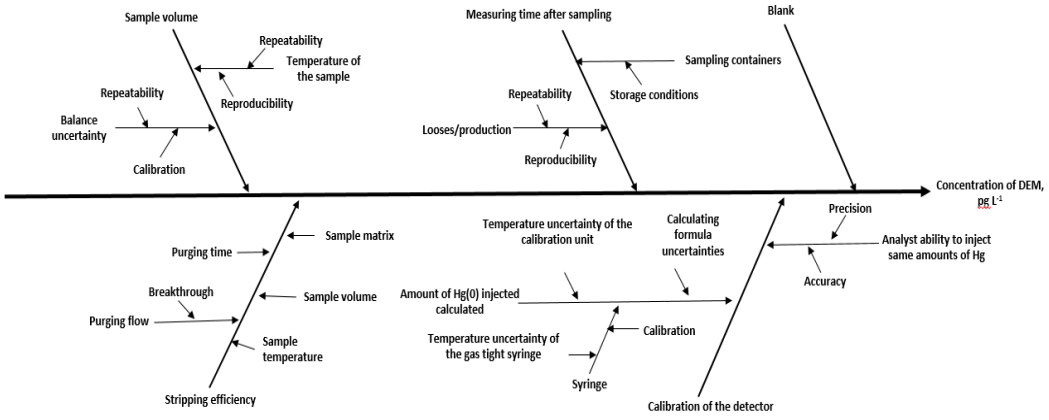


Figure 4.46: An example of the 'fish bonne' representing the possible uncertainty sources for DEM and RHg measurements with the manual method.

Factors to be taken into account when the uncertainty is calculated involve: removal efficiency, trapping efficiency, desorption efficiency, possible losses in the tubing, possible interferences of the CV AFS, repeatability of the standards. Regarding the calibration of the detector, parameters to be estimated and evaluated include: the uncertainty of the value for the Hg(0) amount, temperature stability, the uncertainty from the Dummarey equation and adsorption of the Hg(0) on the syringe walls. However, if the method is properly validated, the effect of stripping efficiency, losses in tubing and desorption efficiency are not a source of uncertainty. We calculated the expanded uncertainty of the manual method with a 95 % confidence interval and it ranged from about 10 to 15 %.

The calculation of the total combined uncertainty of the method was done by considering the uncertainties of the parameters included in Eq. 4.1. The uncertainty due to the amount of Hg(0) vapours injected was calculated by combining the uncertainties due to the calibration of the syringe, repeatability of the gas-tight syringe and the temperature of the calibration unit. Additionally, the repeatability of the method was taken into account (4 % expressed as RSD). The major uncertainty components contributing significantly to overall uncertainty for DEM measurements in water samples by manual method were the repeatability of the method (about 30 % of total uncertainty) and the calibration with Hg(0) vapours (about 8 % of total uncertainty).

The uncertainty for DEM and RHg determination by continuous method

The calculation of the concentration of DEM in water samples with the continuous method was performed by considering the partitioning coefficient measured by conducting parallel sample measurements in the manual method. As a result, the uncertainty from the manual method is included in the overall uncertainty of the continuous method. Additionally, the uncertainty originating from the calibration of UT 3000 detector with Hg(0) vapour was considered. The possible uncertainty sources affecting the results obtained by the continuous method are summarised in Figure 4.47.

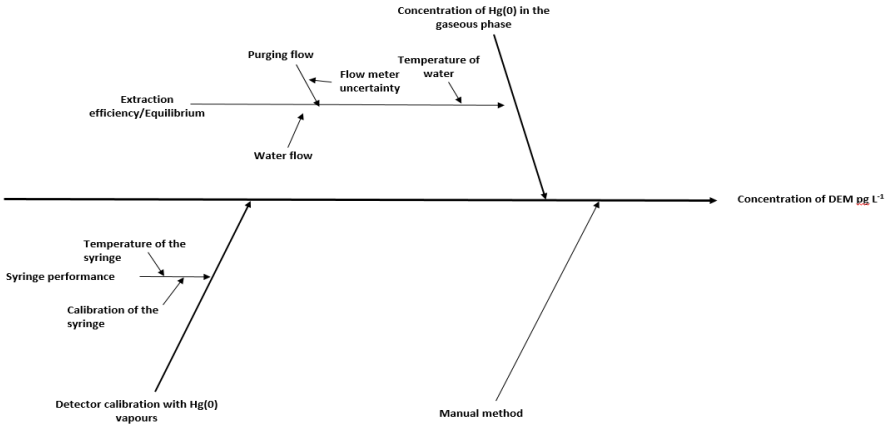


Figure 4.47: An example of the 'fish bonne' representing the possible uncertainty sources for DEM and RHg measurements with the semi-continuous method.

The overall uncertainty of the method varied from 18 to 22 %. The largest uncertainty contribution to the overall uncertainty of the method was attributed to the use of the manual method (60 %) and a lower but significant contribution was attributed to the calibration of the UT 3000 detector (5−8 %).

4.5 Application of the Validated Methods

After optimisation and validation, the manual and semi-continuous methods were used to conduct measurements in surface seawater and in the scrubber solution of the WFGD system.

The presence of DEM in the WFGD scrubber solution may indicate that Hg(0) from flue gas is not sufficiently oxidized and/or that Hg(II) already present in the scrubber solution is reduced to Hg(0). These processes can be altered by controlling the chemistry of Hg in the scrubber solution. The semi-continuous method optimized in this work was primarily developed for continuous monitoring of DEM concentrations in the WFGD solution as an indicator of Hg removal. In order to verify the suitability of the semi-continuous method for this purpose, we checked the performance of the method at a laboratory-scale pilot plant. The experimental apparatus is described in detail elsewhere (Stergaršek et al., 2010). Hg(0) was measured semi-continuously in the outlet gas while in this work, Hg(0) dissolved in the scrubber solution was measured. Initial experiments were carried out with a column filled with distilled water.

4.5.1 DEM in the Tyrrhenian Sea (Mediterranean)

The Tyrrhenian Sea is situated between the Apennine peninsula on its eastern side, the island of Sicily to the south and the islands of Sardinia and Corsica to the north-east. The sea floor in this area has a high geothermal activity (Kotnik et al., 2007), which is a natural source of Hg in the water. Most of this Hg is emitted through geothermal phenomena, which is indicative of tectonic processes.

Besides the natural sources of Hg to the Tyrrhenian Sea, there are potential human emissions near the city of Piombino in the northern part of Tyrrhenian Sea, where dense heavy industry, particularly steel production, may be important.

The sampling points and the main (possible) reactions occurring in the water column are depicted in Figure 4.48. The intention of this PhD is not to identify the possible factors affecting the chemistry of DEM in surface waters, but to test the ability of the developed method to track changes.



Figure 4.48: A map of the sampling points during the cruise.

We installed the continuous and manual systems for DEM measurements on board the research vessel *R/V*MINERVA used to perform a cruise measurement campaign in the Mediterranean Basin which took place in June-July 2015 in the framework of MEDOCEANOR measurement program (funded by the Italian National Research Council – CNR) and as support to the Global Mercury Observation System (GMOS) objectives. Manual and continuous DEM measurements were performed. The samples were taken from 3.5 m depth. During the cruise campaign all meteorological data (air temperature, wind speed, wind direction, relative humidity, solar radiation, atmospheric pressure) and water column parameters (temperature, conductivity, salinity) were monitored by the systems on board the vessel. In order to conduct measurements in surface waters of the Tyrrhenian Sea, the developed semi-continuous method was used and the manual method was used as a reference. Given that the semi-continuous method measures the DEM stripped from the water phase, the calculation of DEM concentration in water was done by considering the partitioning coefficient. The partitioning coefficient did not change during the measurement time. An example of comparison of DEM results measured at different times of day is given in Figure 4.49.

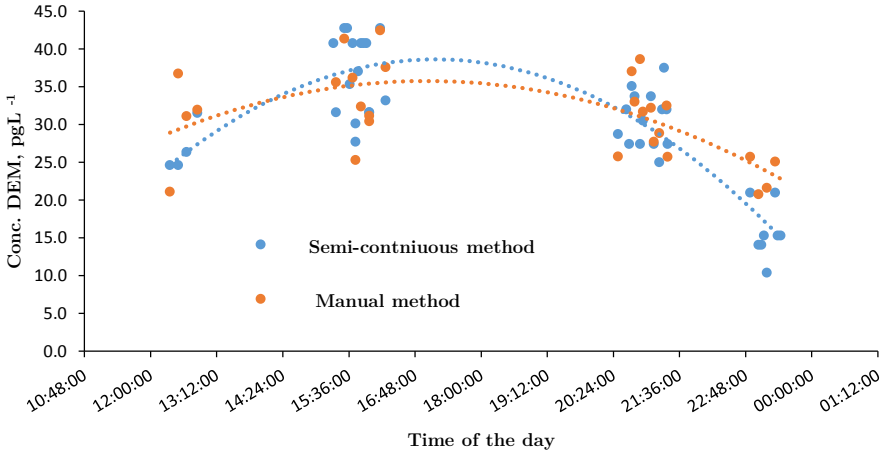


Figure 4.49: The ability of the semi-continuous method to track diurnal changes in DEM concentration in seawater.

The differences between both methods ranged between 1 and 10%. We also noticed a decrease in DEM concentrations during daylight hours, although water temperature was not drastically changed (about 1°C). This highlights once more the role of light in the formation of Hg(0) (Lalonde et al., 2001, Pehkonen et al., 1998, Lanzillotta et al., 2002, Garcia et al., 2005, Costa and Liss, 1999, Qureshi et al., 2010) in natural surface waters.

Figure 4.50 shows the regression line of the comparison of the two methods.

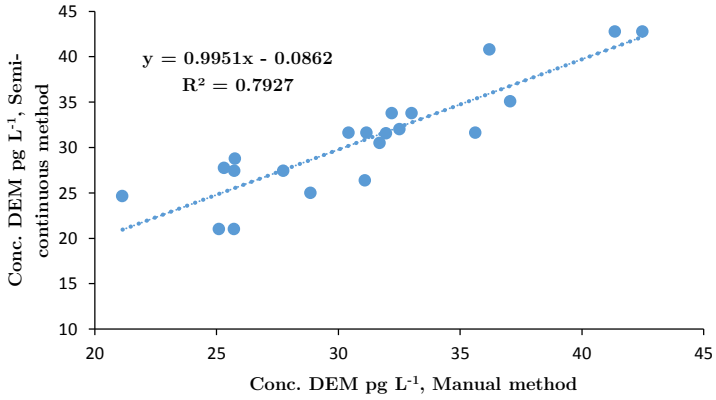


Figure 4.50: Linear regression of the results obtained by manual and semi-continuous methods for DEM measurements in seawater.

Good linearity and comparability was found. In this case, the semi-continuous method demonstrated to have the ability to track diurnal changes of DEM in surface marine waters. In addition to natural waters, the method was successfully applied also in industrial systems. In this case, not only DEM, but also RHg was measured. The intention of the experiment was to track the changes in the chemistry of these species in the scrubber solution of the WFGD.

4.5.1 DEM in reduction column of the WFGD system (distilled water) and in the scrubber solution

Initially, the semi-continuous method was applied in an experimental laboratory setup for testing the oxidation of Hg(0) in water by air. The detailed description of the experimental setup and the working conditions can be found in Stergaršek et al. (2008), and Stergaršek et al. (2013) but will also be briefly described here (Figure 4.51). The installation simulated the water column of the industrial FGD absorber tank in which the air for SO_2 oxidation is introduced (detailed description given in Stergaršek et al., 2008). It was composed of a thermostatic bubbler column with a diameter of 40 mm and 1.5 m high. An agitated reactor with a volume of 500 mL was added where chemicals were introduced and pH, redox potential and temperature were measured and controlled. In addition, a system for the preparation of a gaseous mixture spiked with Hg(0) vapour was also installed. To perform the test, the column was filled with about 1.5 L of distilled water and purged by a gaseous mixture of nitrogen and air introduced at the bottom of the bubbler glass column through a glass frit. To this mixture a small stream of air saturated with Hg(0) was dosed by means of a peristaltic pump.

In an industrial FGD absorber tank, the air for SO_2 oxidation is introduced through dispersing perforations at a depth of 6 to 12 m of solution. Therefore, an aqueous solution of SO_2 was constantly added and the pH kept constant by the addition of a solution of Na_2CO_3. Other chemicals were also added. The gaseous Hg(0) content in the inlet and outlet gaseous mixture was measured continuously with a Lumex Zeeman Mercury Spectrometer, model RA-915$^+$. The basic parameter measured was the percentage of Hg(0) removed from the gaseous mixture entering and passing the bubbler column and the influence of different parameters on this removal efficiency. The parameters included the constituents of and additives to the solution, the composition of the gaseous mixture and the operating conditions of the bubbler column (pH, redox potential, oxygen supply and temperature). A schematic view of the entire system and the sampling point for DEM determination is presented in Figure 4.51.

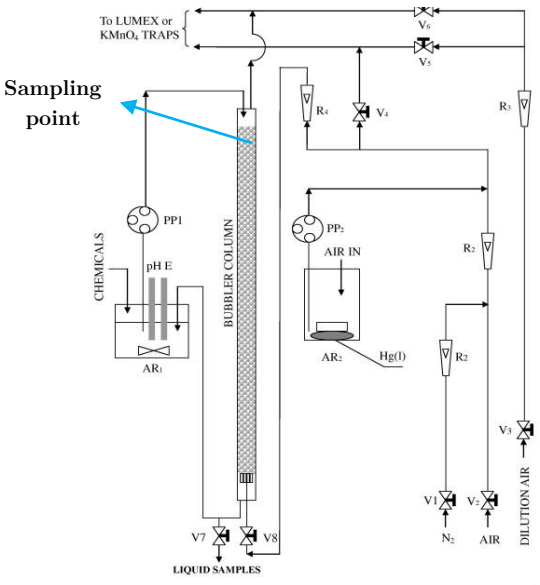


Figure 4.51: The setup system scheme for the oxidation of Hg(0) with air in a column.

The amount of Hg(0) introduced into the bubbler column is measured by the Lumex detector in the inlet and outlet of the system. The amount of Hg(0) retained in the solution is calculated as the difference between the concentration in the inlet and outlet gas. An example of the results is given in Figure 4.52.

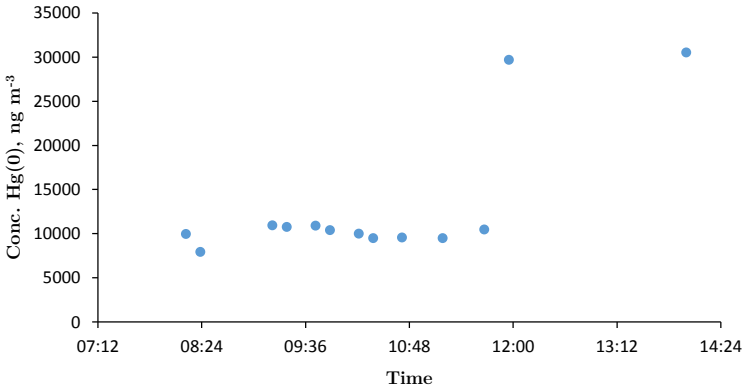


Figure 4.52: The values of Hg(0) represent the difference in concentration between inlet and outlet.

The retained Hg(0) in the solution was also measured in the form of DEM by the manual and continuous methods. For this reason, the sample was continuously taken from the upper part of the column (as demonstrated in Figure 4.51) by using a 1.5 m Teflon tube with an external diameter of 3 mm. The chemistry of Hg(0) in the aqueous phase was altered by changing the physico-chemical properties, namely redox potential, temperature, the addition of oxidants, etc.

Figure 4.53 shows a comparison between results obtained by both methods (manual and semi-continuous) during the saturation of the column with Hg(0) vapour.

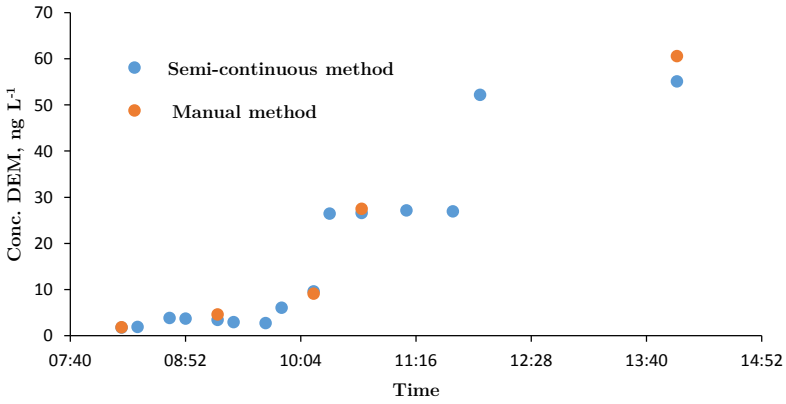


Figure 4.53: The capability of the semi-continuous method to track rapid changes in Hg chemistry due to different physico−chemical conditions applied in a column using distilled water.

The concentration of DEM increased as a result of saturation of the solution with Hg(0). The results of the continuous method were compared with the manual measurements and excellent agreement was obtained (Figure 4.54).

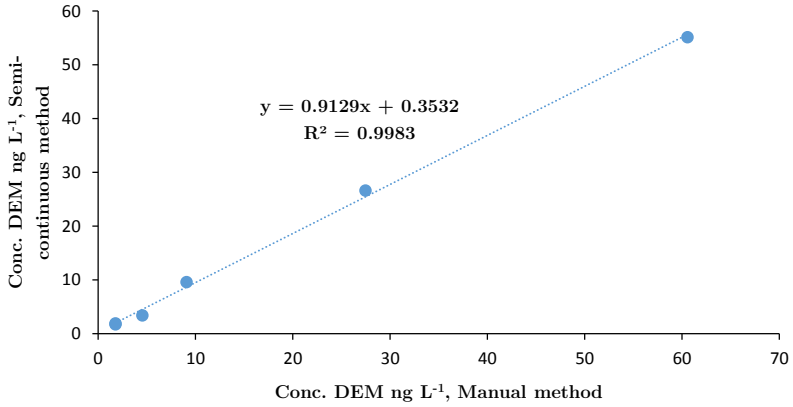


Figure 4.54: Linear regression of the results obtained by the manual and semi-continuous methods.

The differences between results obtained with the two methods ranged from 2 to 12%. The good correlation is demonstrated by the linearity of the regression line. By choosing a measurement cycle time of 3 min, we were able to detect changes in Hg chemistry in the bubbler column depending on quick changes in the physico−chemical conditions.

We continued the experiment by running the whole experimental setup system (the column and the absorber tank) of the WFGD with forced oxidation (Figure 4.55). The main part of the design consists of a reaction vessel (tank) with a capacity of 150 L equipped with a mixer to assure the homogeneity of the sample during operation. The temperature is kept unchanged (not affected by room temperature) by isolating the tank with a sponge layer surrounded by another aluminium layer. Initially the sample was only tap water and additional compounds were added in order to reproduce the working conditions of a TPP. A gas flow of sulphur dioxide (SO_2) is continuously passed through the scrubber solution (in the tank), where the temperature of the solution (about 36 °C) is rigorously and constantly controlled, the same as other parameters (pH, redox potential). The pH (about 5.5) is adjusted by adding calcium carbonate ($CaCO_3$) with another peristatic pump which introduces the reagent only when it is needed.

The Hg(0) vapour which was introduced into the WFGD system was produced in a closed glass vessel containing liquid Hg under controlled temperature and with constant magnetic stirring. To do that, a peristatic pump with controlled speed and Teflon tubes were used. Forced oxidation with air was performed. The inlet and outlet flows (air, SO_2, Hg) were measured by appropriate flowmeters throughout the experiment. The concentration of Hg(0) entering and leaving the WFGD was measured by the Lumex Zeeman Mercury Spectrometer, model RA-915$^+$ detector.

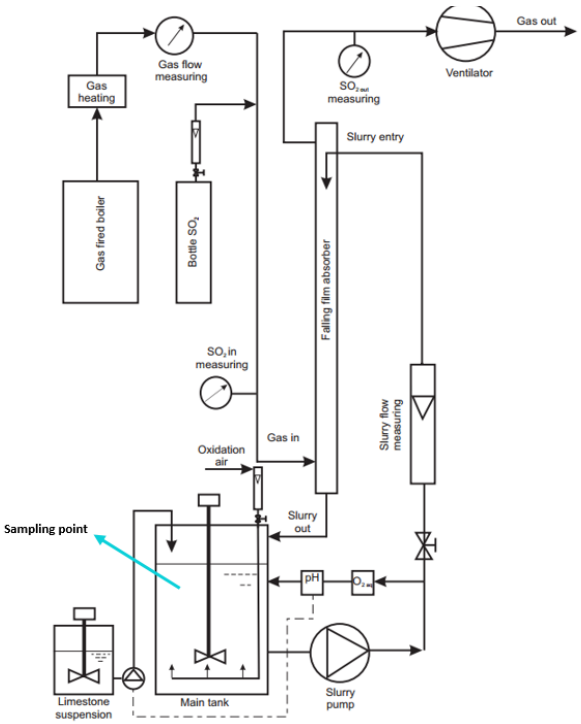


Figure 4.55: The setup of the pilot plant WFGD system; the sampling point is indicated.

In this case, not only the behaviour of DEM was followed but also the RHg. A similar parallel system was installed in order to conducted measurements of RHg. The same principles were followed as for DEM measurements and the calculation of the results in ng L^{-1} was done by considering the partitioning factor. The only difference was the installation of one line for $SnCl_2$ introduction.

The samples for continuous measurements of both Hg species and for THg in the scrubber solution were taken in the tank of the WFGD system by using a 2 m Teflon tube (3 mm). The frequency of measurements was 3 minutes and the absorbance values measured by the UT 3000 detector were converted into concentration in ng L^{-1} by using the partitioning coefficient calculated as demonstrated in previews experiments. A summary of the results obtained for DEM measurements for a period of about 2 months, is shown in Figure 4.56.

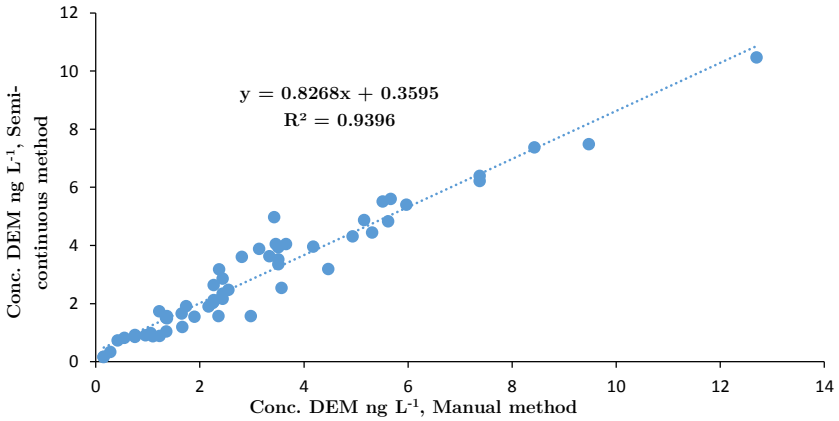


Figure 4.56: Linear regression of the results obtained by the manual and semi-continuous methods during pilot plant WFGD experiments.

The linearity of the semi-continuous method for long-term measurements was shown to be good. The differences in DEM concentrations achieved by both methods ranged mostly between $3-10$ %, but in some cases exceeded 20 %. Moreover, the method was very sensitive to changes of DEM concentration in the scrubber. (Figure 4.57).

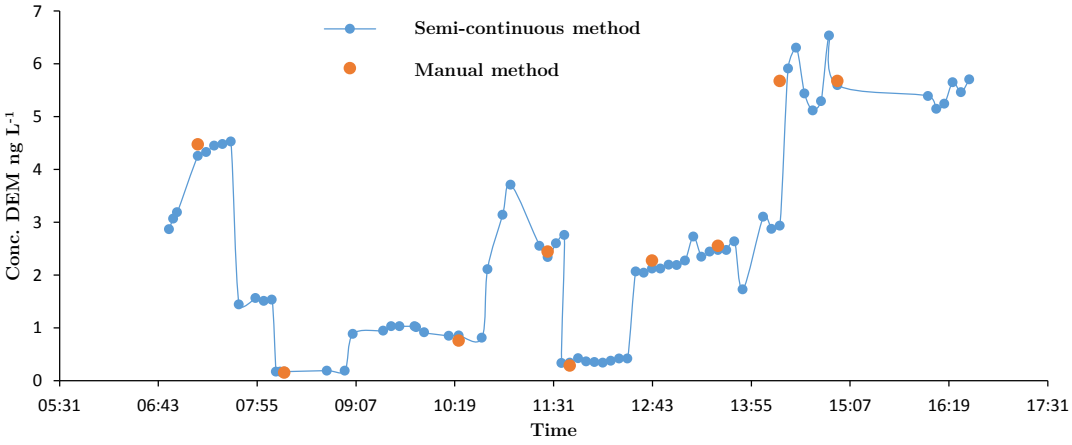


Figure 4.57: A demonstration of the ability of the semi-continuous method to track fast changes in Hg chemistry in the scrubber solution of the pilot plant WFGD.

The differences in results between methods range mostly between 3-10 % but in some cases exceed 20 %. The semi-continuous measurements of DEM in the scrubber solution may not provide precise results, but at this stage, it can be used as a very good method to show the trend of DEM chemistry in WFGD systems. Long -term measurements of RHg, in addition to DEM, demonstrated good comparability with the conventional manual method. A summary of the results for about 2 months of measurements is given in Figure 4.58.

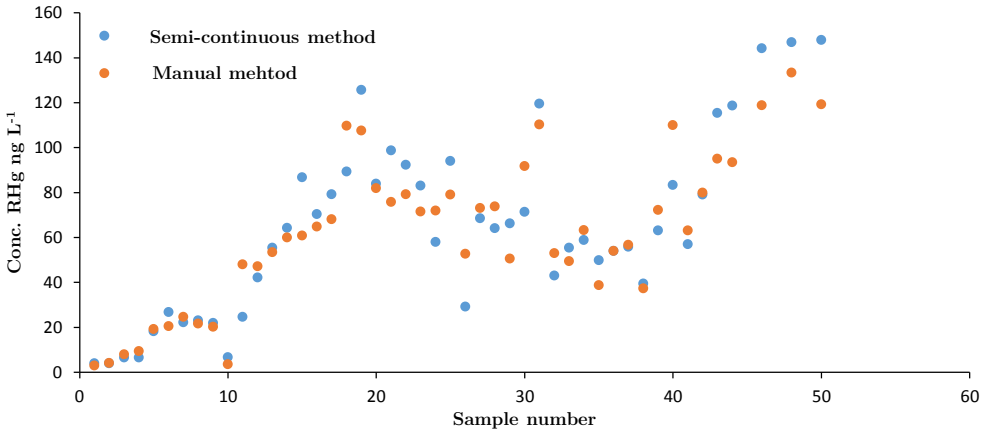


Figure 4.58: A demonstration of the ability of the semi-continuous method to track fast changes in Hg chemistry in the scrubber solution of the pilot plant WFGD.

The average difference in RHg results of the two methods in the concentration range from 3 to 130 ng L^{-1} was about 16 %. The linearity of the methods is demonstrated in Figure 4.59.

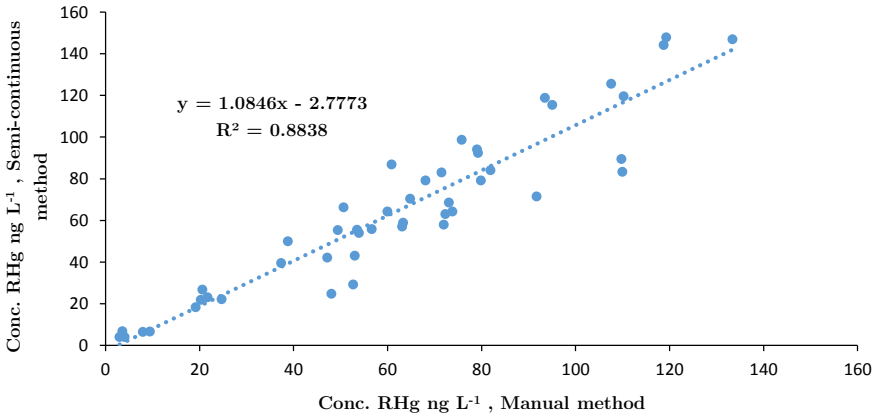


Figure 4.59: Linear regression of the results for RHg obtained by the manual and semi-continuous methods during pilot plant WFGD experiments.

The linearity in the concentration range from about 2 to 160 ng L^{-1} was satisfactory.

For a wider range of measured concentrations (180 to 3000 ng L^{-1}), the results are given in Figure 4.60.

A. B.

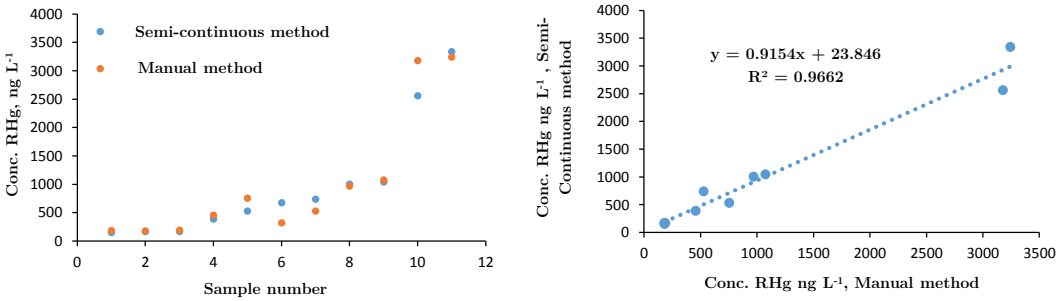
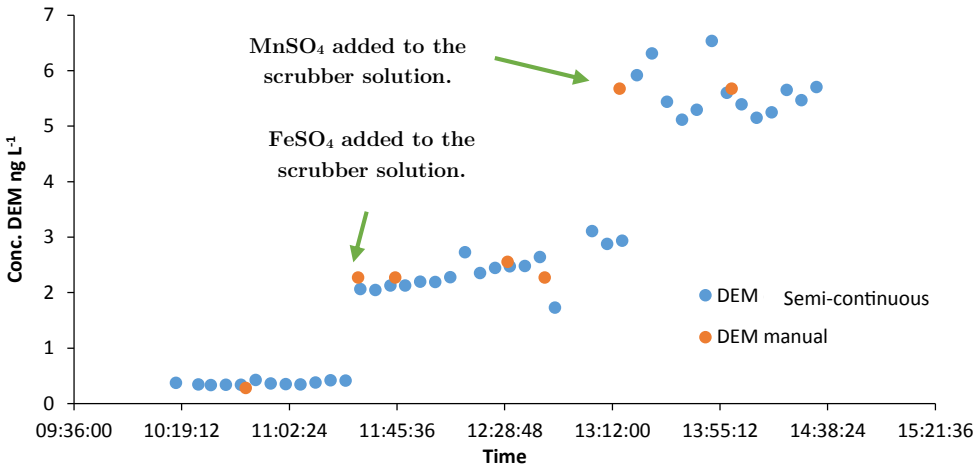


Figure 4.60: (A) RHg measurements in the scrubber solution in the concentration range of 200 to 3200 ng L^{-1}. The capability of the semi-continuous method to track rapid changes in Hg chemistry due to different physico-chemical conditions in the column using distilled water; (B) Linear regression of the results obtained by the manual and semi-continuous methods.

The differences between results ranged from 3–25% (with an average of 13% and one exception of about 50% mostly related to the sample matrix and possible problems with either of the methods). The regression line (Figure 4.60 B) showed once more the good correlation between results obtained with both methods. As previously mentioned, the semi-continuous method does not give equal results to the manual method but at this stage of development, it is suitable to show the trend of changes in Hg chemistry. The factors affecting the chemistry and the behaviour of Hg in the scrubber solution, as described by Stergaršek et al. (2010), could be due to iron and manganese, which are very effective catalysts for Hg(0) oxidation in the WFGD system. In the following experiment, we studied the effect of these catalysts (Fe^{2+} and Mn^{2+}) on the behaviour of DEM and RHg in the scrubber solution (Figure 4.61).

A.



B.

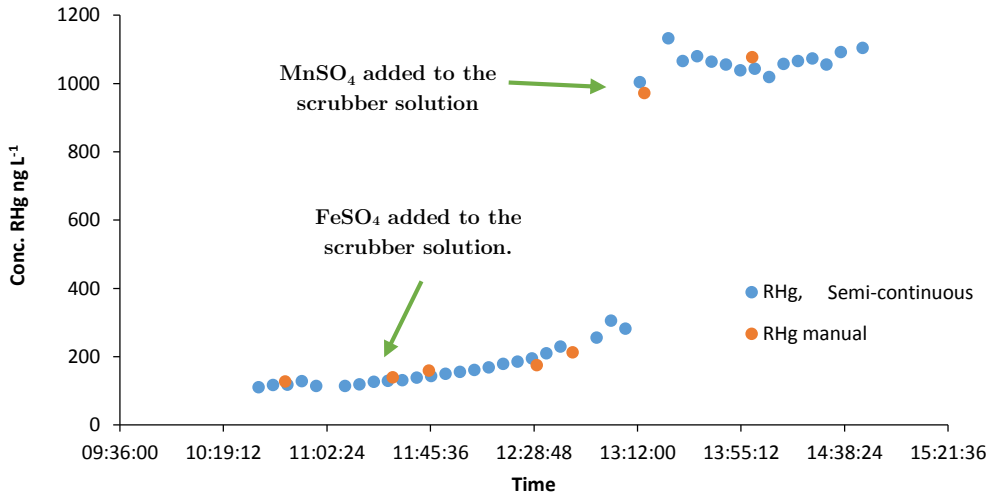


Figure 4.61: The effect of Fe^{2+} and Mn^{2+} on the chemistry of (A) DEM and (B) RHg in the scrubber solution.

The semi-continuous method was able to track the quick changes occurring with DEM as a result of the oxidation in the scrubber solution. At the same time, the increased Hg(II) concentration as a result of the addition of Mn^{2+} ions into the system was successfully detected by both methods. Clearly the effect of Fe^{2+} ions is not as significant as Mn^{2+}. Based on THg measurements, the elevated levels of Hg(II) in the scrubber solution after the addition of Mn^{2+} could be connected to desorption of Hg from particles (the redox potential in this case increased two times while pH remained constant).

The pH and the redox potential of the scrubber solution also play important role in DEM and RHg chemistry. An example of the changes occurring to these Hg species due to the changes in pH and redox potential when all other parameters remain equal is shown in Figure 4.62.

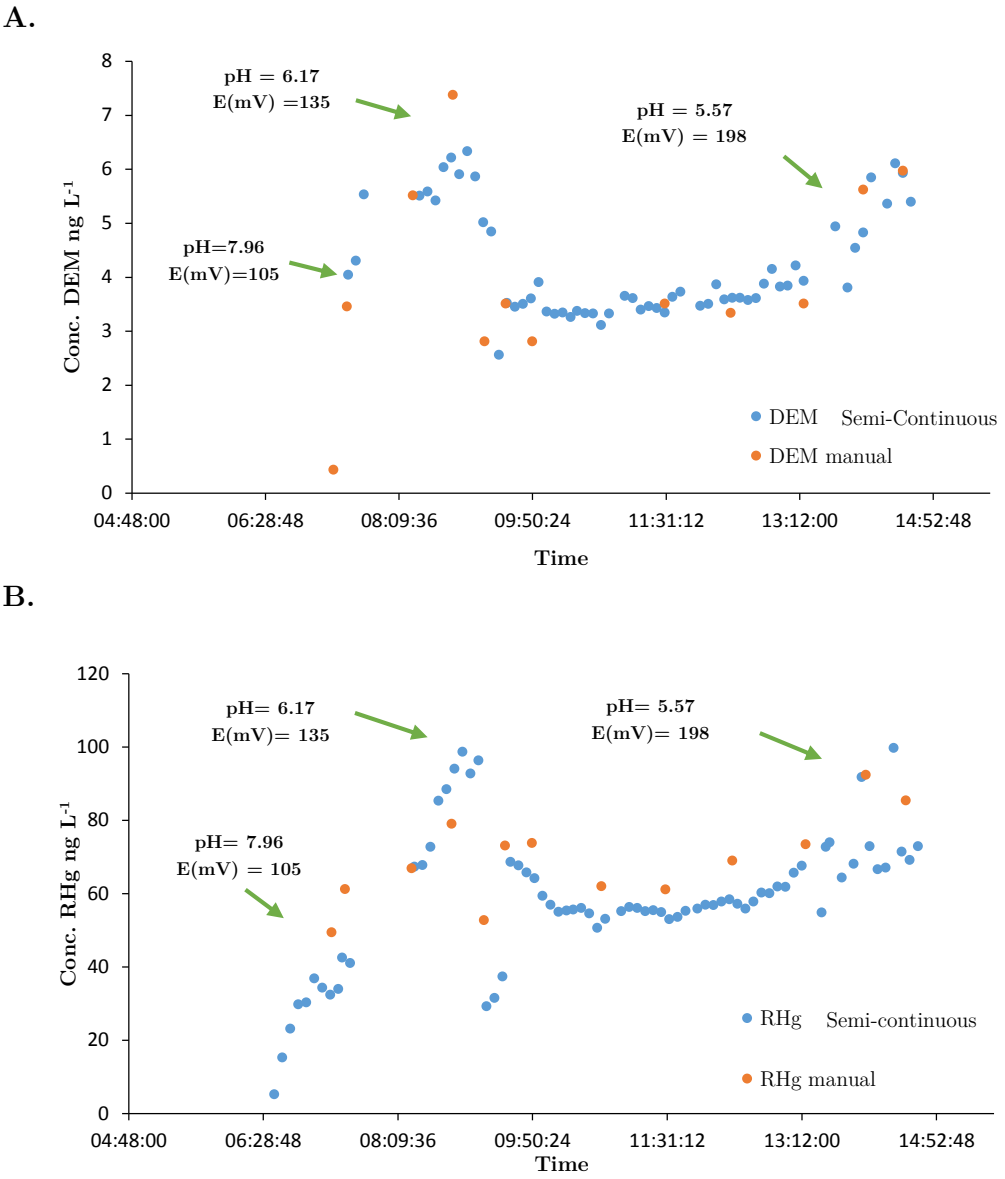


Figure 4.62: The effect of physical parameters (pH and redox potential) on the oxidation/reduction of Hg in the scrubber solution.

It is clear that the semi-continuous method is able to follow the chemistry of DEM and RHg in the scrubber solution and despite the low stripping efficiency that the method has shown, the concentrations of the species in the scrubber samples are high enough to assure a significant analytical response from the UT 3000 detector.

Chapter 5

Conclusion

Several issues related to DEM and RHg measurements in natural and industrial waters have been addressed in this PhD. They include the stability of DEM and RHg in natural and industrial waters, interferences during partitioning and pre-concentration on gold traps, as well as aspects related to proper calibration and uncertainty evaluation of the results.

The experiments on the stability of the species in aqueous solutions demonstrated variability of the results with the storage conditions and sample composition. DEM and RHg in freshwater samples stored in glass bottles in the fridge (at 4°C in the dark) did not show significant changes up to 5 hours after sampling. The same was observed of the seawater samples. When $AuCl_3$ and HNO_3 were added to the sample, oxidation of Hg(0) into Hg(II) was observed and the latter was stable in the solution for at least 3 days. The stability of the species was also checked in the scrubber solutions of WFGD systems. A drastic decrease was noticed immediately after the first hour. During routine work done we noticed a decrease in concentration even 15 minutes after sampling. Generally, scrubber samples are very reactive; therefore, the stability of the species is highly time-dependent. It is strongly recommended to conduct the measurements of DEM and RHg in natural or industrial waters at the sampling site.

Apart from the stability, another widely discussed issue is related to the pre-concentration materials. One of the biggest problems associated with Hg measurements is the passivation phenomenon of pre-concentration materials resulting in poor sensitivity and repeatability. The results obtained in this work showed that the main cause of passivation was the agglomeration of the Au nanoparticles on the substrate surface (in this case silica oxide) as a results of heating. The hypothesis of the formation of compounds on the surface was not confirmed. A new substrate was coated with Au, namely alumina, and tested for Hg measurements in different water matrixes. Despite good repeatability, sensitivity and linearity obtained with the newly developed materials, a longer performance is needed to determine the passivation time. This would be of great relevance for their further use in Hg measurements not only in water media but also in gases. Humidity is a very important parameter which we also addressed. After comparing three different materials as the most suitable for application in DEM and RHg measurements, soda lime was chosen as being better than the rest, economical and very practical for use. We further addressed a very important topic, the calibration of instruments. Three calibration techniques which might be used to increase the performance were tested and compared. The results were similar when either pure Hg(0) vapour (produced by a drop of liquid Hg)

or the reduction of Hg(II) in aqueous solution were used for calibration. The differences between them varied from 2 to 5 %. Therefore, either of the procedures can be used for routine work. The calibration of the system with Hg(0) produced from the reduction of Hg(II) standard solution in gas-tight vials did not provide comparable results with the other tested calibration procedures.

The main purpose of this work was not only to improve the performance of the existing methods of DEM and RHg determination, but also to develop new ones that would facilitate the determination the two species. Therefore, a semi − continuous method for measuring DEM and RHg in aqueous media was developed and optimised to conduct measurements in natural surface waters and in the scrubber solution of the WFGD. Continuous measurement of DEM in waters, especially industrial waste waters, is very important in mercury biogeochemistry. Because of difficulties in collecting real-time representative samples from industrial processes it is impossible to use the traditional bubbler purge/trap method to obtain continuous data.

Two novel approaches were developed:

a. A semi-continuous method based on flow-injection system was applied for the first time for natural waters and validated on a filed expedition.
b. Measurements of DEM in WFGD slurry have not been done so far. Both methods were validated, the manual and the semi-continuous. They offer a simple and easy way to be used as a diagnostic tool in the control of the efficiency of WFGD to oxidize Hg(0) entering the system.

In the two developed systems, the sample is introduced continuously by a peristatic pump and carried through the system by a constant flow of nitrogen. The optimization of the method was accomplished by adjusting sample and gas flow rates, equilibration times, matrix effects, linearity range, LOD, and precision of the method. Estimation of uncertainty was conducted robustly, and the level of uncertainty of this method is acceptable. The sample volume and the nitrogen flow ratio were important to establish the highest possible stripping efficiency of the species from the solution. The stripping efficiency in natural waters was higher than in the scrubber solution due to the presence of particles in the scrubber. Direct calibration of the method using standard addition (of DEM or Hg(II)) was not possible due to significant losses of Hg(0) and Hg(II) due to oxidation/reduction processes. Therefore, the manual method was used as a reference method in order to verify the data. The method is applicable to a wide range of concentrations, from a few tens of pg L^{-1} up to several tens of ng L^{-1}.

The method was applied to natural surface waters only for DEM measurements. The repeatability of the measurements for seawater expressed as relative standard deviation ranged from 1 to 7% (average 4 %). The limit of detection was calculated as three times standard deviation of the sample with the lowest concentration and was between 3.2 and 8.5 pg L^{-1} with an average of 5.4 pg L^{-1}. The semi-continuous method was able to detect changes in DEM concentrations in response to physico-chemical factors affecting the oxidation/reduction processes in aqueous media. However, the method is highly sensitive to the composition of the aqueous sample and the presence of particles. As a result, the stripping efficiency of DEM from the scrubber solution decreased to about 25 % (when compared to about 50 % in natural waters). The stripping efficiency of RHg was up to 64%. The LOD of the method was 14 pg L^{-1} and the repeatability ranged from 0.5 to 12 % (with an average of 6 %). As for natural samples, direct calibration of the method using standard addition of Hg(II) was not possible due to adsorption of Hg(II) onto particles. Further development of this method would require improved stripping of DEM and RHg from aqueous to gaseous phase. The determination of RHg in parallel with Hg(0) would

reveal important information regarding the chemistry and availability of these species in natural waters. On the other hand, determination of DEM and RHg in the scrubber solution of WFGD systems can serve as tool to control the efficiency of redox reactions and thus control Hg emissions into the atmosphere.

In conclusion, mercury behaviour in aqueous media is extremely complex and is different for different water bodies. Another difficulty when measuring Hg in natural water samples is related with the low levels. Even more difficult is to perform Hg speciation, particularly when the species are in the gaseous form and no reference materials are available, as in the case of DEM and RHg. However, much has been done to improve the analytical methods as the main tool to improve the knowledge of Hg behaviour in water systems.

For future work, longer testing of the gold-coated substrates would be crucial to determine their performance for long-term use and the occurrence of passivation. In addition, further development of the semi-continuous method would primarily require an increase of the extraction efficiency for both Hg species (DEM and RHg). This could be achieved by changing the system design such as the length of the separation reaction coil or by using multiple reaction coils. Moreover, the use of a Lumex detector which enables the measurement frequency of 1 s^{-1} would allow completely continuous measurements of DEM and RHg. In order to make the system independent of the manual method, an improved calibration procedure is required. A very important and crucial step would be the change of the detector. The use of a detector with high frequency of measurements (e.g every second such as Lumex), would make the method continuous.

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Publications Related to the Thesis

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