

**The on line determination of mercury in process
streams using atomic spectrometry**

by

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fulfilment for the degree of

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ABSTRACT

The on line determination of mercury in process streams using atomic spectrometry

On-line systems for monitoring mercury in liquid and gaseous production and waste streams have been developed, utilising atomic fluorescence spectrometry (AFS) as the basis for detection.

Instrumentation has been designed for unattended continuous operation. Laboratory chemistries for the vapour generation of mercury, normally performed off-line in batch mode, have been adapted and optimised for continuous, flow-injection analysis for varying sample types and chemical forms of mercury. The system has typical analysis cycle of 7 minutes, a limit of detection of 10 pg ml^{-1} , a linear range up to $100 \text{ } \mu\text{g ml}^{-1}$, and has been applied in industrial environments for the continuous monitoring of mercury in incineration wastewater and sulphuric acid. The system was validated by on-site trials for periods of one week, during which time comparative off-line laboratory measurements showed good agreement.

An automated system for monitoring mercury in natural gas streams has also been developed and validated by laboratory and on-site industrial trials. A heated pressure let-down system was designed in order to facilitate sampling of high-pressure gas streams without condensation of heavier fractions. The heated sampling line was interfaced with an automated system for trapping mercury, from variable volumes of gas, onto gold amalgamation traps, with subsequent desorption and analysis by AFS. The method detection limit for a 58 litre sample of natural gas was 30 pg m^{-3} which was sufficient to determine residual mercury in natural gas streams even after mercury scrubbing had been performed. The system was validated by laboratory trials and spiking experiments during on-site trials at a gas processing facility, which resulted in complete installation and commissioning.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescence spectrometry
CV	Cold vapour
CVAAS	Cold vapour atomic absorption spectrometry
CVAFS	Cold vapour atomic fluorescence spectrometry
CWI	Clinical waste incineration
DDW	Doubly distilled water
DTC	Dithiocarbamates
DTI	Department of Trade and Industry
EC	European Community
EDL	Electrodeless discharge lamp
EPA	Environmental Protection Agency
FI	Flow injection
FIA	Flow injection analysis
FIV	Flow injection valve
GLS	Gas liquid separator
IPC	Integrated Pollution Control
ISO	International Standards Organisation
LOD	Limit of detection
MW	Mega watt
MWI	Municipal waste incineration
PMT	Photo multiplier tube
PSA	PS Analytical Ltd
PTFE	Polytetrafluorethylene
PVC	Polyvinyl chloride
RSD	Relative standard deviation
SSI	Sewage sludge incineration
TCS	Teaching Company Scheme
TMT	Trimercaptotriazine
UK	United Kingdom

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Publications

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"The at-line determination of mercury in process streams using atomic fluorescence spectrometry"; N.K. Brahma, W.T. Corns, P.B. Stockwell, L. Ebdon, and E. H. Evans, *J. Anal. At. Spectrom.*, 1997, Vol. 12, 611-616.

Presentations

"A new approach to the on-line determination of mercury in process streams using atomic fluorescence spectrometry"; N.K. Brahma, W.T. Corns, P.B. Stockwell, L. Ebdon, and E. H. Evans, presented at the *Eighth Biennial Atomic Spectroscopy Symposium*, July 1996, Norwich, UK.

"Instrumentation for on-line mercury monitoring"; N.K. Brahma, W.T. Corns, P.B. Stockwell, presented at the *Process Control and Instrumentation Seminar*, June 1997, Prague, Czech Republic.

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"A fully automated atomic fluorescence system for the determination for the determination of mercury in the environment from 10^{-14} – 10^{-5} g l⁻¹"; N.K. Brahma, W.T. Corns, P.B. Stockwell, poster presented at the *Fourth International Conference on Mercury as a Global Pollutant*, August 1996, Hamburg, Germany.

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Signed.....

Date.....*12th March 2000*

CHAPTER 1

MERCURY IN THE ENVIRONMENT

1 MERCURY IN THE ENVIRONMENT

1.1 INTRODUCTION

Mercury is one of the most toxic elements known to man. Concern about mercury pollution in aquatic environments started with the celebrated case of Minimata Bay in Japan [1] where many people died after consuming contaminated fish and shellfish which was later found to contain large amounts of methylmercury. It is now well documented that fish and shellfish contribute appreciably to the total mercury intake by humans. 95% of mercury in fish is present as methylmercury, of which approximately 90% is absorbed by the human body [2]. Its toxicity to aquatic organisms and hazard to human health has resulted in many countries setting maximum mercury concentrations for discharges to the environment.

Inorganic mercury is known to be toxic at microgram per litre concentrations. However, organomercury compounds (e.g. methylmercury, which is teratogenic) are toxic at nanogram per litre levels. As a result, mercury has been designated a List 1 substance by the EC and its presence in effluents is controlled by two EC directives [3, 4].

1.2 MERCURY OCCURRENCE AND DISTRIBUTION

Mercury is probably the most ubiquitous of all heavy metals. It is the only metal that can exist as both a liquid and gas at ambient temperatures [5], so it cycles readily and continuously in nature. The mean abundance of mercury in the earth's crust is approximately $5 \times 10^{-5} \%$, it thus comes 62nd in order of abundance [6]. Its concentration in seawater is usually very low – about 0.15 ng l^{-1} , *i.e.* the oceans potentially hold about 2×10^8 tonnes of mercury [7]. Despite this overall rarity, mercury usually occurs as concentrated deposits, almost always as the

sulphide HgS (Cinnabar). More recently Livingstonite (HgSb₄S₇) has become an important ore for mercury.

World production of mercury is largely centered in Spain, the USA, Italy and China. World production of mercury has gradually declined since the early 1970's. In 1971 world production was 9.6×10^3 tons, but by 1987 it had dropped to 6.1×10^3 tons. This has partly been due to increased recycling and concern over environmental pollution [8].

1.3 PROPERTIES OF MERCURY

There are three valence states for inorganic mercury. Metallic mercury, Hg⁰, exists as a liquid at room temperature and pressure. Due to its high vapour pressures almost all 10⁴ tons of mercury in the atmosphere is monatomic Hg⁰. Hg⁰ is virtually insoluble in water (K_s is $\cong 10^{-7}$ M). Its appearance in sediments and rocks is difficult to document due to the propensity of mercury to absorb into a variety of materials. Since most atmospheric mercury is either Hg⁰ or CH₃Hg⁺, it is very likely that microbial activity is responsible for much of the transfer of mercury in the atmosphere. Inorganic mercuric and mercurous ions exist in equilibrium due the disproportionation:



Mercuric ions form complexes such as [HgCl₄²⁻]. In addition mercury is methylated in nature to mono- and dimethylmercury [9].

1.3.1 Biomethylation of mercury

The methylation of inorganic mercury in the sediments of lakes, rivers and other waterways, as well as the oceans is a key step in the transport of mercury in the environment and ultimately to aquatic food chains. Two biochemical pathways

have been identified for the formation of methylmercury in organic sediments. Non-enzymatic as well as enzymatic transfer of methyl groups from methylcobalamin ($\text{CH}_3\text{-B}_{12}$) to inorganic mercury has been shown to occur in living cells as well as cell-free extracts. Bacteria living in bottom sediments and sludge can methylate mercury by excreting methylcobalamin, which serves as an *in vitro* methyl donor.

1.3.1.1 Enzymatic transfer

It appears that organisms methylate mercury as a means of detoxification and that the microorganisms do not seek mercury, but rather deal with it when present in their food supply. Indeed, bottom dwelling bacteria, soil anaerobes, fungi and yeast have shown the ability to methylate mercury as a detoxification mechanism.

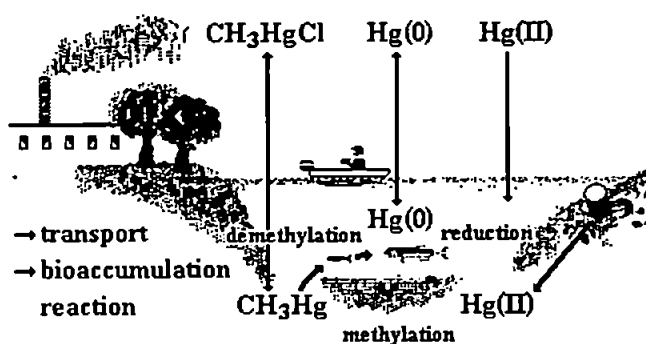


Figure 1.1. Mercury cycle in lakes and wetlands

Jensen and Jernelov first demonstrated biomethylation of mercury in 1967 [10], they proved that microorganisms in lake sediments could methylate mercury. In 1969 they showed that the degree of methylation correlated well with the microbial activity in the sediment. Thus, methylation rates increase with temperature and with increasing nutrient content of the substrate, roughly

following the Q10 rule. The rate is also higher in upper layers of sediments than those of lower layers.

1.3.1.2 Non-enzymatic transfer

Experiments on the influence of oxygen on the rate of methylation of mercury have shown that the rate of methylmercury formation in mixed aerobic and anaerobic sediment and its subsequent accumulation in fish is higher at lower levels of dissolved oxygen [10]. Also, when sediments have been exposed by dredging or by tide fluctuations in the water level, the rate of biomethylation can be extremely high, 10^3 - 10^4 times higher than "normal" rates in aquatic environments [10].

1.3.2 Mercury affinity

Mercury laden effluents are often discharged to watercourses that also receive other pollutants. When anaerobic conditions prevail, hydrogen sulphide may also be found in these receiving waters. The periodic occurrence of H_2S in bottom waters and sediments is of importance for the turnover of mercury in aquatic systems. In the restoration of mercury contaminated watercourses the artificial binding of mercury as the sulphide has been suggested [11], laboratory tests have shown that microorganisms producing H_2S can remove mercury by precipitation of insoluble mercuric sulphide. This virtually prevents the formation of methylmercury from the sediment.

However, mercury has also been shown to be available from mercuric sulphide. The very low solubility product of mercuric sulphide ($K_s = 4 \times 10^{-53}$ M) raises the question of how mercury is available from this compound for methylation [11]. However, the threshold solubility product does not strictly apply to natural systems due to redox potentials, pH and concentrations of complexing

agents, all being typical factors that will affect equilibrium and create an extremely complex system.

The affinity of mercury for the sulphide is further complicated when organic sulphur is present. Many of the substrates that constitute protoplasm contain sulphhydryl groups (-SH). In particular, proteins contain available free sulphhydryl groups through the incorporation of amino acids and cysteines.

Organic compounds that contain sulphur bound mercury exist in non-equilibrium states relative to the water, but are stable whilst they are in the living organisms [12]. Upon release, either by excretion or death of the organism these compounds will decompose and the mercury will ultimately reappear in the inorganic form. The situation is further complicated by the presence of an affinity of mercury for complexing groups such as the amino group (-NH₂). This increases the organic matter's capacity for mercury and also increases the strength at which mercury is bound.

Organic sulphhydryl complexes exist at redox potentials higher than those at which sulphide sulphur is stable relative to sulphate sulphur, apparently because of the stability afforded by the bonding of sulphur to the organic residue. The combination of mercury with sulphhydryl groups explains enzyme inhibition of microorganisms [13], since most organisms contain sulphhydryl groups. Chelating agents often used to combat mercury-poisoning use the fact that the thiol or sulphhydryl groups bind to mercury.

1.3.3 Mercury-carbon bond

There are two types of mercury-carbon bond that predominate, *i.e.* those in which mercury is joined to a single carbon atom and those where it is joined to two

carbon atoms. The former act as substituted salts and are fairly soluble, whilst the latter are covalent compounds and are comparatively insoluble.

The first type includes methylmercuric chloride (CH_3HgCl) that exists as CH_3Hg^+ ions and Cl^- ions in solution. Jensen and Jernelov [10] showed that mercuric chloride could be readily converted to methylmercury by organisms in sediments. Mercuric chloride is a relatively strong oxidising agent and can be reduced by many organic materials.

The second type of mercury-carbon bond includes dimethylmercury (CH_3HgCH_3), a volatile covalent substance that remains undissociated in solution. The mercury-carbon bond is relatively weak, its strength being comparable to the carbon-carbon bond. These compounds are not readily dissociated when in water.

There is no readily apparent pathway for the formation of compounds with Hg-C bonds in aquatic systems. It was originally thought that these were present in natural waters as pollutants, either in their use as agricultural fungicides, or from industrial wastes. This idea was enforced when the methylmercuric ion (CH_3Hg^+), the root cause of Minamata disease, was identified in the waste streams of the chemical manufacturing plant discharging into Minamata Bay.

There is some debate as to the actual reaction mechanism involved and also as to whether monomethyl or dimethylmercury is the primary product. Nevertheless, methylation *via* methylcobalamin is very likely to be the primary route for methylation and mobilisation from bottom sediments in polluted waters. As a result, methylation in sediments is of serious concern in the streams and rivers downstream from paper mills, incineration sites and chlor-alkali plants discharging large amounts of contaminated effluent. However, this does not

explain the concentrations of methylmercury in fish from deep waters. Furthermore, the level of mercury (mainly all methylmercury) in deep-sea fish has not changed the last 100 years, making it very unlikely that the level of mercury in fish is entirely from human origin [14].

1.3.4 Toxicity effects of mercury

Mercury is a general protoplasmic poison; it can be absorbed through the gastrointestinal tract, and also through the skin and lungs [6]. After absorption it is circulated through the blood and is stored in the liver, kidneys, spleen and bone. Elimination takes place only slowly through urine, faeces, sweat and saliva. Very mild exposure to the vapour may produce dryness in the throat and mouth, while the main symptoms of more prolonged exposure are inflammation of the mouth and gums (gingivitis), loosening of the teeth, tremors and physical disturbance.

A number of biological changes have been detected as a result of occupational exposure to mercury vapour in the air. These include plasma galactosidase and catalase activities in red blood corpuscle cholinesterase activity. Physical disturbance is usually of the type known as erythism and is characterised by loss of memory, lack of confidence, irritability, insomnia, urinary complications and ultimately death.

Most attention over the last thirty years has been devoted to the toxicological effects of alkyl and methylmercurials. Much this research was as a result of the Minimata Bay incident 1953. The term Minimata disease has been used to describe many of the toxic effects of methylmercury poisoning.

The principal source of methylmercury to humans is from contaminated fish. The target organ of methylmercury in humans is the brain, where it disrupts the blood-brain barrier, upsetting the metabolism of the nervous system. In

addition mercury forms very strong bonds with sulphur groups in proteins and enzymes, disrupting various enzymatic systems and synthetic mechanisms. Methylmercury can cross the placenta much more easily than inorganic mercury, as it is lipid-soluble, it affects the foetus and accumulates in tissues, thus damaging the central nervous system. In the poisoning incident at Minimata, twenty-two infants born with serious brain damage were born to mothers who showed slight or no sign of mercury poisoning [15].

Most methylmercury is completely absorbed in the gastrointestinal tract and is fairly stable once in the body. Biological half-life of mercury compounds is approximately 70 days.

1.4 ANTHROPOGENIC RELEASES TO THE ENVIRONMENT

Various estimates have been made of the amount of mercury released to the environment by both man and nature. Figure 1.2 shows a model of the biogeochemical cycling of elemental mercury. It has been estimated that the global weathering of mercury amounts to 800 tons a year, whilst the release from fossil fuels for the period 1900-1990 has been estimated at 5×10^3 tonnes. During the period 1945 -1958, more than 10,000 tonnes of mercury were "lost" to the environment from industrial uses in the USA alone.

It has been estimated that 2.5 Kg of mercury a day is discharged to the atmosphere from one 700 MW coal-burning power station alone. Global releases of mercury from coal-burning power stations have been estimated to total 3000 tonnes per year. The mercury content of bituminous coals averages around 3000 $\mu\text{g Kg}^{-1}$, with anthracite coals and crude oils ranging from 1200 to 21,000 $\mu\text{g Kg}^{-1}$ [16]. If one assumes a world crude oil production of approximately 2.8×10^9 tons

per a year an additional 10,000 - 60,000 tonnes of mercury will be released by burning crude oil alone.

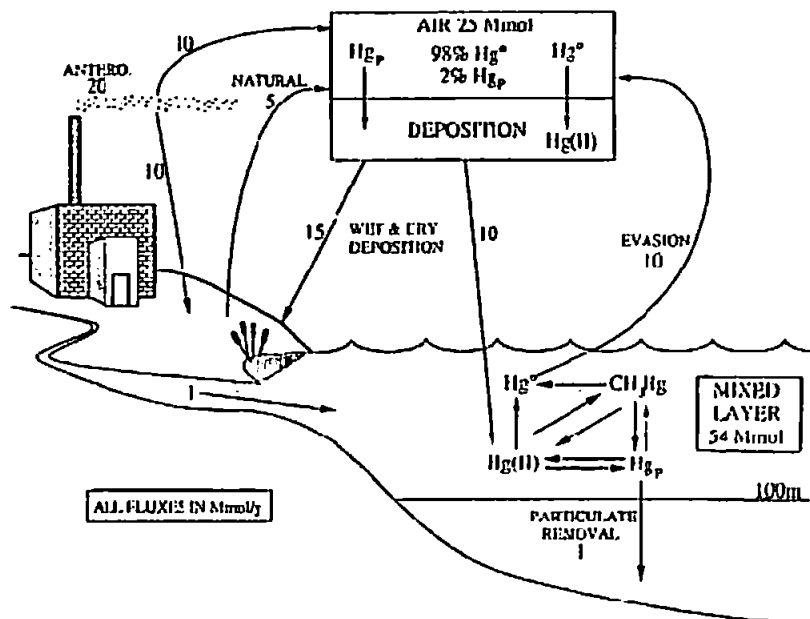


Figure 1.2. Cycling of elemental mercury [20]

Human activities over the last 100 years have added no more than 10^6 tons of mercury to the environment, or less than 1% of that which is presently in the oceans. Analysis of polar ice cores has shown that mercury levels were of the order 100 ng Kg^{-1} since 800 B.C., unlike those of lead, which have risen from 10 ng Kg^{-1} in 1750 to around 200 ng Kg^{-1} in 1980 [17].

It has been suggested that the majority of mercury in the atmosphere is as a result of terrestrial degassing of the earth's crust. Summers, [18] suggested a different balance for mercury. He notes that the bedrock and deep-sea sediments contain most of the world's mercury. Indeed the high concentrations of mercury from degassing of the earth's crust are reflected by mercury vapour being used to indicate the presence of ore bodies. Mercury is described as a "pathfinder element" where its vapour is used to detect for lead-zinc-silver mineralisation, levels of up to $160 \mu\text{g m}^{-3}$ have been found in the air above mercury mines [19].

However, global volcanic emissions have recently been estimated to be around 20-90 T/yr based on studies of Mount Etna in Sicily and Kilauea in Hawaii, this being equal to approximately only 1-5% of the annual emissions from human activities [20].

1.4.1 Past uses of mercury

Much of the mercury distributed in the environment today has been as a result of anthropogenic activities that have taken place over the last few centuries. In the past mercury was used as a pigment in Vermilion, for cosmetic or decorative purposes, or superstitiously for medical purposes. Early use was for the treatment of syphilis and skin diseases [21]. It was common practice in the nineteenth century for hat makers to heat mercuric nitrate into a paste when gluing fur on to hats. The resulting poisonous mercury vapour led to many hat makers suffering from emotional problems, this later coined the phrase "mad as a hatter".

1.4.2 Small-scale uses of mercury compounds in the UK

The small-scale manufacture of mercury compounds has declined significantly over recent years; this is as a result of both legislative and voluntary following concern over the environmental effects of their use. Mercury based pesticides and biocides, formerly widely used, have been progressively replaced by non-mercury alternatives. The final prohibition of all mercury containing plant protection products was made effective by the EC in 1992 [22].

The majority of mercury products still used in the UK are imported. A limited number of mercury compounds are, however, manufactured for certain non-prohibited uses, e.g. in pharmaceutical products such as soaps, creams and for certain fungicidal applications such as in paints used in tropical climates.

1.4.2.1 Organomercury compounds

Phenyl mercury compounds have been used for many years as bactericides or fungicides, e.g. in paints and wood preservatives. Although their use in products formulated and used in the UK is believed to have ceased, manufacture for export to developing countries continues at a significant level and is steadily increasing. The production of phenyl mercuric dodeceny succinate remains significant in the UK. A licensed process using a two-stage reaction of mercuric oxide, benzene, acetic acid and dodeceny succinic anhydride in an organic solvent medium makes the fungicide [23].

Releases to air from this process include mercury vapour and particulate matter containing mercury compounds from the reactor ventilation systems. Releases to water include mercury containing condensates, distillates and washings. These effluents are normally treated by addition of sodium bisulphide to reduce most of the compounded mercury to the element. After a long settling period the supernatant liquor is transferred, neutralised and disposed of to a suitable waste-handling specialist, where it typically undergoes incineration or landfill. The elemental mercury is retained for re-use. Releases to land include contaminated packaging, pipes, process equipment and clothing, once again treated by either landfill or incineration [22].

1.4.2.2 Mercury battery manufacture

Mercury is used in certain primary battery cells, although the manufacturers are progressively reducing the quantity used. Elemental mercury has been an essential part of all cells using zinc powder anodes (Le Clanche cells), it is amalgamated with the zinc oxide by the supplier. Recently the proportion of mercury in these cells has been reduced to 0.025% m/m and was due to be

removed entirely from all European general-purpose batteries by 1998, however an extension for a further 4 years has been granted [23].

The majority of the mercury now used in batteries in the UK is found within the mercuric oxide containing cathodes of small mercury button cells. Here, the mercuric oxide is an essential part of the electrochemical couple powering the cell. In the UK these cells are primarily used for powering hearing aids, with approximately 30 million a year manufactured on one site only. Alternative non-mercury button cells are available and production of mercury cells is due to be completely phased out by 2001.

During the manufacture of button cells releases to the air include mercury oxide present as fine particulate matter in the exhaust ventilation air from the blending process. Releases to water include effluents containing mercuric oxide from the cell washing process; this effluent is treated via an ion exchange column to remove the majority of mercury. Releases to land include spent ion exchange resins absorbed with mercury compounds and scrap/reject cells, both are either land-filled or incinerated.

1.4.2.3 *Electrical equipment and instruments*

Although declining in use generally, mercury retains a number of essential applications in a variety of equipment and instruments, including fluorescent discharge lamps, manometers and thermometers, control/switching devices, certain vacuum pumps, AC/DC rectifiers and gas filled valves. These processes typically involve the filling of a specified quantity of mercury, ranging from a few milligrams to hundreds of grams, into the device, which is then sealed to contain the mercury [23].

1.4.2.4 Fluorescent discharge lamps

Mercury is used in all current mass production of discharge lamps worldwide and non-mercury alternatives are believed to be many years away from development to the stage of commercial viability. Mercury has a high vapour pressure at ambient temperatures and its use gives a high efficiency of luminosity/power consumed for white light applications. When excited electrically the mercury vapour atoms emit blue/green visible light and ultra-violet radiation. The latter subsequently excites the internal phosphorous coating of the lamp to emit red/yellow light and produce a balanced output approaching that of natural daylight.

UK low-pressure discharge lamps typically each contain 10-20 mg of mercury, which is all vaporised when the lamps are made. Gradually the mercury vapour reacts with parts of the lamp until there is insufficient vapour to generate a complete discharge circuit, thus the amount of mercury present in a lamp dictates the lifetime of the lamp.

Releases to air during lamp manufacture are mainly from mercury vapour in the exhaust ventilation systems around the vacuum filling stage. Providing that adequate cleanliness and control is employed in the handling of liquid mercury then no release to water should occur. Releases to land include rejected filled lamps and waste vacuum pump oil contaminated with mercury.

At present there is only one European lamp recycling facility and this is located in Belgium, it recovers spent lamps from France, Belgium, Netherlands and Germany. The incineration site is the subject of chapter 3 as it now operates an on-line effluent analyser to monitor mercury levels leaving the site and entering the local river [24]

1.4.3 Chlor-alkali industry

The primary industrial use of inorganic mercury is in the chlor-alkali industry. Here, chlorine is produced via the Castner-Kellner process, from the electrolysis of molten sodium chloride by the use of a flowing mercury cathode. The chloralkali industry produces chlorine and caustic soda for a wide range of industrial uses. Caustic soda (NaOH) is industry's most important alkali. There are three technologies used for the manufacture of caustic soda, these are mercury cell, diaphragm cell and membrane cell. The mercury cell process is historically the oldest technique and predominates with over 350 plants worldwide [25] in the USA there are 13 plants, whilst the UK currently has 3 [26].

It has been estimated that 50-200g of mercury was present in every tonne of chlorine produced before 1970. Current levels are in the region of less than 10.0g per tonne of chlorine. Since the Minimata Bay incident (1950's) the use of mercury cell technology has been forced into decline. Strict emission controls have been introduced which have resulted in alternative membrane processes being developed for the chlor-alkali industry. Although effective, membrane technologies are extremely expensive and replacement of the mercury cells has been slow on the uptake. In most cases, conversion costs of existing mercury cells to alternative techniques are estimated to be more expensive than the complete replacement of the plant.

The 1992 Rio Conference stipulated that all mercury cell plants should be phased out by the year 2010 [20], although this deadline has already been subject to several extensions over the last twenty years. Approximately 72% of the UK chlorine capacity is based on the mercury cell process [26].

Although environmental factors do not favour the mercury cell process it has several significant advantages over the membrane and diaphragm technologies [27, 28], namely:

- lower energy consumption.
- toleration of lower grade brine feedstock's.
- higher purity caustic soda and chlorine gas.
- higher throughput process with cheaper operating costs.

1.4.4 Wastewater treatment

The discharge of heavy metals in effluents to receiving waters has important implications for the quality of water for a variety of uses, including abstraction for potable supply, irrigation, amenity and support of the aquatic biota. Heavy metals present in effluents are of concern, especially in densely populated and industrialised areas where water re-use is practised. European Community (EC) countries have set stringent limits for the concentration of metals in industrial discharges or have introduced integrated pollution control (IPC) policies as in the United Kingdom [3,4,23].

The most important concern for heavy metals discharged to surface waters lies in the possible harmful effects to human health as a result of drinking water abstraction. Although processes such as ion-exchange and sulphide and carbonate precipitation are effective in eliminating heavy metals from drinking water at rates greater than 90%, metals such as cadmium, manganese, mercury, selenium and zinc are sometimes removed with much lower efficiencies in precipitation or activated-carbon processes [29]. There is evidence that conventional drinking-water treatment e.g. sedimentation in clarifying basins, sand

filtration and bank filtration are not well suited to safeguard against the passage of trace metals [30].

There are two stages in conventional wastewater treatment where metal ions may be removed, primary sedimentation and activated sludge treatment. Primary sedimentation removes a portion of the metals that are either insoluble or adsorbed onto large particles. Normally during primary sedimentation the suspended solids concentration is reduced by between 50-70% and the BOD reduced by between 30-50% [30].

Further metal removal occurs in the activated sludge process by adsorption of metal or metal particulates onto sludge flocs [31]. Most literature reports that the activated-sludge process is more efficient at metal removal than the primary sedimentation stage [31,32]. Primary sedimentation of raw sewage is employed to remove most of the settleable solids prior to treatment of the primary effluent by the activated sludge process. The removal of metals during primary sedimentation is a physical process, which is dependent on the settlement of precipitated metal or the association of metals with settleable particulate material.

1.4.4.1 Treatment of wastes containing heavy metals

Wastewater containing heavy metals can be divided into two categories; soluble and particulate bound metals. Free ions or soluble metals can be removed by simple hydroxide precipitation. Complex or particulate bound metals require more detailed attention. In many instances this can be solved by using precipitating agents containing sulphur, i.e. with inorganic or organic sulphur compounds. Complexing agents are used in many processes for treating metal laden waters, their aim is to dissolve metals or metal compounds and keep them in solution. Even under conditions in which nearly insoluble compounds such as

metal hydroxides, carbonates and sulphates would be formed under normal circumstances. Complexing agents can be classified into inorganic and organic substances. The inorganic substances include cyanides, ammonia, phosphates and thiosulphates. The organic complexing agents include polyamides, polyalkonoamines, polyamino-polycarboxylic acids and polycarboxylic acids [33]. If the complexing agents are not destroyed or their effect masked when the wastewater is treated, then the heavy metals can pass on as a highly stable complex to drains and water supplies. Here they can only be degraded by slow biological mechanisms releasing heavy metals back into the watercourse to continue their cycle in the hydrosphere.

1.4.4.2 Separation of heavy metals from wastewater

Heavy metals are usually precipitated from wastewater by so called neutralisation using caustic soda, soda or slaked lime to form metal hydroxides and carbonates with low solubility, which can be removed from wastewater by settling or filtration. However, when complexing agents are present in the wastewater, such processes are not effective. This is due to the high stability of the metal complexes reducing the concentration of heavy metal ions to such an extent that the solubility product of the hydroxide is not reached. In such instances alternative wastewater treatment methods such as oxidation, ion exchange, electrolysis and precipitation with special precipitating agents containing sulphur are necessary.

1.4.4.2.1 Sulphur based precipitating agents

Precipitating agents containing sulphur include sodium sulphide, sodium polysulphide, various dithiocarbamates (DTC) and trimercapto-s-triazine tri sodium salt (TMT). These products combine with heavy metals to form highly

insoluble compounds, with solubility products far below that of the hydroxides of the corresponding metals. Table 1.1 shows the solubility product of metal-TMT compounds, sulphides and hydroxides. The lower the value the more insoluble the compound. This table also clearly illustrates the difference between the organic and inorganic metal sulphides in relation to the hydroxides.

Each of the various precipitating agents has its shortcomings. Although sodium sulphide is relatively inexpensive, it always forms a certain quantity of hydrogen sulphide when added to wastewater. Both sodium sulphide and hydrogen sulphide are extremely toxic to both humans and fish. Another problem is that frequently metal sulphides with very small particle sizes are formed which result in long settling times or difficult filtering processes. Sodium polysulphide suffers from similar drawbacks as sodium sulphide except less hydrogen sulphide is produced.

Dithiocarbamates are again relatively inexpensive precipitating agents. DTC-metal compounds with coarse floccular shapes are generally easy to filter out, they also have the advantage of not producing hydrogen sulphide, however they do have a high toxicity to fish. In acidic media they also decompose to produce highly toxic and flammable carbon disulphide.

Trimercaptotriazine (TMT) is comparable to dithiocarbamate in terms of price; it does not form toxic hydrogen sulphide or carbon disulphide when added to wastewater. Its toxicity to fish is also extremely low. Metal TMT compounds also have coarse floccular shapes and are hence easy to filter out [33].

Table 1.1. Solubility products of heavy metal complexes [33]

Metal	TMT compounds	Sulphides	Hydroxides
Hg ²⁺	1.4 X 10 ⁻⁴⁷	4 X 10 ⁻⁵³	1.7 X 10 ⁻²⁶
Cd ²⁺	7.7 X 10 ⁻³³	3.6 X 10 ⁻²⁹	1.3 X 10 ⁻¹⁴
Cu ²⁺	1.3 X 10 ⁻³¹	8.5 X 10 ⁻⁴⁵	2.0 X 10 ⁻¹⁹
Pb ²⁺	3.6 X 10 ⁻²⁹	3.4 X 10 ⁻²⁸	1.0 X 10 ⁻¹³

1.4.4.2.2 Precipitation procedure

As a general rule precipitating agents containing sulphur are used in the pH range 6 -10, which is fortunately in the range allowing disposal of the effluent without further treatment. This eliminates the necessity of correcting the pH following precipitation. Basically, the wastewater is brought to the correct pH by adding acid or alkali solutions. The precipitating agent is added to the wastewater as required by the metal concentration.

If necessary a flocculent is added to increase the particle size of the precipitate formed, this will greatly facilitate the sedimentation or filtration process. Non-ionic or anionic polyelectrolytes, usually long chain polyacrylamides are preferred as flocculents. These are added to the wastewater in the form as highly dilute aqueous solutions (0.05 to 0.1%) [33]. The quantity added depends upon the type of sludge containing the heavy metal. In addition iron or aluminium salts are frequently added to wastewaters containing very low concentrations of heavy metals. These trivalent metals form highly soluble hydroxide flakes with small particle sizes and active surfaces, which adsorb and bind the metal sulphide precipitates. The resulting agglomerates can then be flocculated well with polyelectrolytes. The quantity of precipitating agent required is frequently calculated potentiometrically with redox electrodes.

1.4.4.3 Soluble and suspended metals

Although the soluble forms of heavy metals are an important component of effluents discharged to surface waters, particulate forms associated with solids, which do not undergo settlement in final sedimentation processes, also have a significant impact on the receiving waters. Particulate forms of heavy metals become associated with bottom sediments, resulting in localised enrichment, or are transported long distances before settling out. In either case metals associated with bottom sediments may not be immobilised for long [30].

An important consequence of heavy-metal pollution in surface waters is their toxic effects on aquatic organisms. A significant degree of bioaccumulation/bio-magnification can occur resulting in the uptake of metals by lower organisms and their mobilisation through the food chain. Ramoorthy *et al.*, [34] found that the cell culture *Pseudomonas fluorescens* was capable of accumulating approximately 20 times more mercury than its surrounding sediment. Higher organisms, especially those that live and feed on bottom sediments such as eels, can accumulate metals to a much higher degree.

1.4.4.4 Sludge disposal

In normal methods of wastewater treatment, metals are concentrated in the sludges produced in both primary sedimentation and activated sludge treatment. Metals that are strongly adsorbed or complexed to suspended solids or which form sparingly soluble salts with the matrix of the effluent will be removed in the sludges, either primary or secondary treatment.

The treatment and disposal of these sludges poses problems in themselves. Dumping sludge at sea by the UK water companies is no longer an alternative as it was phased out in 1998. One practicable alternative is

agricultural spreading on land used for short rotation coppicing. Disadvantages of this method are long the lead times necessary to cultivate the coppice, large tracts of land and the limitation of the types of sludge that can be applied.

A second alternative is anaerobic sludge digestion, yielding compost and methane. Sludge digestion may well minimise the amounts of NO_x and CO produced, but chlorides, sulphur, indigestible organics and heavy metals that are normally captured or destroyed in an incineration processes remain in the cycle.

As a consequence, the incineration of contaminated sludges in high temperature furnaces has become an increasingly more popular method of disposal. The irony of sludge incineration is that a secondary sludge or ash is produced from the wastewater treatment plant from the stack gas scrubber water. This secondary sludge ultimately requires disposal by speciality landfill sites. If not stored properly landfill can lead to long term leaching of heavy metals back into watercourse continuing the cycle of the pollutant.

1.5. AIMS AND OBJECTIVES

Mercury pollution has become a global concern due to its wide occurrence in the environment and its toxicological effects. Consequently, mercury monitoring is of particular concern amongst the monitoring of heavy metals. Industrial and municipal wastewater treatment plants have become an integral part of the hydrological cycle, since they can control the vast dispersion of heavy metals. Careful control of mercury levels entering and leaving these plants allows for environmental compliance through minimal release.

The aim of this programme of research was to first of all understand the occurrence and behaviour of mercury during the various stages of the manufacturing process and waste treatment systems of the following industries:

- Waste incineration
- Sulphuric acid manufacture
- Chloralkali manufacture
- Natural gas processing

In order to control mercury levels they must be accurately and frequently measured. Hence the aim of this thesis was to develop mercury monitoring instrumentation, allowing accurate and rapid unattended continuous measurement of mercury levels in process or effluent streams.

Ultimately, the intention was to take the laboratory based measurements to the sample and perform the analysis in-situ at the sampling point. Essentially, the aim of this research is to translate manual laboratory based analysis techniques into a fully automated system, capable of sample collection, preparation, determination and calculation of the mercury level.

The collection, delivery and pre-treatment of samples will be discussed along. The analysis system will be based on continuous flow principles combined with flow injection analysis. Mercury determination will be based upon the cold vapour principle combined with atomic fluorescence spectrometry. It is intended to develop mercury monitoring systems for both aqueous and gaseous process and effluent streams. Sample pre-treatment will be fully automated by combining the appropriate switching valves, pumps, heaters, reaction coils and control software into a complete stand alone continuous mercury monitoring system that requires minimal operator intervention.

Systems will be designed and tested off-line in the laboratory, prototype systems will then be installed on-line at the manufacturing site and developed further. After optimisation on-site, systems will be ultimately commissioned to the

manufacturing/waste treatment process. The intention is to design a system that enables plant operator's to monitor mercury accurately, reliably and confidently. By providing an additional tool in the monitoring of the mercury cycle plant operators can minimise its release into the receiving environment thus, giving them a greater degree of confidence, control and compliance.

CHAPTER 2

DEVELOPMENT OF INSTRUMENTATION FOR ON-LINE DETERMINATION OF MERCURY BY ATOMIC FLUORESCENCE SPECTROMETRY

2 DEVELOPMENT OF INSTRUMENTATION FOR ON-LINE DETERMINATION OF MERCURY BY ATOMIC FLUORESCENCE SPECTROMETRY

2.1 INTRODUCTION

The toxicological effects of mercury compounds on environmental systems have been well established over the last few decades resulting in many techniques for its detection. Originally, calorimetric and spectrophotometric methods, which were based on mercury ions forming chelates with dithizone and dinaphthylthiocarbozone were used. These methods are troublesome and suffer from contamination and poor sensitivity. Additionally, these methods detect mercury by concentration rather than by mass, and are limited to laboratory conditions that do not lend themselves economically or operationally to continuous monitoring applications.

Colorimetric analysis can be conducted in two ways. Gas containing mercury can be passed through an acidic potassium iodide or iodine solution, resulting in the quantitative formation of mercuric iodide. A more common colorimetric technique is the use of a Draeger tube. Here, gas is passed through the tube, which forms a colour change as a copper/mercury complex is formed. The greater the volume of gas required for a complete colour change reaction, the lower the mercury concentration. Draeger tubes are generally used to detect high mercury concentrations in the range 50-2,000 mg m⁻³.

Differential conductivity techniques include gold film mercury detection based on the amalgamation of mercury on a low surface area gold wire or film. The system is designed to accept a gas flow of a few millilitres per a minute, and measurement is based on the concept of resistance increasing linearly across the gold film as mercury is adsorbed, i.e. measurement of the change in resistance is

a measurement of the mass of mercury. Wheatstone bridge instruments of this type are compact, inexpensive, easy to operate and offer the operator a fairly accurate measurement technique.

Today, the most commonly used method for determining mercury is cold vapour atomic absorption spectrometry (CVAAS), a method originally developed in 1963 by Poluetov and Vitkun [35]. However the technique was under used until Hatch and Ott [36] refined and popularised the method in 1974.

West [37] in 1974 showed theoretically CVAAS should be more sensitive and produce considerably less spectral interference from non-specific absorption compared with the corresponding AAS technique.

Thompson and Godden [38] were the first to use the cold vapour technique for the determination of mercury in 1975. They modified a conventional atomic absorption spectrometer. More recently (1989) Godden and Stockwell [39] developed a non-dispersive fluorescence spectrometer specifically for mercury determination. Their system is based on a conventional molecular fluorescence spectrometer coupled to a vapour generation process.

The process of atomic fluorescence is a very sensitive and selective method for the determination of a number of environmental and biochemical elements such as mercury, arsenic, selenium, bismuth, antimony, tellurium, lead and cadmium. The technique has been adopted as a standard analytical tool for the determination of trace metals in environmental samples. Its advantages over other methods include sensitivity, selectivity, linearity and the low cost of equipment.

Fluorescence radiation is emitted when a radiatively excited atom returns to the ground state. The main types of atomic fluorescence are shown

diagrammatically in Figure 2.1. These are characterised by the excitation and de-excitation mechanism involved in the transitions from the ground state E_0 to an intermediate energy state E_1 , and a higher energy state E_2 [40, 41, 42].

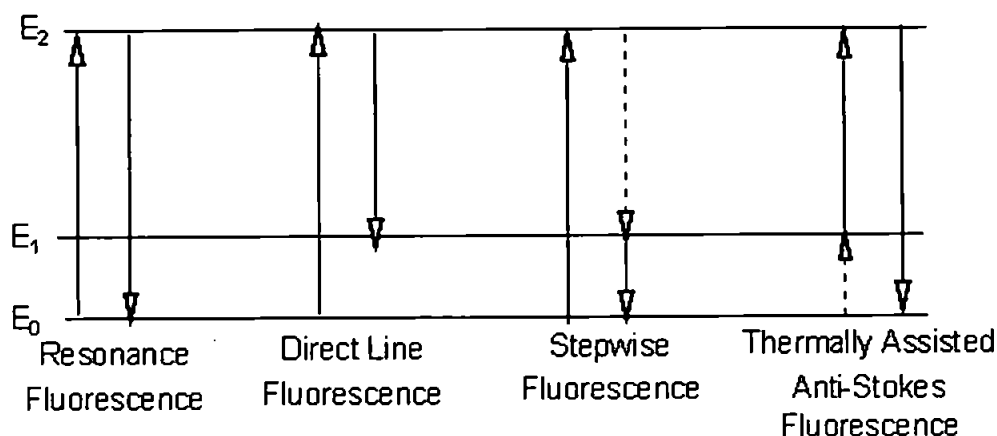


Figure 2.1. Different types of atomic fluorescence

Resonance fluorescence occurs when atoms absorb and re-emit radiation of the same wavelength, i.e. E_0 to E_2 and then desorption E_2 to E_0 , it occurs when atoms re-emit the same wavelength as that used for excitation. Analytical chemists most commonly use resonance for quantitative analysis, as it is the most intense type of fluorescence. Energy transitions for resonance fluorescence are shown Figure 2.1.

Direct line fluorescence occurs when transitions between the excited state E_2 of the resonance line and the lower intermediate level E_1 , are allowed by the selection rules. Consequently, this type of fluorescence occurs at a higher wavelength than the initial excitation radiation. This process is shown in Figure 2.1.

Stokes and anti-Stokes fluorescence occur when the excitation and fluorescence wavelengths are different. If the photon energy of fluorescence is less than the photon energy of absorption, i.e. $\lambda_F > \lambda_A$, the process is called Stokes

type fluorescence. If the photon energy of absorption is greater than that of fluorescence then anti-Stokes type fluorescence is obtained [43, 44].

Stepwise line fluorescence occurs when the upper energy levels are involved in the excitation and de-excitation process. The atoms usually undergo de-excitation by collision to a lower excited state E_1 , rather than directly to the ground state E_0 . This process is shown in Figure 2.1.

Thermally assisted fluorescence is the opposite of stepwise line fluorescence. It occurs as a result of a stepwise absorption of energy by an atom to reach an excited state. A simple mechanism involves an atom which is thermally excited by a flame (atom cell) into a more excited energy state E_1 . Absorption of radiation by this excited state promotes the atom to an even higher energy level E_2 . This process is shown in Figure 2.1.

2.2 ATOMIC FLUORESCENCE OF MERCURY

The majority of mercury determinations are based on the resonance transition line that occurs at 253.7nm. Electronic transitions at this wavelength correspond to movement from the 6^3P_1 excited state to the ground state of 6^1S_1 of mercury. Excitation of mercury to the 6^1P_1 excited state, followed by a Stokes stepwise fluorescence transition is also utilised used for mercury determinations, however, this line has limitations in that most flames at this wavelength (185.0nm) absorb very intensely, [45, 46].

Fluorescence intensity is directly proportional to the intensity of the radiation source, I_0 as shown by equation 2.1:

$$I_f = K \phi I_0 C \quad \text{(Equation 2.1) [47]}$$

Where $K = \text{Constant } (1/4\pi)$

$l = \text{path length in the direction of the detection system, m}$

ϕ = Fluorescence (quantum efficiency)

I_0 = intensity of the source at the absorption wavelength

C = concentration of atoms

Consequently, the sensitivity of atomic fluorescence is governed by the intensity of the irradiation source rather than the wavelength of the absorption line [48].

The concentration of the analyte in the atom reservoir or fluorescence cell is defined within the term C and the fluorescence intensity I_f , which is linearly proportional to the concentration of mercury present at low concentrations.

Assumptions of this equation include:

- the atom under consideration has only two energy levels, the ground state and the excited state.
- atoms are uniformly distributed within the atomiser
- the concentration of the analyte atoms is low,
- the temperature of the atomiser and the radiation density of the source are spatially uniform

2.2.1 Instrumentation

The basic layout of an atomic fluorescence spectrometer is similar to AAS and AES except that the light source is located at right angles to the detector around the atom cell. A block diagram of an AFS system is shown in Figure 2.2. The basic components of an AFS system consist of a radiation source, an atomizer, a wavelength selection system, a signal detector and an electronic readout system.

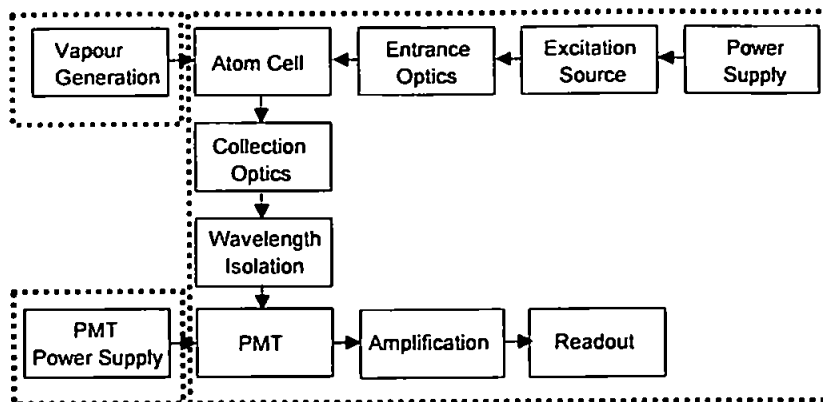


Figure 2.2 Major components of an AFS system

2.2.1.1 Excitation sources

Ideally, for an AFS system the source should be stable and provide intense radiation at the particular wavelength of interest. A number of excitation sources have been used in AFS, these can be divided into two types, spectral line sources and continuum sources. As the intensity of AFS radiance is proportional to the intensity of the exciting radiation, sources with high radiance are necessary for good sensitivity and a wide linear range. Indeed, much effort in AFS research over recent years has been to improve the intensity of excitation sources. Winefordner discussed the criteria for choosing a good excitation source in detail [49]. In summary, Winefordner suggests that a source should have good short term and long-term stability in addition to having a high radiance over absorption line.

The most often-used conventional light sources are hollow-cathode lamps (HCL) [49, 50, 51], the electrodeless discharge lamp (EDL) [52], vapour discharge lamps [53], and the continuum source lamp. Significant advances in recent years have been focussed around the replacement of conventional excitation sources with lasers. Lasers provide high intensity which are capable of complete saturation of atomic transitions and hence provide the maximum fluorescence signal [54,53].

Mercury arc lamps are a type of vapour discharge lamp that provide simple and robust line spectra. The low-pressure mercury vapour discharge lamp equipped with a fused silica window is the most common source for filter fluorimeters. This type of source provides intense lines at 254, 366, 405, 546, 577, 691, and 773 nm. Individual lines can be isolated with absorption or interference filters. Most commonly, the mercury lamp is commercially used in instruments with a 254nm filter for mercury analysis.

2.2.1.2 Atom Cell

The atom cell converts the sample into gaseous atoms. Many atomisers used for AFS are similar to those of atomic spectrometry and emission spectrometry. Commonly used atom cells for AFS include flames, plasmas and electrothermal atomisers. The basic requirements of an atomiser for AFS are:

- efficient and rapid production of free atoms with minimum background noise
- long residence time of the analyte atoms in the optical path,
- low quenching properties
- low operating costs
- and ease of use

Mercury is the only metallic element that exhibits an appreciable atomic vapour pressure at ambient temperatures. Mercury has a vapour of 0.00016 mbar at 20°C, corresponding to a concentration of about 14 mg m⁻³ in air [54]. This unique property allows mercury to be measured without the need for additional thermal energy supplied by a flame or by eletrothermal heating. Consequently, this method has been categorized as the cold vapour technique for mercury and is frequently hyphenated with AAS and AFS. As a result, the purpose of the atom

cell for mercury determination is ultimately to channel the gaseous mercury in front of the excitation source.

2.2.1.3 Wavelength Selection and Detection

Wavelength isolation ultimately depends on the type of excitation source used. With conventional line sources such as HCL, EDL or laser excitation, low dispersion monochromators or non-dispersive systems such as filters are most commonly used. It should be noted that excitation sources should be free from contaminating lines from other elements which contribute to background radiation. Background radiation can however be minimised, by the simple insertion of filter between the excitation source and the detector. Detection is usually by means of a photomultiplier tube.

2.2.2 Vapour Generation of Mercury

For vapour generation to occur, mercury contained within a sample needs to be converted to elemental mercury gas, Hg^0 , i.e. mercury vapour must be generated. Once in the gas phase the elemental mercury can then be delivered to an AFS detector for measurement.

However, before conversion to the elemental state, mercury contained in the sample must first be converted to a readily reducible form. Essentially, all mercury contained within a sample must be converted to the divalent state, once in the divalent state it can then undergo reaction with a reducing agent to produce elemental mercury vapour.

Once in the elemental state, the appreciable vapour pressure of mercury allows it to be rapidly volatilised from solution by agitation, usually with an inert carrier gas such as argon. The liberated mercury is then swept out from the solution and delivered by a carrier gas to an AFS detection system for

measurement. This combination of oxidation and reduction at room temperature to produce a mercury vapour is termed the cold vapour technique.

In order for total mercury measurement, the first requirement is to liberate all mercury compounds from the sample matrix. Liberation of the mercury from the sample is usually termed the digestion or oxidation stage. Mercury contained within a sample must be converted into the divalent, inorganic form, usually by use of the appropriate oxidising agent. When the oxidant is in excess, complete oxidation to mercury (II) species is possible. If no oxidation or reduction is performed on the sample then the proportion of Hg^0 can be calculated. The oxidised mercury can then be reduced to elemental mercury Hg^0 , by the addition of an excess of reducing agent.

2.2.2.1.1 Oxidation – digestion and release of mercury

For natural water samples, several laboratory methods for oxidation/digestion procedures have been reported [55, 56], along with various combustion techniques [57, 58] to decompose organic material prior to obtaining mercury in aqueous solution for final measurement.

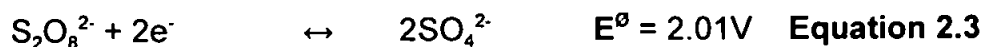
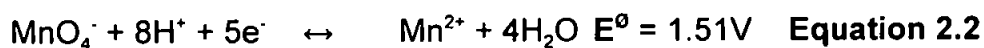
Varieties of combinations of acids such as hydrochloric, sulphuric, nitric and perchloric (HCl , H_2SO_4 , HNO_3 , and HClO_4) and oxidants such as permanganate, persulphate, dichromate, and peroxide (MnO_4^- , $\text{S}_2\text{O}_8^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$ and H_2O_2) have been used for mercury breakdown and oxidation of mercury in environmental samples. Table 2.1 shows the various combinations of oxidants most frequently used in routine environmental laboratory applications.

Table 2.1. Commonly used oxidation chemistries for mercury determinations

H ₂ SO ₄ /HNO ₃	HNO ₃ / H ₂ O ₂	H ₂ SO ₄ /HNO ₃ / HCl
H ₂ SO ₄ /HNO ₃ / HClO ₄	HNO ₃ / HCl	H ₂ SO ₄ / HF
H ₂ SO ₄ /HNO ₃ / KMnO ₄	H ₂ SO ₄ / KMnO ₄	NaOH / KMnO ₄
3HCl/ HNO ₃	HCl / KI / KIO ₃	HCl / KBr / KBrO ₃
HNO ₃ / K ₂ S ₂ O ₈	HCl / NaOCl	CuSO ₄ / K ₂ S ₂ O ₈ / H ₂ SO ₄
H ₂ SO ₄ /HNO ₃ / KMnO ₄ / K ₂ S ₂ O ₈		

The efficiency of these reactions can be predicted by calculation of the electrode potentials. However, standard electrode potentials at 298 K, 1 atm and 1mol l⁻¹ concentrations, only serve as a guide to predicting the various forms of mercury in aqueous solution.

The one drawback with all of these oxidations is that the excess oxidant, - permanganate, bromine or persulphate etc has to be reduced prior to detection, *i.e.* a pre-reductant is required. A common pre-reductant is hydroxylamine hydrochloride, however this too has its drawbacks, as it liberates nitrogen on reduction, which is a quenching gas in atomic fluorescence and suppresses the signal.



For natural water sample analysis, a hot oxidising method based upon a mixture of potassium permanganate and persulphate has traditionally been used, however this combination is frequently unsuitable for low-level mercury determination, due to the high blanks found in the reagents. One favoured method used with aqueous samples is the oxidation using an acid bromate with bromide mixture [59, 60]. Bromine monochloride has been found to be an excellent oxidant and preservative for total mercury in water samples, working

faster and more efficiently on many organomercurials [61, 62]. After oxidation, the solution is then pre-reduced using a solution of hydroxylamine hydrochloride to destroy the excess bromine before complete reduction using an excess of reducing agent.

Both open and closed vessel techniques have been proposed for mercury digestion. Open vessel techniques such as hot-plate based methods are frequently prone to lose of the analyte due to volatilisation at elevated temperatures or by incomplete oxidation of the sample matrix at ambient temperatures. The open vessel method also requires large amounts of glassware and scrupulous cleanliness.

The drawbacks of the open vessel system can be overcome by use of a closed decomposition system at elevated temperatures such as a microwave or an autoclave system. These techniques have been reported to obtain complete oxidation whilst minimising losses of mercury. By using closed vessel methods the preparation of aqueous samples is effective and allows large batches of samples to be prepared rapidly and routinely in the laboratory environment.

2.2.2.1.2 Reduction of divalent mercury

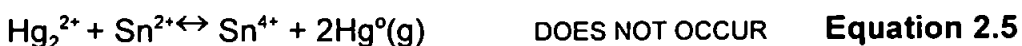
Once all forms of mercury have been converted to the divalent form, Hg^{2+} , the solution is reduced to produce elemental mercury, Hg^0 . Table 2.2 shows a range of reduction regimes available for mercury vapour generation.

The reduction process is most commonly performed by the addition of excess stannous chloride, Sn(II)Cl_2 , either acidified or alkaline, occasionally sodium borohydride is used, however, this liberates hydrogen which is both explosive and quenches the fluorescence signal.

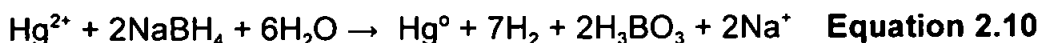
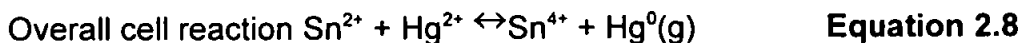
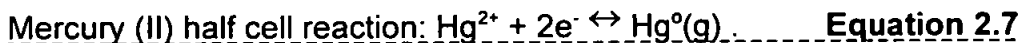
Table 2.2. Reducing solutions for mercury vapour generation

Reductants	Conversion
SnCl ₂ / HCl	Hg ²⁺ → Hg ⁰ ↑
SnCl ₂ / NaOH	Hg ²⁺ → Hg ⁰ ↑
NaBH ₄ / NaOH	Hg ²⁺ → Hg ⁰ ↑
OHNH ₃ Cl / NaOH	Hg ²⁺ → Hg ⁰ ↑
SnCl ₂ / CdCl ₂ / NaOH	Hg ²⁺ → Hg ⁰ ↑
	RHg → Hg ²⁺ → Hg ⁰ ↑
SnCl ₂ / KI / Ascorbic acid	Hg ²⁺ → Hg ⁰ ↑
SnCl ₂ / OHNH ₃ Cl	Hg ²⁺ → Hg ⁰ ↑
NaBH ₄ / CuSO ₄	RHg ⁺ → RHgH ↑
NaBEt ₄	Hg ²⁺ → Et ₂ Hg ↑
	RHg ⁺ → RHgEt ↑

Mercury (I)



Mercury (II)



2.2.2.2 Interferences

Chemical interference caused by chemicals within the matrix are of concern during vapour generation. This type of interference can be reduced by the use of complexing and releasing agents, when these measures are coupled with vapour generation techniques the problem can be reduced significantly [63]. Chemical interferences can be divided into those occurring in the gas phase and those in the liquid phase [63].

2.2.2.2.1 Gas phase interferences

This type of interference consists of quenching of the mercury fluorescence and absorption of the mercury excitation line in the 253.7nm region. Investigations have shown argon to be the best carrier gas for mercury AFS, this is due to its small cross-sectional area for quenching [44]. Replacement of air by argon results in approximately a one hundred-fold decrease in fluorescence signal [47, 48,]. Replacement of argon by nitrogen resulted in an decrease of the fluorescence signal by 4-15 fold. Other gases such as H₂, CO, D₂, CH₄ and CO₂ have also been observed to cause quenching [50]. Mercury atoms excited at the 253.7nm line are de-excited much more rapidly by H₂ than by N₂, consequently tin (II) is a much better reductant than NaBH₄ for AFS mercury determination.

Organic solvents with a high vapour pressure such as benzene, acetone and ethanol have also been observed to cause a decrease in the fluorescence signal [44]. The vapour of unsaturated and aromatic organic compounds which absorb at the 253.7nm region also interfere with the fluorescence signal for mercury.

2.2.2.2.2 Liquid phase interferences

As mercury vapour is produced at room temperature and no thermal assistance is required, the term "cold vapour" is often used for mercury determination. The mercury vaporisation step undergoes almost complete separation from the other constituents within the solution. Depressive interferences can be caused by noble metals such as Au, Pt, Pd and Ag and also by certain transition metals [64]. These types of interference effects are concentration dependant. Certain substances that produce very stable complexes with mercury ions interfere with the reduction process and prevent the

formation of elemental mercury gas. Examples of such interferents include bromide, iodide, cysteine, sulphide, thiosulphates and Se (IV).

2.2.3 Reaction valves

The reduction reaction starts when the two solutions of oxidised sample and reductant are mixed together. In older systems this reaction is performed manually by injection of the reductant into a closed reaction chamber containing the oxidised sample, the resulting gas/liquid solution is then purged of elemental mercury and delivered to an AFS or AAS detector for measurement.

Modern systems use fully automated vapour generators coupled to valve manifolds that deliver and mix the oxidised sample with the reducing agent. A peristaltic pump delivers the solutions to an electronically controlled d.c. switching valve where the reduction reaction commences. The oxidant is mixed with the reductant solution at right angles, sometimes referred to as butt-mixing. Mixing of the solutions at right angles ensures the maximum reaction of the reagents.

The switching valve alternates between delivering either a blank or oxidised sample solution for reaction with a reductant. In this way a steady baseline or equilibrium can be obtained when the valve is in the standby position (blank mode), i.e. mercury vapour entering the detector is from the reagent blank solution and should produce a constant signal. When the switching valve is activated, the blank solution is diverted to waste or recycled, whilst the oxidised sample solution is mixed with the reductant inside the switching valve. Upon activation, any oxidised mercury present in the sample reacts with the reductant and generates mercury vapour. Figure 2.3 shows an internal view of a simple 5-way D.C switching valve configured for both tin (II) chloride and sodium borohydride reductants.

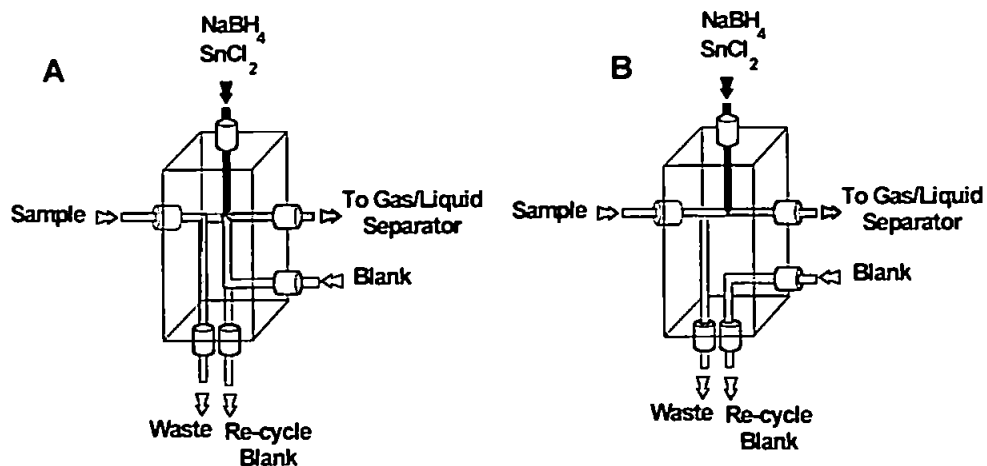


Figure 2.3. Switching valve positioned in A. Standby mode (blank) and B. Sample analysis mode (reduction) [65]

2.2.4 Gas/liquid separators

During the reduction process the majority of reduced mercury is formed instantly inside the switching valve, however some elemental mercury is left remaining in solution and requires agitation to be released into the gas phase. Agitation is normally performed with the use of a gas/liquid separator, as shown in Figure 2.4. The reacting solutions and mercury vapour are pumped out from the switching valve and into the closed reaction chamber. By purging the reaction solution with an inert carrier gas such as argon, almost instantaneous measurement of mercury is possible at the detector.

High purity argon is frequently used as a carrier gas to both sweep the mercury from solution and to deliver it to the detector. Argon is more expensive than alternative carrier gases such as helium and nitrogen, but has the advantage of offering minimal quenching of the fluorescence signal and hence greater sensitivity. The gas liquid separator shown in Figure 2.4 has been specifically designed for use with a continuous flow cold vapour generation process coupled with an argon carrier gas. Argon is used to purge the elemental mercury from the reaction solution and in to the headspace of the gas/liquid separator. As the

system is closed, the gaseous products are contained within the carrier gas and delivered to the AFS detector for measurement.

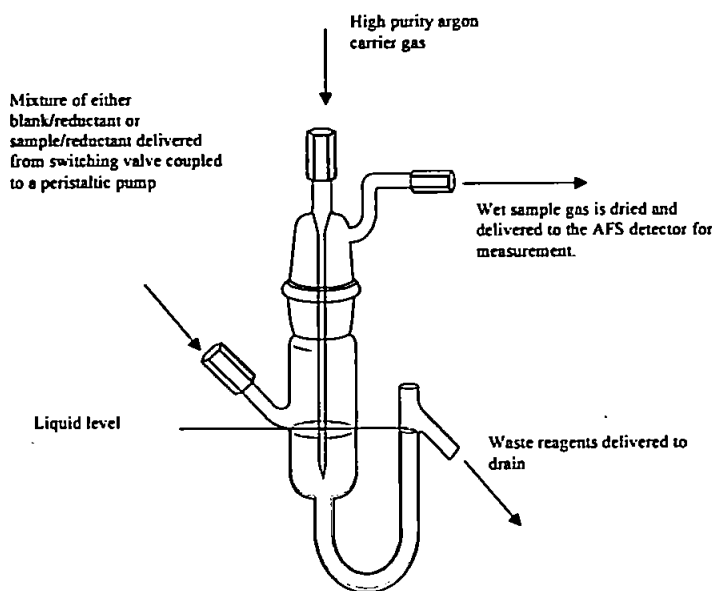


Figure 2.4. Gas/liquid separator for purging elemental Hg from solution [65]

2.2.5 Removal of moisture from sample gas

A common problem often encountered with the cold vapour technique during prolonged periods of operation is that of moisture carry over from the vapour generation stage to the detection stage. Moisture is often present as a fine aerosol composed of a complicated mixture of reagents and the sample matrix. Moisture often forms on the walls of the gas/liquid separator and eventually condenses on the transfer-tube walls and enters the detection system. If excessive moisture is carried over to the detection unit fogging of the optics and atom cell windows will occur, causing severe baseline drift with a corresponding loss of sensitivity.

Usually, moisture is removed with a desiccant such as concentrated sulphuric acid, magnesium perchlorate, anhydrous calcium chloride or activated silica gel. All of these desiccants are effective but they all become rapidly saturated and need to be changed regularly.

The problem of moisture carry over can be eliminated by use of a semi-permeable Nafion membrane dryer tube after Corns *et al.* [65]. This basically consists of two concentric tubes; the outer tube is made from PTFE whilst the inner tube is made from a hygroscopic Nafion membrane. This essentially desolvates the wet gaseous stream continually. As the wet gas from the separator passes through the inner membrane the moisture is removed and transferred to the outer tube. In the mean time a dryer gas flows in the opposite direction to that of the wet gas removing any moisture that has condensed on the outer surface of the membrane. The dried gas is then passed to the detector for measurement.

2.3 MANUAL CV-AFS SYSTEM USED FOR DEVELOPMENT OF AN ON-LINE SYSTEM

2.3.1 Continuous flow vapour generation manifold

A schematic diagram of the PSA continuous flow vapour generator for mercury is shown in Figure 2.5. [66]. In this set-up, a variable speed multi-channel peristaltic pump delivers blank, sample and the reductant solutions. The solutions are pumped to a reaction chamber located inside an electronically controlled D.C. switching valve. When the valve is switched to the sampling position, the reaction mixture is pumped to the gas/liquid separator and the gaseous products purged from solution and passed through a membrane dryer tube. In the mean time, the waste liquid products are continually pumped out through the waste exit of the gas/liquid separator. After removal of the water vapour the dried gas is presented to the detector for measurement.

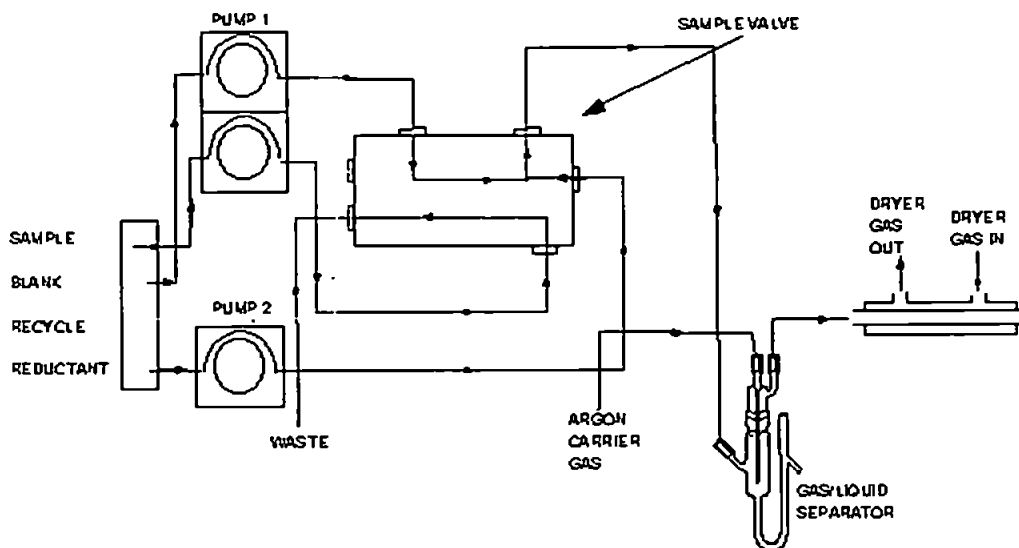


Figure 2.5. Schematic flow of vapour generation manifold (blank position) [66]

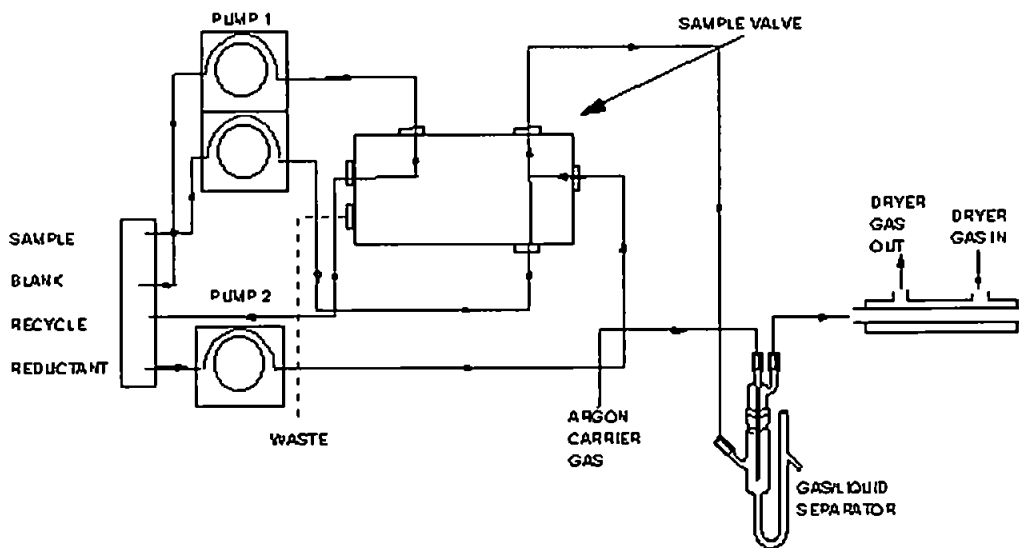


Figure 2.6. Switching valve in sample position [66]

As the solutions are continuously pumped into the gas/liquid separator, an equilibrium is established and continuously monitored by connection to an AFS detector. When the electronic valve is activated a steady state signal is produced as the divalent mercury is reduced by the reductant solution. The duration of the reaction can be controlled and optimised by observing the reaction kinetics indicated by the signal obtained at the AFS detector.

2.3.2 AFS detector

The design of the AFS detector for mercury analysis is relatively simple due to the absence of the thermal atomiser [67, 68]. In most systems a UV mercury vapour lamp is used as the excitation source and the fluorescent light is detected by a PMT that is perpendicular to the excitation source. Figure 2.7 shows the schematic optical arrangement of Stockwell's AFS system [66]. Here, a Teflon chimney is used for introduction of mercury vapour in to the optical path. Around the chimney, a jacket of argon encapsulates the carrier gas so as to focus a plume of gas in front of the collecting lens. A 253.7 nm interference filter is then positioned between the chimney and the PMT to keep stray light away from the detector. An internal view the AFS detector is shown in Figure 2.8

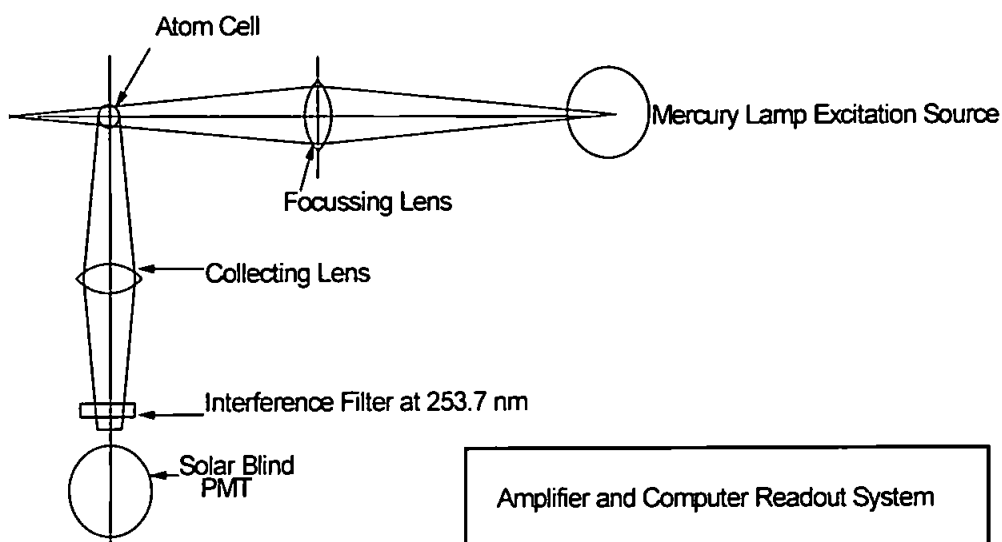


Figure 2.7. Commercially available atomic fluorescence detector

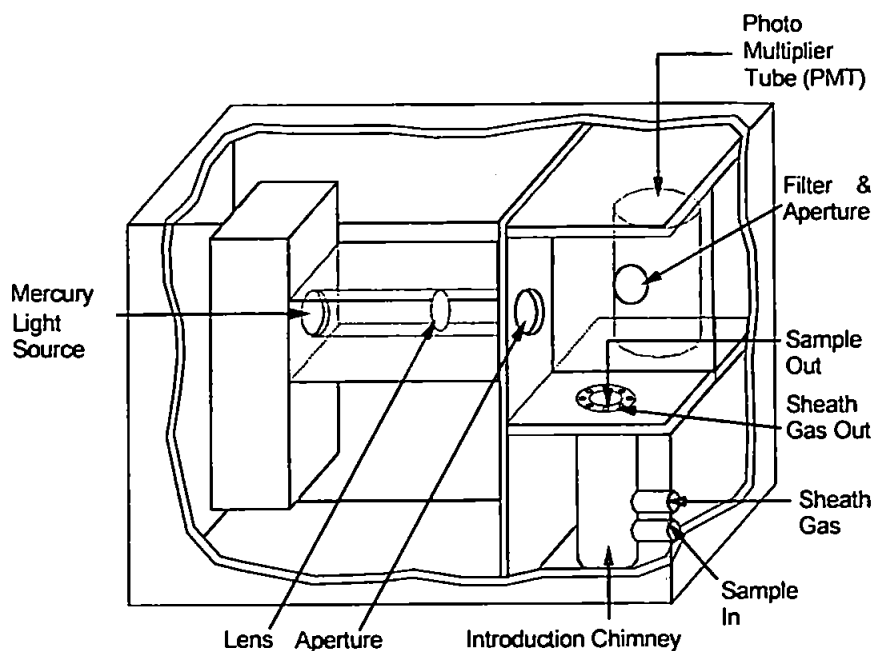


Figure 2.8. Side view of PS Analytical 'Merlin' AFS mercury detector [64]

The AFS signal is usually plotted as a function of peak area against time. A simple vapour generation and AFS detection system designed by Stockwell *et al* [66] was used to obtain the peak profile shown in Figure 2.9.

The Stockwell vapour generation system uses electronic valve timings of:

- Delay time, (10 seconds) - the sample line is flushed through with the blank.
- Rise time (30 secs) - the valve is activated so that the sample and reductant start to mix and an AFS signal is generated.
- Analysis time, (30 secs) - the reaction in the gas liquid separator has reached equilibrium so that the reaction is in steady state; the signal has reached its plateau so that a steady reading can be obtained.
- Memory time, (60 secs) - the valve is closed so that the sample is pumped to waste; and the blank remixed with the reductant so that the signal returns to the original baseline.

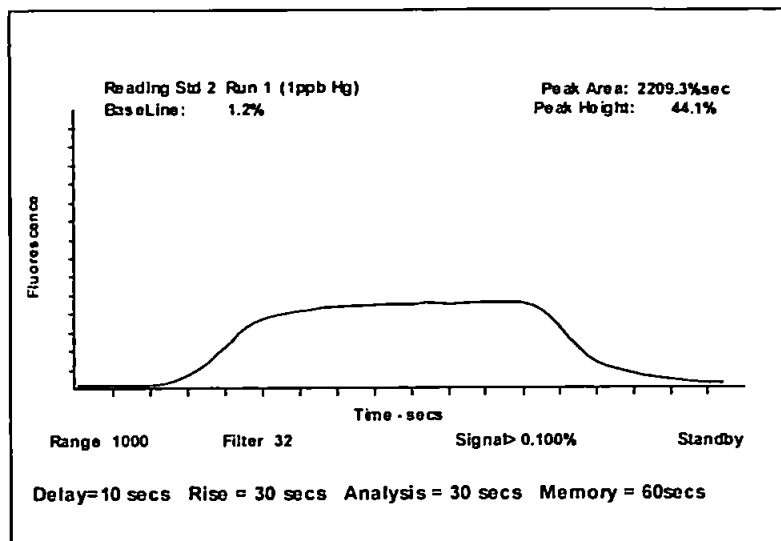


Figure 2.9. Continuous flow vapour generation peak for a 1 ng ml^{-1} Hg standard obtained from a PSA vapour generator coupled to a PSA Merlin AFS detector

The switching valve ensures a steady transfer from the reagent blank to sample and minimises the inherent noise on the generated signal. The peak shape is frequently specific to the type of sample being analysed, in fact the presence of interferents can sometimes be recognised from the peak profile.

Automated continuous flow systems are ideal for laboratory applications where reagent consumption and operator attention are not limited. They provide excellent sensitivity with detection limits in the region of $1\text{-}2 \text{ pg ml}^{-1}$ and linearity up to $10 \text{ }\mu\text{g ml}^{-1}$, the linear range stretching over seven orders of magnitude, sufficient to span most environmental applications.

One fundamental problem with conventional continuous flow systems is that the water sample still needs to be digested prior to analysis, i.e. the rate-determining step in the measurement of mercury is the pre-treatment of the sample. The measurement stage is relatively straightforward, taking generally no more than 3-8 minutes with the apparatus described. The sample pre-treatment stage often takes up to 2 hours before the oxidised mercury is presented to the

vapour generation stage for measurement. The laborious tasks of sample collection, preparation and delivery to the detector lend themselves ideally to an automated, continuous flow vapour generation process. By use of an appropriate manifold a simple continuous flow vapour generation process such as that shown in figures 2.5/6 can be adapted into an automated oxidation, reduction and detection system for continuous mercury monitoring.

2.3.3 Sampling and Reaction Manifolds

Sample preparation is currently being replaced by flow injection analysis (FIA), which is computer compatible and allows automated handling of sample and reagent solutions with a strict control of the reaction conditions. Ruzicka and Hansen of Denmark [69] first described FIA in 1975. FI is a common method for online and laboratory processing of wastewater, soil testing, and other environmental applications where trace level measurements in difficult matrices are required. For example, FIA can dilute by factors up to tens of thousands, and can enrich/preconcentrate by factors of several hundred. It can perform chemistry on an analyte to generate a detectable species and can transfer an analyte from one medium to another, for example from an effluent sample or natural gas sample to a carrier gas such as argon. FIA is also used widely for solvent extraction, matrix modification or matrix elimination.

Flow Injection (FI) analysis systems usually consist of a high quality multi-channel peristaltic pump, an injection valve, a coiled reactor, and a detector such as a photometric flow cell. The reagents are added continuously to a carrier stream near after an injection zone, allowing the sample/reagents to mix. The resulting reaction product forms a concentration gradient corresponding to the concentration of the analyte throughout the entire sample zone length [69]. Figure

2.10 shows the basic components and principles of FIA. The pump is used to propel one or more streams through a detector via narrow bore tubing (0.5 - 0.8 mm ID). The injection valve is used to periodically introduce a small volume (<500 μ l) of sample into the carrier stream. As the sample is carried to the detector, the fluid dynamics of flow through narrow-bore tubing mix the sample and reagent together. The generated species is then measured at the detector as a transient peak. The height and area of the peak is proportional to the concentration, and is used for quantification by comparison with samples of known concentration to produce a calibration curve.

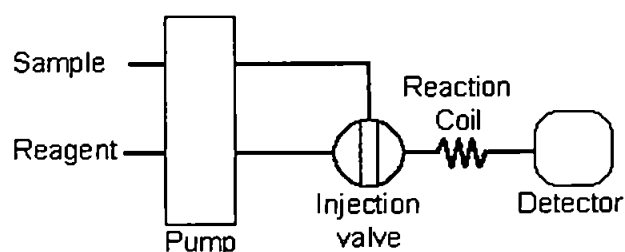


Figure 2.10. Basic components of an FIA manifold

When adapting a manual method to an FIA manifold it is worth considering that manual methods are generally equilibrium based while FIA methods are non-equilibrium based. The most common manifold configurations are often called single-stream, two stream, and three stream manifolds [70]. A single-stream manifold is shown schematically in Figure 2.10. In this set up, a stream containing a reagent is pumped through the system. A volume of sample is injected into the stream, and dispersion causes mixing of the reagent with the sample zone leading to reaction between the analyte and the reagent as the zone passes through the reactor and to the detector.

2.3.3.1 Two-stream FIV manifold

Figure 2.11 shows a two-stream manifold, which can be used in two different ways. The first is with a single stage chemistry, similar to that described for the single-stream application. However, in the two-stream approach, the sample is injected into a reagentless carrier, R1, and the reagent stream R2 is merged with it downstream. This provides a more uniform mixing of the reagent with sample over the length of the sample zone, and often provides better sensitivity and performance compared to the single-stream approach. For this reason, the two-stream manifold is often preferred over the single-stream manifold for simple chemistries.

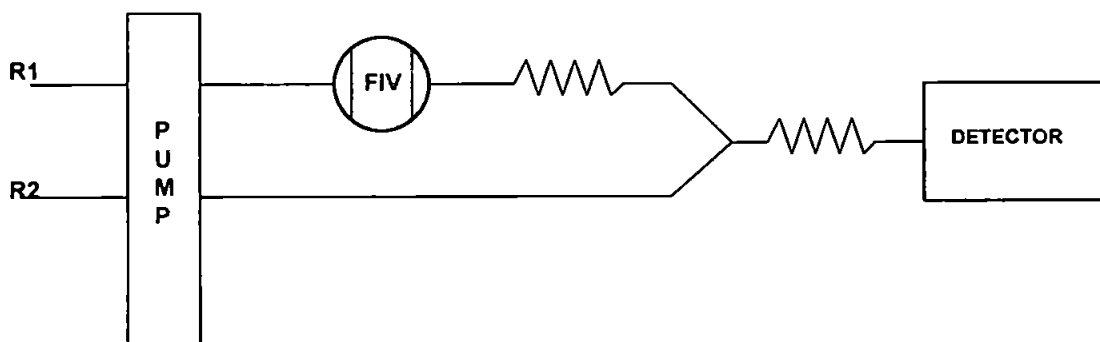


Figure 2.11. Two-stream FIA manifold

The second set-up involves a two stage based chemistry; the sample is injected into the first stream containing reagent R1, the analyte reacts with the reagent R1 to produce an intermediate, on merging with stream R2 downstream, the intermediate reacts with reagent R2, forming the product that is measured by the detector [71].

2.3.3.2 Three-stream FIV manifolds

Three stream manifolds are generally used for two stage or three stage chemistries [71]. When used for two stage chemistries the sample is injected into

a reagentless carrier and merges downstream with the first reagent, further downstream it merges with the second reagent.

For three stage chemistries the sample is injected into a stream containing the first reagent R1. The product of this reaction merges with the second reagent R2 downstream to form a second intermediate. This intermediate then merges with the third reagent R3, downstream to form the final product that is measured at the detector [71].

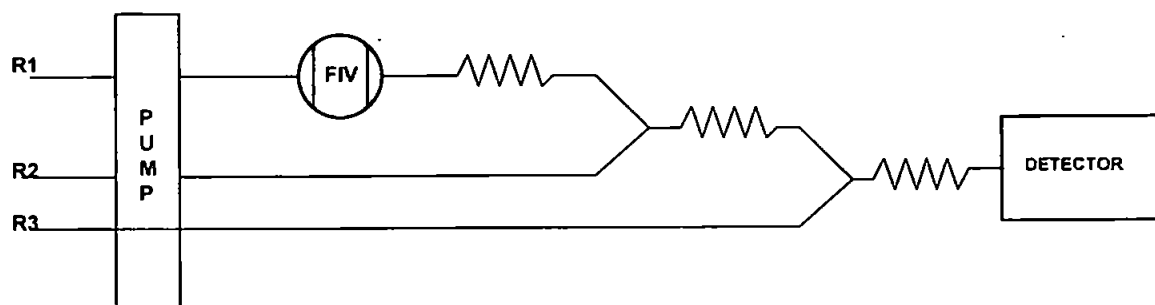


Figure 2.12. Three-stream FIA manifold

2.3.3.3 Simple FIV manifold for mercury determination

The flow injection approach has been utilised by Corns *et al.* [72] to extend the linear calibration range of the continuous flow cold vapour generation range procedure. Figure 2.13 shows a FIV manifold for mercury oxidation, reduction and determination [73]. In this simple manifold the sample/standard is pumped to a six-port flow injection valve where a fixed volume of the sample is introduced to the mixing manifold. At the mixing manifold chemical pre-treatment takes place whereby the sample is mixed with oxidants so as to get all the available mercury into the divalent state Hg^{2+} . Finally the mercury is reduced to the gaseous phase by reduction with tin (II) chloride. The gaseous mercury is then stripped from solution in a gas/liquid separator by a carrier gas and then passed through a Perma Pure membrane dryer. The dried sample gas is then introduced to a

fluorescence detector for determination. The detector returns a transient peak, which is forwarded, to the computer in BCD code.

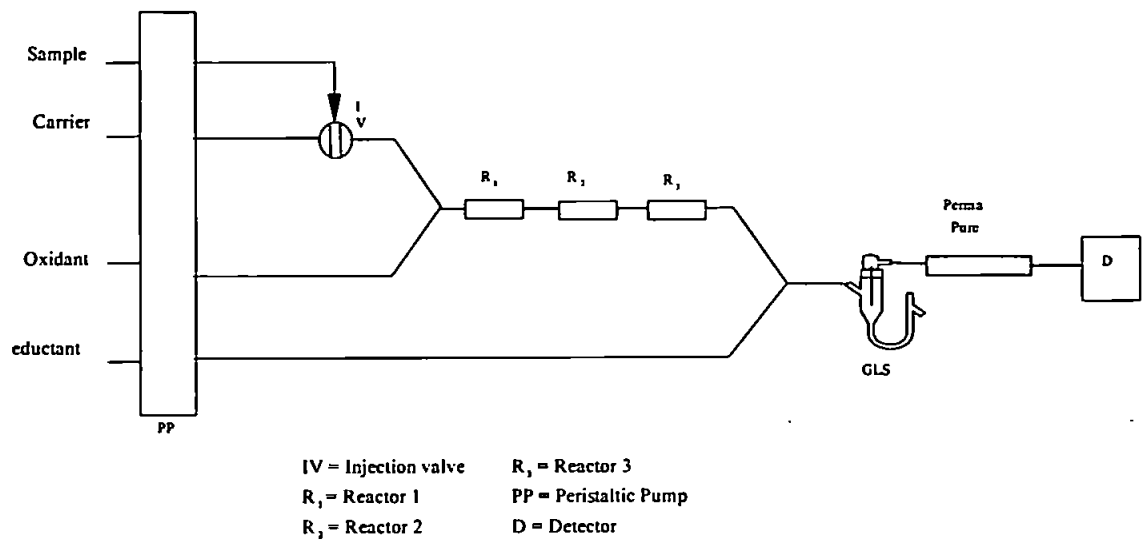


Figure 2.13. FIV manifold for mercury oxidation, reduction and determination

2.4 DEVELOPMENT OF AN ON-LINE FIA MANIFOLD FOR MERCURY DETERMINATION

An on-line system has been specifically designed to determine mercury in liquid samples with full process and data control via an IBM compatible computer. The main components of the system consist of a stream selection valve, a peristaltic pump, a six port switching valve, a gas liquid separator, an atomic fluorescence spectrometer and a computer, the basic features of this configuration are shown in Figure 2.14.

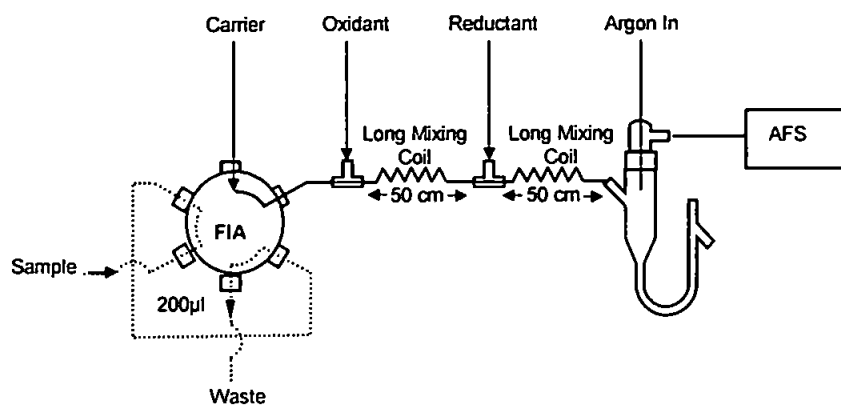


Figure 2.14. Basic features of the on-line mercury manifold

The software allows the operator to fully customise the instrument to suit the application; automatic calibration and analysis protocols can be fully programmed within the software. The unit also employs an error monitoring system which checks for the flow of sample, reagents and gases, as well as for leaks within the system. Should any of the reagents or gases fail to be present an alarm would sound and the instrument shut down.

2.4.1 On-line mercury monitoring system

A schematic diagram of the on-line system is shown in Figure 2.15. With the standard instrument set up the stream selection valve is fitted with four valves, only one of these valves can be selected at any one time. Table 2.3 shows the reagents used in Figure 2.15

Line 5 (Figure 2.15) shows the carrier stream of HCl in the standby mode; here the carrier is flowing into the FI six-port valve through port 1 and exiting from port 2. The carrier then enters the mixing manifold where it is butt-mixed (Port 1 on mixing manifold). The resulting reaction oxidises any mercury present to the divalent Hg^{+2} state. The standard/sample is then dispersed through the reaction coil to ensure oxidation. The length of the mixing coil can be altered accordingly.

The six-port valve is switched pneumatically (activated at 30 psi). When the valve switches the standard/sample is diverted from the waste position by the carrier stream through port 6 on the FIV. The standard/sample loop (typically 300 μl) is then carried as a slug in the acidic carrier stream to the mixing manifold. By using small loop sizes matrix interference and heating effects can be overcome, however the loop size can also be increased for greater sensitivity, thus the balance between dilution and sensitivity.

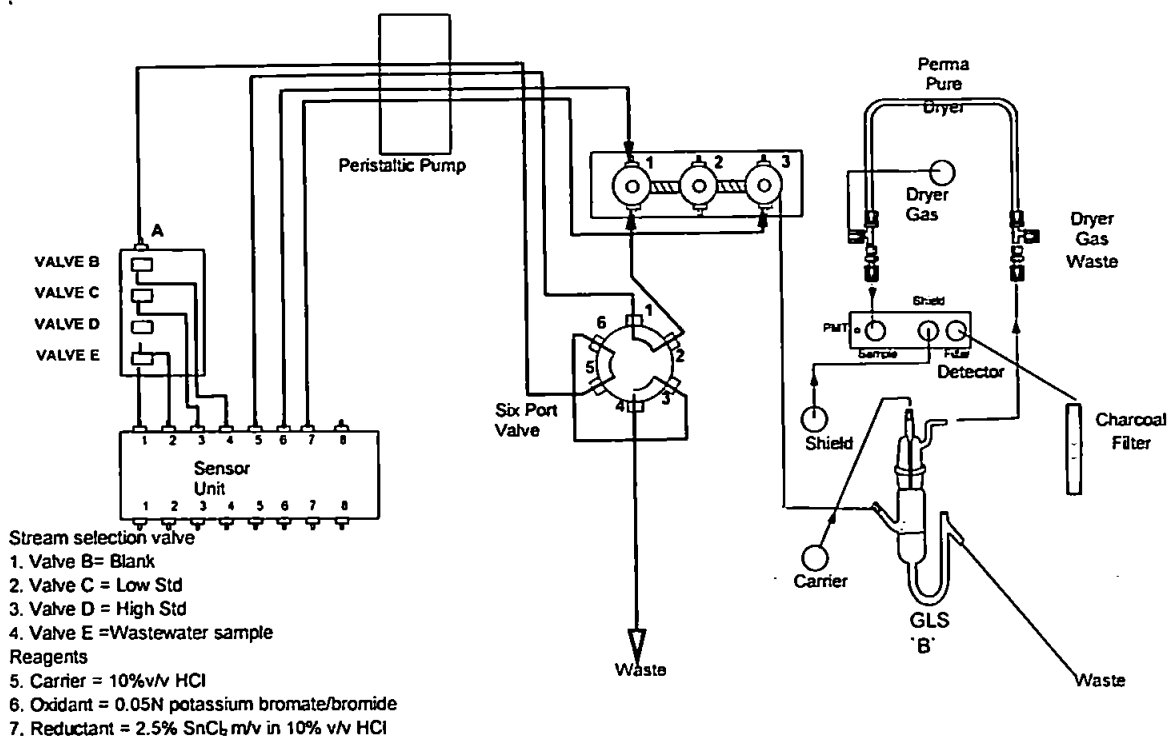


Figure 2.15. Schematic diagram for on-line mercury determination

The oxidised sample is then mixed with an acidic solution of 2% (m/v) tin (II) chloride at port 3 on the mixing manifold. Here the divalent mercury is reduced to mercury Hg⁰ gas through the mixing coil, and then passed to the gas/liquid separator (GLS) for purging. The carrier gas strips the mercury Hg⁰ out from the solution through the Perma Pure membrane dryer tube at a rate of 300 ml min⁻¹. Here the damp sample is continuously de-solvated as it passes through the Nafion membrane. The flow rate of the dryer gas has been simplex optimised at 2.5 l min⁻¹. The dry sample then arrives at the Merlin detector for fluorescence detection. Figure 2.16 shows a typical transient peak obtained by a 10 µg l⁻¹ mercury standard delivered through the on-line manifold.

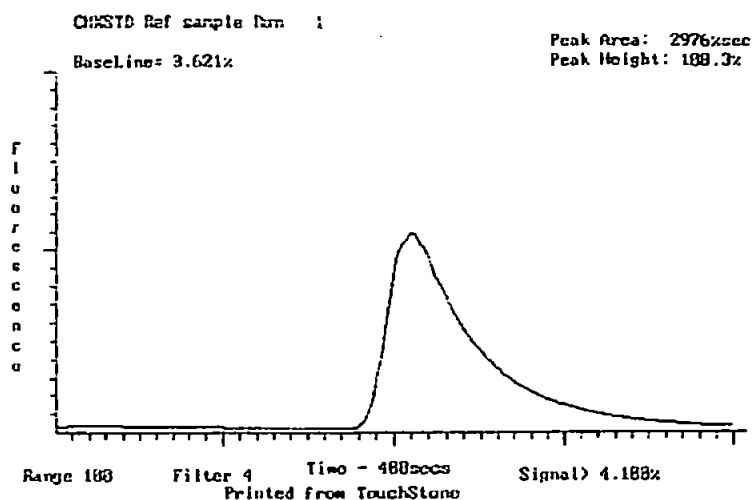


Figure 2.16. Typical peak shape obtained for a 10 mg t^1 Hg standard using the on-line mercury manifold shown in Figure 2.15

Table 2.3. Chemistries and valve timings used in Figure 2.15

Carrier:	10% HCl	0.9 ml min^{-1}	Delay time: 100 s
Oxidant:	0.05N $\text{Br}^-/\text{BrO}_3^-$	0.9 ml min^{-1}	Analysis time: 300 s
Reductant:	2% SnCl_2	0.9 ml min^{-1}	Memory time: 300 s

The on-line manifold has been designed using the basic principles of cold vapour mercury generation. The simple modular based principles of cold vapour mercury vapour generation have been integrated with a flow injection manifold. Laboratory chemistries normally performed off-line have been transferred to a manifold that allows complete automation of each stage of the sequence. The fully automated system is capable of performing all the manually performed sample preparation tasks, to provide a complete continuous mercury monitoring system. A photograph of the on-line wet chemistry manifold is shown in Figure 2.17, whilst Figure 2.18 shows the complete monitoring system.

By altering the configuration of the manifold, different chemistries can be developed allowing the continuous on-line monitoring of mercury in effluent and

process streams. Applications of the manifold are described in the subsequent chapters for incineration wastewater, sulphuric acid and caustic soda. Additionally, many of the principles of the aqueous manifold have been extended further, to produce an on-line manifold for the analysis of mercury in gaseous streams such as natural gas, ambient air and stack gas.

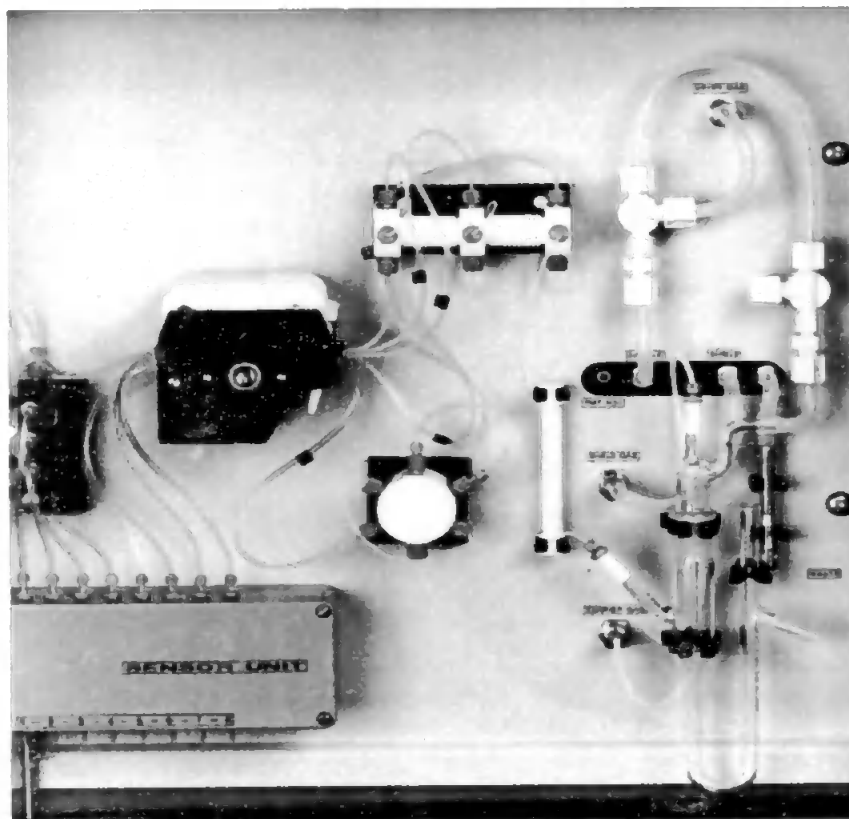


Figure 2.17. Photograph of on-line FIV manifold for continuous mercury monitoring



Figure 2.18. On-line mercury monitoring system

CHAPTER 3

ON-LINE DETERMINATION OF MERCURY IN INCINERATION WASTEWATER

3 ON-LINE DETERMINATION OF MERCURY IN INCINERATION WASTEWATER

3.1 INTRODUCTION

The *Royal Commission on Environmental Pollution's 17th Report* [74] suggests, "where ever possible avoid creating waste, where wastes are unavoidable recycle them if possible. Where wastes can't be recycled...recover energy from them" such that incineration is proving to be the Best Practical Environmental Option (BPEO) for many types of waste. Incineration handles a variety of wastes, which can be broadly classified into the following types:

- Hazardous and non-hazardous chemical waste
- Municipal waste
- Animal carcasses
- Clinical waste
- Sewage sludge.

Incineration is often the most practicable means of dealing with waste generated from the above industries; it also has local and global benefits. In particular, reduced consumption of landfill capacity, the destruction of potentially harmful substances and, where combined with energy production the reduction in the use of fossil fuels. Disadvantages of incineration techniques include the formation of harmful substances that can be released to air and water and which may require special disposal conditions when land-filled [74].

3.1.1 Incineration processes

All incineration techniques are generally comprised of the same steps. Figure 3.1 shows the basic stages of the incineration process.

Each involves:

- Incoming waste reception, storage and handling
- Means of charging the waste to the incinerator
- An incinerator – of which there are many types
 - Possibly a waste heat recovery process
 - Flue gas cleaning plant – of which there are many configurations
 - A stack for final dispersion of the cleaned gases
 - A form of wastewater treatment plant.
 - A means of handling solid residues such as sludges and ash.

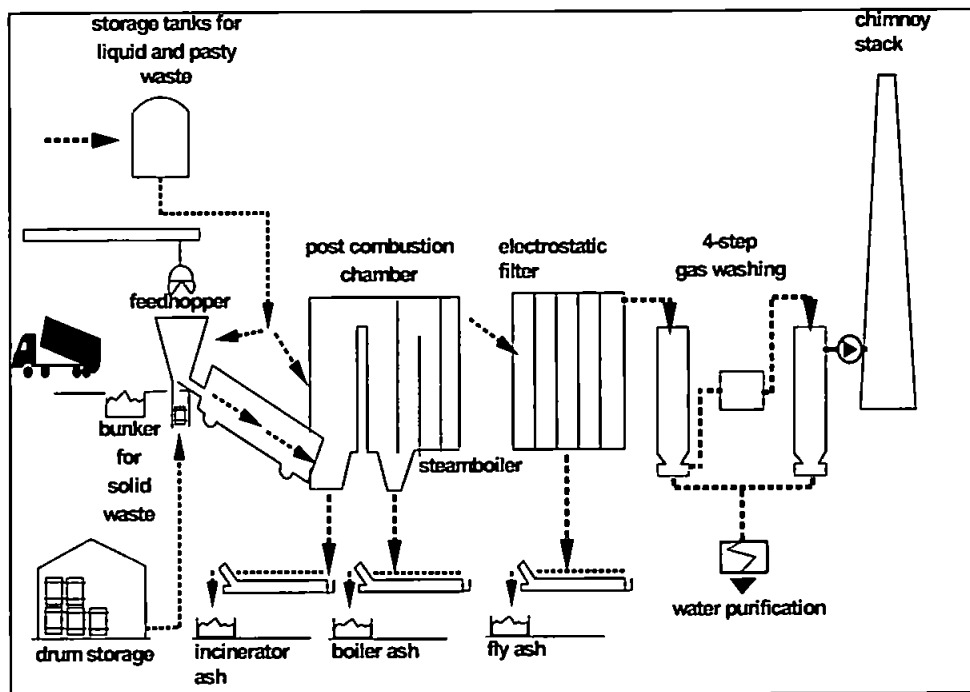


Figure 3.1. Basic stages of the incineration process

3.1.1.1 Waste chemicals

Waste chemicals in bulk or liquid form are handled by pipeline or tanker and are often burned on the site where they arise. Waste chemicals can also be in solid form or in drums containing either liquid or solid. They are often suitable as a fuel for raising heat or generating power, in some cases these types of fuel

can be of less harm to the receiving environment than some of the fossil fuels they displace. Gaseous waste chemicals can cover a wide spectrum from a high calorific value (CV) gas which could be used as a fuel, to VOC's at concentrations of a few mg m⁻³ which can cause odour problems. Typical waste compositions are summarised in Table 3.1

Table 3.1. Typical incoming waste composition [74]

WASTES	TYPICAL CONSTITUENTS - % OF DRY WEIGHT										
	Hydro-carbon content	Oxygen	Chlorine	Sulphur	Fluorine	Nitrogen	Phosphorus	Mercury	Cadmium	Other heavy metals	Iron
Chemical waste	Very variable										
Clinical waste	42-56	21	1-4	0.07-0.17	-	0.07-0.45	-				
Municipal waste	18-36	12-21	0.25-0.8	0.08-0.6	0.01-0.02	0.4-0.8					0.5-2.4
Animal carcasses	7		as salt	in fur	-	in protein	-	-	-	-	-
Sewage sludge	35-57	13-19	0.07-1.0	0.2-1.3	0.03-0.06	3-5		*	*	*	
Drum recovery	Very variable										

*Mercury – typically <1.0mg kg⁻¹ DS (Dry Solids) in non-industrialised areas. Average of 3 mg kg⁻¹ rising to EC land spreading limit of 25 mg kg⁻¹ in industrial areas. However the trend is for the industrial cases to diminish as dentistry becomes the major source for rural and industrial values

3.1.1.1.1 Municipal waste

Municipal waste can vary in composition both seasonally (e.g. garden refuse in the autumn) and geographically (industrial and rural areas) depending on the type of commercial operations within the catchment area.

Municipal waste may be contaminated by a variety of materials that can be a hazard to the environment, e.g. waste paint, oil, pesticides or household cleaners. The waste may contain batteries, plastics, and packaging containing toxic constituents such as lead, cadmium and mercury.

3.1.1.1.2 Clinical waste

Clinical waste includes any waste which consists wholly or partly of human and animal tissue, blood or any other bodily fluids, excretions, drugs or pharmaceutical products, swabs or dressings, syringes, needles or any other sharp instruments. Clinical waste also covers material arising from medical, dental, veterinary and pharmaceutical industries.

3.1.1.1.3 Sewage sludge

Sewage sludge arises from two sources, either of which first requires dewatering. The first is primary sludge, which has a solids content of around 5% and consists of both organic and inorganic substances. The second arises from the settlement of solids produced during the biological treatment processes, i.e. surplus activated and humus sludges or secondary sludges.

3.1.1.1.4 Drums

Drums containing residual chemical wastes, which are usually made of steel and are around 210 litres in capacity. The drums are usually used for storing solids, liquids, powders, waxes and greases etc. In preference drums are washed rather than burned, as it is much cheaper. However, in many cases drums can not be cleaned adequately by this method and incineration is the only method of cleaning.

3.1.1.1.5 Animal carcasses

Animal carcasses (which include remains) come typically from domestic pets brought in by individuals, animals from veterinary practises and currently contaminated livestock such as BSE bovine stock.

3.1.1.2 Flue gas cleaning

In incineration processes scrubbers are used for:

- Heavy metal precipitation;
- Acid gas scrubbing;
- Residual particulate removal;
- To a lesser extent VOC removal, some dioxin and NO_x removal.

Wet scrubbing systems are not normally used for simple dust removal, as they are less efficient in capturing sub-micrometer particles. A further disadvantage of gas scrubbers is that they give rise to a liquid effluent requiring extensive treatment for the removal of contaminants and may require reheating of the stack gases prior to discharge. Normally scrubbers are located downstream of particulate arrestment in order to give more flexibility to the type of scrubber and to ease the problems of scrubber liquor treatment.

An example of a multi-stage scrubbing sequence that covers most types of incineration waste would be:

Stage 1 - a water scrubber into which HCl and HF will readily dissolve to produce an acidic liquor whose pH can be maintained to dissolve heavy metals out of the gas stream (typically pH 2). A single stage water scrubber can remove 99% of HCl and 90% of HF. Subsequent changes of pH can then be used to precipitate the metals from the liquor. The advantage of this process is that it separates out the pollutants most likely to cause landfill problems (*i.e.* attract high landfill charges) into a relatively small volume that can be readily stabilised if required.

Stage 2 - an alkaline scrubber for the removal of SO_x and any remaining HF and HCl. A single stage alkaline scrubber can remove up to 80%+ of SO₂.

Stages 3 - using sodium sulphite to polish out the remaining SO_x.

3.1.1.2.1 Wet scrubbing of heavy metals

Mercury arises in the sewerage system from a variety of sources. In the absence of control of releases at source (especially dentistry) the main protection for the receiving waters is that the sewage treatment works absorbs the mercury into either primary or secondary sludges. When the sludge is incinerated the mercury will be abated by the scrubber, and passed, with the liquor back to the sewage treatment works (STW).

Depending on the capture rate of mercury in the STW (which can be as low as 45%) and the capture rate in the scrubber, it is possible that mercury, which had been originally caught in the sewage sludge, will subsequently be re-released to controlled water. The incineration process would therefore be negating the effect of the sewage treatment works.

3.1.1.2.2 Treatment of scrubber liquors

Whether scrubber liquors are to be re-used in the process or discharged, there is normally a need to separate out the pollutants that have been captured. If this is not done, and the water is re-injected into the incinerator the indestructible matter will simply build up in the system, as it is repeatedly recycled. When discharges are to the sewerage system it should not be forgotten that releases to sewer are ultimately releases to controlled waters. The efficiency and capacity of the sewage treatment works should therefore be taken into account when discharging such an effluent. Attention is drawn to the toxic effects of heavy metals on the sewage treatment works as outlined in Chapter 1.

Scrubber liquor treatment typically comprises of neutralisation, flocculation, coagulation and settling. Settling is much more effective when equipment such as lamella plates are used. Filtration may also be necessary for removal of fine

particulate matter. For mercury, cadmium and the other heavy metals, precipitating the metals as either hydroxides or sulphides followed by the appropriate solids separation can remove up to 90% or more of the heavy metals but probably less than 70% of the cadmium and nickel [33].

The use of specialist complexing agents such as TMT (trimercapto-s-triazine tri sodium salt) can settle similar percentages and have the added advantage of forming stronger bonds with the metals and therefore result in a lower leaching capability, they are however significantly more expensive than hydroxide or sulphide precipitation agents [33]. The settled solids can then be dewatered by filter, centrifuge or evaporation to make them easier to handle and subsequently stabilise prior to landfilling.

Organics, including dioxins, furans, PAH's and mercury should be measured in the treated effluent and if present, are best removed by passing the effluent over activated carbon beds. The spent activated carbon can then be returned to the incinerator for destruction. Alternatively, if the heavy metals have been removed then the treated water itself can be returned to the incinerator, if salt concentration does not prevent it. The final effluent liquor will still contain salts, in particular chlorides and sulphates. If the receiving water can cope with this level of salinity the treated water can be discharged. If not, then ion exchange resins, micro-filtration, evaporation and reverse osmosis techniques are normally used. If treated to this standard, the water would be of too good a quality for discharge and would normally be recycled on-site.

3.1.1.3 Source control for mercury capture

Heavy metals are present in most wastes either as the metal or metal compound. For the most part the plant operator has no control over their presence. However in the case of mercury there is some scope for control.

From Figure 3.2 it can be seen that most metals have returned to the solid phase at around 300°C, with mercury being the exception. (Tin has a lower melting point but its boiling point is such that it remains in the grate ash). For these metals the primary control is particulate capture.. It should be noted that some metals may be present as a fine fume whilst others will adhere to fine particulate matter.

While wet scrubbing is not effective for particulate removal, at low pH's heavy metals can be dissolved in the liquor. While this results in a waste stream which needs to be treated, it does have the advantage that the metals will be present as soluble salts which are therefore not readily leachable, it also separates the majority of metals from the fly ash residues, thereby simplifying disposal. Since metals are bound more securely to grate ash than fly ash it is preferable that as much as possible remains there [74]. Thus, furnaces systems with the lowest peak temperatures consistent with effective combustion are preferable for mercury capture.

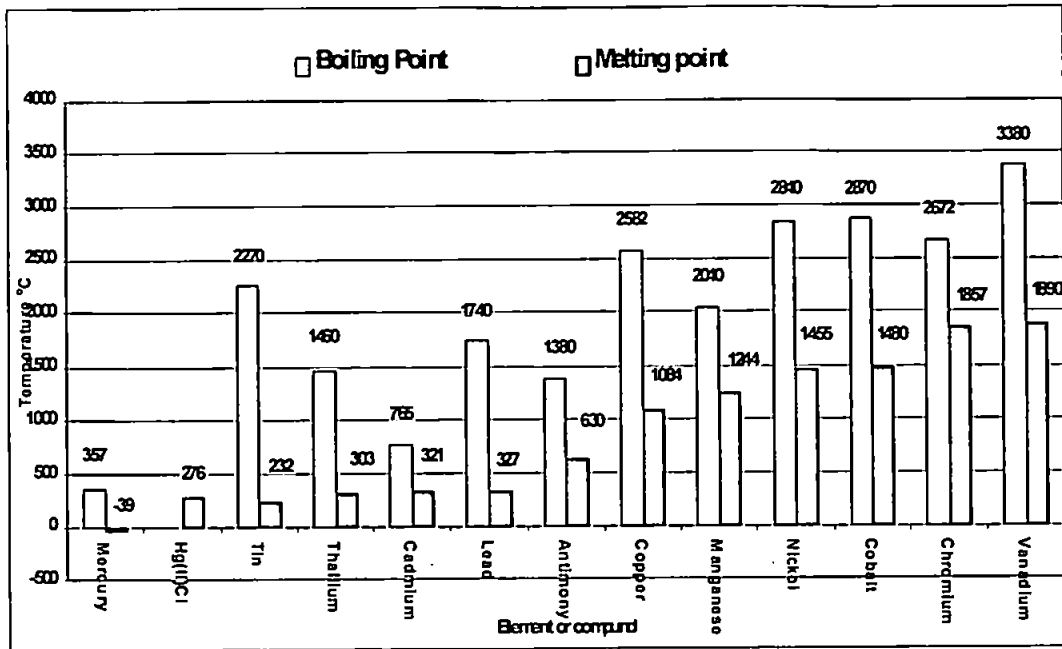


Figure 3.2. Boiling and melting points of heavy metals and their salts

3.1.1.3.1 Clinical waste incineration (CWI)

In CWI mercury arises from thermometers and dentistry work in particular. Incineration operators normally maintain pressure on their customers to use non-mercury alternatives. There is also some evidence that mercury collected from filters at dental units (to avoid releases to sewer) end up for incineration instead of being sent for recovery – this is a likely source of intermittent large mercury releases.

3.1.1.3.2 Municipal waste incineration (MWI)

In MWI the main source of mercury was batteries, however over the last few years the problem has been all but eliminated. Almost 90-95% of the UK battery market now has zero mercury and cadmium content. Of the remainder, such as NHS hearing aid batteries, collection schemes are now in operation for their proper disposal. However, mercury may still arise from miscellaneous sources [84].

3.1.1.3.3 Sewage sludge incineration (SSI)

In SSI a significant source of mercury is from dental premises. As water companies operate most SSI units they usually apply pressure on dental practices to fit mercury collection filters before their effluents are discharged to the sewerage system for treatment.

3.1.1.3.4 Minimising volatilisation

Depending on their boiling points metals will either be found in the grate ash or be volatilised into the flu gas where they will later condense as the gas cools. Figure 3.2 shows boiling (volatilisation) and melting (condensation) temperatures for common heavy metals and their salts often found in incineration wastes. Metal partitioning is also affected by other factors such as the presence of sulphates, chlorides and whether there are appropriate condensation nuclei present (usually inert particulates) onto which metals can condense and agglomerate.

Mercury and most of its salts do not solidify at normal flu gas temperatures. Its natural state is liquid with some of the material existing as a vapour. At 220°C, 8% of the metal and its halides will be in the vapour phase (Hg^0), at 180°C (1.4%) and at 120°C (0.13%). Reduction in temperature may not, however be sufficient as a form of removal. Water-only scrubbing at low temperatures (10-20°C) has shown only about 50% capture of mercury vapour. Capture by scrubber liquors can be improved by conversion to soluble mercury (II) chloride, this is achieved by scrubbing with a strong acid (pH 1-3) or high chloride liquor (80-95% removal), or with sodium hypochlorite solution (90-95% removal) [74]. This can then be precipitated from the liquor as an insoluble salt or complex. This has the advantage of stabilising the mercury in the residue. Alternatively, reasonably

high capture rates can be achieved when adequate condensation nuclei are present. This can be provided by a lime injection system coupled to a filtering process. If sodium sulphide is added to the lime feed, the effects are enhanced as the formation of mercuric sulphide is between 87-98%. The insoluble sulphide can then be readily collected via a bag or electrostatic filter. Similarly the injection of activated carbon with lime should give removal rates greater than 90%, although the stability of the waste is less certain.

3.1.2 Monitoring requirements for mercury in incineration effluents

EC legislation currently requires that waste incineration plants should monitor their discharge effluents to receiving watercourses daily for mercury content [75]. This is normally performed manually, whereby a sample is collected from the exit of the wastewater treatment process and taken back to the laboratory for analysis. The collection of a representative sample, its delivery to the laboratory and its subsequent preparation and determination can take up to several hours before the mercury concentration is known. There is therefore potential situations where unnoticed breaches of discharge consent take place in-between analysis intervals, in such cases large volumes of contaminated effluent may have already entered the receiving water system and then efforts to minimise or contain the pollution incident are necessary. Thus, many environmental protection agencies such as Her Majesty's Inspectorate of Pollution (HMIP) and the Environment Agency (EA) have expressed a preference for continuous monitoring programmes, i.e. on-line mercury monitoring systems [74].

At present there few commercially available on-line mercury-monitoring systems capable of measuring mercury at the levels required for effluent monitoring. The few systems that have been developed have been constructed

in-house and although effective for short periods of time are generally unreliable, leading to a lack of confidence by the operator; who must subsequently resort to manual sampling and analysis.

Thus, there is a clear requirement for the development of an on-line effluent monitoring system for mercury. The remainder of this chapter covers the development of such an instrument based on the manifold described in Chapter 2. Evaluation of various laboratory procedures suitable for the determination of mercury in incineration wastewaters is described. The translation of the optimum chemistry to an on-line manifold is also presented. Results from short-term laboratory trials through to successful long-term on-site trials with a European waste incineration company are presented.

3.2 OFF-LINE DETERMINATION OF MERCURY IN INCINERATION WASTEWATER

3.2.1 Introduction

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

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

The effluent sample is analysed using the EPA 7470 method for mercury in industrial wastewaters [76]. This involves a two-hour digestion stage on a hot-plate using a mixture of KMnO_4 , H_2SO_4 , and $\text{K}_2\text{S}_2\text{O}_8$ before being analysed using conventional cold-vapour AAS detection. The whole process can take as long as 5 hours before the mercury concentration in the effluent is known. In-between analysis intervals, plant maintenance, wastewater treatment failures and variations in incoming waste composition are all factors which can lead to

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

3.2.2 Method Development

Before any on-line analysis could be performed on the effluent sample it was first necessary to compare and contrast the various available laboratory chemistries. There are a range of laboratory chemistries that can be used for mercury determinations, these have been discussed in detail in Chapter 2.

Ideally the on-line manifold should replicate the analysis procedure used within the companies' own laboratory. However, the company's samples digestion procedure involved a two-hour heating stage, which was clearly unfavourable for an on-line system, designed for rapid response. Thus, a procedure which replicates the off-line technique or which ultimately produces the same result was required in order for rapid continuous monitoring. Several established sample preparation techniques could potentially be used with the on-line manifold. Each of these was evaluated for their performance on a laboratory based AFS system.

3.2.3 Experimental

3.2.3.1 Reagent preparation

The sample was collected from the effluent outfall in a 5.0 litre HDPE sample bottle (Azlon, Merck, Pool, UK). The bottle was rinsed three times with the sample prior to collection. The sample was then refrigerated at 4°C until required for analysis.

All solutions were prepared from ultra-pure distilled deionised water (17 M Ω) (Elga Option 3, High Wycombe, UK). All glassware was made of borosilicate (Volac Class A, Merck) and pre-cleaned in 50% v/v HNO₃ acid (AnalaR[®], Merck).

Calibration standards were made by the appropriate dilution of a 1000 mg l⁻¹ mercury stock solution (SpectrosoL[®], Merck) to produce a working stock of 100 µg l⁻¹. Standards were prepared in the same matrix as the sample, *i.e.* 10% v/v HNO₃ acid (AristaR[®], Merck). The reductant was 2% m/v SnCl₂ (AR, Aldrich, Gillingham, UK) in 10% v/v HCl (AristaR[®], Merck). All reagent transfers were performed using a Gilson Pipetteman P5000 (Anachem, Luton, UK).

3.2.3.2 Method 1 – no sample pre-treatment

Before any total mercury determinations were performed, the sample was first evaluated for its readily reducible mercury concentration (Hg²⁺ & Hg⁰). This is done simply by acidifying an aliquot of the sample and then analysing directly using only against acidic tin (II) chloride as a reductant. Tin (II) chloride's reduction potential is only capable of reducing Hg²⁺ species whilst Hg⁰ does not require reduction; so the value obtained using this method was not a total mercury result; as it took no account of any mercury (I) or organomercury compounds which may have been present in the sample.

The sample was first brought to ambient temperature after refrigeration and left in the laboratory for ~3 hours to warm up. The sample was shaken for approximately 1 minute to re-suspend the settled particulate matter. Five or 10 ml aliquots of the shaken sample were then immediately transferred to 100 ml volumetric flasks by pipette. Two aliquots of the sample was spiked with a known quantity of mercury from a 100 µg l⁻¹ working stock solution and 10 ml of concentrated HNO₃ acid was then added to each flask along with approximately 30 ml of DDW. After standing for 10 minutes the solutions were made up to 100 ml by further addition of DDW and analysed immediately. Standards were prepared in the same matrix as the sample along with a reagent blank.

3.2.3.3 Method 2 - EPA 7470 method

The customer's procedure was based on the EPA 7470 method for mercury in industrial wastewaters [76]. This method is designed to give a total mercury concentration, i.e. it is strong enough to oxidise mercury (I) and organomercury compounds using a mixture of strong acids and oxidants to break down the sample matrix. The customer utilised this method due to the type of instrumentation used, namely an automated sample digestion system with subsequent CVAAS detection, (Leeman Labs® PS 200 II automated mercury analyser). Although this system was fully automated the same procedure was replicated manually for comparison with the other sample pre-treatment techniques in order to assess which would be the most effective for on-line translation.

The sample was shaken for approximately 1 minute to re-suspend the settled particulate matter then, 50 ml aliquots of the shaken sample were immediately transferred to acid cleaned 100 ml digestion flasks. Two aliquots of the sample were again spiked with a known quantity of mercury from the 100 µg l⁻¹ working stock solution. An aliquot (1.25 ml) of concentrated HNO₃ acid was added to the sample flask followed by 2.5 ml of H₂SO₄ (AristaR®, Merck), 12.5 ml of 0.5% m/v KMnO₄ in DDW (Spectrosol® low in mercury, Merck) and 4.0ml of 5% m/v K₂S₂O₈ (AristaR®, Merck) in DDW.

The resulting solution was then mixed thoroughly and heated in an aluminium digestion block (BD 26, Lachat Instruments, Milwaukee, USA) at 95°C for two hours. After heating, the digested solution was left to cool for approximately 20 minutes before being made up to the mark with DDW in the digestion flask. Mercury standards were prepared in the same manner as the

samples along with a reagent blank for matrix matching. Prior to analysis each sample/standard was de-colourised by adding 60 μ l of 12% NH₂OHHCl (AristaR[®], Merck) to pre-reduce the excess oxidant. The samples were then analysed immediately with 2% SnCl₂ as the reductant.

3.2.3.4 Method 3 - acid permanganate method

Another commonly used pre-treatment technique is the use of acidified potassium permanganate [77]. This is also capable of complete conversion of all mercury forms but is not as aggressive as the EPA method. After digestion the oxidised mercury can then be reduced using conventional stannous chloride.

The wastewater sample was again brought to ambient temperature and re-suspended. Aliquots (5 or 10 ml) of the shaken sample were immediately transferred to acid cleaned 100 ml volumetric flasks and 5.0 ml of 0.5% m/v KMnO₄ solution in 5% v/v HCl was then added to each flask and thoroughly mixed. Two aliquots of the sample were spiked from the 100 μ g l⁻¹ Hg working stock solution. One batch of solutions were heated at 60°C in the digestion block for 30 minutes while the other batch was left for 30 minutes at room temperature before being made up to mark in DDW. Prior to analysis the samples and standards were decolourised by adding 60 μ l of 12% NH₂OHHCl. Standards were prepared in the same matrix as the sample along with a reagent blank for matrix matching.

3.2.3.5 Method 4 - bromination method

Another sample preparation procedure that could potentially be utilised used on-line is the acid bromate-bromide technique for wastewaters [78].

The wastewater sample was again brought to ambient temperature and particulate matter re-suspended. Aliquots (5 or 10 ml) of the shaken sample were

then immediately transferred to each 100 ml volumetric flask. Two aliquots of the sample were again spiked from the 100 $\mu\text{g l}^{-1}$ Hg working stock solution and 5.0 ml of concentrated HCl was then added to each flask followed by 2.0 ml of 0.1M $\text{Br}^-/\text{BrO}_3^-$ solution (ConVoL[®], Merck). One batch of samples was heated in a water bath at 60°C for 40 minutes and the second batch left at room temperature for approximately 40 minutes. After this time the samples/standards were made up to the mark with DDW and decolourised with 50 μl of 12% hydroxylammonium chloride prior to analysis. Standards were prepared in the same matrix as the sample along with a reagent blank for matrix matching.

3.2.3.6 Method 5 - acid dichromate method [79]

The wastewater sample was again brought to ambient temperature and particulate matter re-suspended. Aliquots (5 or 10.0 ml) of the shaken sample were then transferred to 100 ml volumetric flasks. Two aliquots of the sample were again spiked from the 100 $\mu\text{g l}^{-1}$ Hg working stock solution and 30 ml of concentrated HCl was then added to each sample followed by 10 ml of 0.05 %m/v $\text{K}_2\text{Cr}_2\text{O}_7$ (AnalaR[®], Merck). The samples were then left standing at room temperature for approximately 1 hour before being analysed with a reductant of 2% m/v tin (II) chloride in 10 % v/v HCl. Standards were prepared in the same matrix as the sample along with a reagent blank for matrix matching.

3.2.3.7 Instrumentation

All determinations were performed using a continuous flow vapour generator (PS Analytical. 10.004, P.S. Analytical Ltd, Orpington, Kent, UK) coupled to a mercury atomic fluorescence detector (P.S. Analytical. 10.023 Merlin[®]) – see Chapter 2 for more details. Instrument control and data capture

was fully automated and performed by P.S. Analytical Avalon® for Windows® software.

3.2.3.7.1 Instrumental conditions

AFS Detector settings

Gain = 100.

Fine Gain = 1-9.0 depending upon method

Filter (S/N damping) = 32

Vapour generation settings

Delay = 10 sec. Rise = 30 sec. Measure = 30 sec. Memory = 60 sec

Carrier gas = Argon 300 ml min⁻¹

Sheath gas = Argon 300 ml min⁻¹.

Dryer gas = Air 2.5 l min⁻¹.

Sample/blank flow rate = 8.0 ml min⁻¹

Reductant flow rate = 4.0 ml min⁻¹

3.2.4 Results and Discussion

Results for the various sample pre-treatment techniques are shown in Table 3.2.

Table 3.2. Comparison of Oxidation methods

Method	Customers value ng ml ⁻¹	5% Dilution ng ml ⁻¹	10% Dilution ng ml ⁻¹	1 ng ml ⁻¹ Spike Recovery	2 ng ml ⁻¹ Spike Recovery
No pre-treatment	-	4.8 ± 0.1	4.4 ± 0.38	95%	98%
EPA 7470 Method	17.5	11.3 ± 0.1	12.1 ± 0.2	75%	76%
Acid Permanganate	-	16.3 ± 0.1	15.9 ± 0.2	101%	96%
Acid Permanganate (heated)	-	16.5 ± 0.2	16.1 ± 0.2	97%	98%
Bromination Method	-	17.9 ± 0.1	17.5 ± 0.1	98%	99%
Bromination Method (heated)	-	18.1 ± 0.1	17.7 ± 0.3	99%	100%
Acid Dichromate	-	15.1 ± 0.3	14.1 ± 0.2	89%	86%

All measurements were performed in triplicate (n=3), results reported are based on the mean of two aliquots of the sample for each technique.

Each sample was analysed at both 5 and 10% dilution factors in order to establish for matrix and dilution effects. Standard additions of 1 and 2 ng ml⁻¹ were performed on each 10% diluted sample. The results reported in Table 3.2 are the mean of two aliquots of the sample.

The incineration company retained a portion of the sample for measurement. The company's laboratory found the concentration of mercury in the sample to be 17.5 ng ml^{-1} using the EPA 7470 Method on their CVAAS system. This value has been used as the figure of merit to compare all other results against.

The mean value for the 5 and 10% diluted sample with no pre-treatment was $4.6 \text{ ng ml}^{-1} \pm 0.3$, with a mean spike recovery of 97%. The company would not normally use this technique as it is not a total mercury result. However this value is interesting as it gives an indication as to the amount of readily available reducible Hg^{2+} and Hg^0 in the sample.

The mean value for both dilution factors using the EPA method was $11.7 \pm 0.6 \text{ ng ml}^{-1}$ with a mean spike recovery of 76% compared to the company value. Although this method was identical to that performed by the incineration companies own laboratories the result obtained here was somewhat lower than the expected value. Upon acidifying the sample with concentrated sulphuric acid a white precipitate immediately formed which remained throughout the heating stage of the digestion. It was later found that the sample had a calcium content of 2% which was due to the addition $\text{Ca}(\text{OH})_2$ during the pH correction stage of treatment. This white precipitate formed upon addition of sulphuric acid to the sample was later confirmed to be CaSO_4 . The low result obtained in relation to the customers result could have been due to the absorption of mercury onto the precipitate material, which was not re-released into solution despite the aggressiveness of the digestion procedure (2 hours at 95°C). This could also be confirmed by the spike recoveries. Recoveries in the region of 75% were obtained when the sample was spiked with divalent mercury (II) nitrate suggesting

that mercury in the sample was being complexed by the sample matrix. Discussions with the customer at a later date revealed that they were aware of the CaSO_4 formation and that to avoid the precipitate they omitted the addition of H_2SO_4 .

The next procedure evaluated was the acid permanganate method. Although this method was probably the simplest to perform it gave very encouraging results, the mean value for both dilution factors was $16.1 \pm 0.3 \text{ ng ml}^{-1}$ in relation to the customers value of 17.5 ng ml^{-1} . Spike recoveries were also good with a mean spike recovery of 99% for the room temperature digestion. Very little difference was observed between heating and performing the digestion at room temperature, with recoveries of 99% and 98% respectively. The mean result for this method was $16.2 \pm 0.3 \text{ ng ml}^{-1}$ which was 93% of the expected value (17.5 ng ml^{-1}).

The bromination technique gave an overall mean result of $17.7 \pm 0.3 \text{ ng ml}^{-1}$, which was in excellent agreement with the expected value of 17.5 ng ml^{-1} (101% of expected value). The overall mean spike recovery for both bromination methods was 99%. Once again there was very little difference between the heated and room temperature digestions with mean values of 17.7 & 17.8 ng ml^{-1} respectively.

The final method evaluated was the acid dichromate procedure. The overall mean value for this technique was $14.6 \pm 0.7 \text{ ng ml}^{-1}$ which was 83% of the expected value. Overall spike recoveries for this method were 83%. If the samples were heated the recoveries may have improved slightly. The results were comparable to the acid permanganate method but the spike recoveries were slightly lower, suggesting that some of the available mercury in the sample was

still being complexed to the matrix, i.e. this oxidation stage was not quite as effective in releasing all the available mercury from the sample as either the acid permanganate or bromination methods.

3.2.5. Conclusions

When the results of the untreated sample (no pre-treatment stage) are compared against the other values in Table 3.2 the effects of oxidising the sample are clearly evident. If the customer's value of 17.5 ng ml^{-1} is used for comparison then this would suggest that just over 25% of the total mercury in the sample was present as readily reducible mercury; or that 75% of the mercury was likely to be present as mercury (I) and organomercury complexes bound to TMT, the precipitating agent. Hence the sample clearly needed oxidising in order to produce a total mercury result, as a consequence this technique would not be suitable for translation to the on-line manifold.

The EPA method should have produced a value similar to that of the customer, however the mean value obtained was only 11.7 ng ml^{-1} in relation to the expected value of 17.5 ng ml^{-1} . The low result, poor recoveries, excessive reagent addition and duration of heating, coupled with precipitate formation made this technique unsuitable for on-line translation.

The acid permanganate method produced a mean result of $16.2 \pm 0.2 \text{ ng ml}^{-1}$ which was in close correlation of the expected value of 17.5 ng ml^{-1} . Mean spike recoveries for this method were in the region of 99%. Very little difference was obtained upon heating the sample and performing the digestion at room temperature, with mean results of 16.1 ± 0.2 and $16.3 \pm 0.2 \text{ ng ml}^{-1}$ respectively. This method proved effective in the digestion of the sample. This coupled with the

simplicity; minimal reagent consumption and reagent cost made this method suitable for translation to the on-line manifold.

The bromination technique was the most effective technique of all the methods evaluated. Results produced using this technique were in very good correlation to the customers result, with a mean obtained value of 17.8 ± 0.3 ng ml⁻¹ (expected value of 17.5 ng ml⁻¹). Once again very little difference was observed upon heating the sample and performing the digestion at room temperature. Spike recoveries for this technique were also the best of the methods evaluated, with a mean recovery of 99%. Although this method involves a greater amount of reagent addition than the acid permanganate procedure the overall result was closer to that of the expected value. This method would therefore be ideally suited for on-line translation.

The final method evaluated was the acid dichromate technique, this produced an overall mean concentration of 14.6 ± 0.2 ng ml⁻¹. Although the result was close to that of the expected value spike recoveries were in the region of 85%. This slightly low result and recovery may have been improved upon heating the sample during the digestion stage, which was unfortunately not performed. This method still had its merits as once again it was simple to perform, rapid, reagent consumption and addition was minimal and the obtained value was close to the expected concentration.

The overall method chosen for on-line translation was the bromination technique. This produced the best overall result and spike recoveries. Reagent addition was the only limiting factor for this technique. The subsequent dilution of the sample by the addition of the various reagents could prove challenging when

analysing low-level mercury concentrations in the effluent, however this could be combated by omitting the pre-reductant solution.

3.3 ON-LINE DETERMINATION OF MERCURY IN INCINERATION WASTEWATER

3.3.1 Introduction

A fresh batch of samples was provided by the incineration company, this time the company provided two batches of sample labelled "Samples 1 and 2". The first sample, Sample 1, was a treated effluent, i.e. had been through the wastewater treatment process, while the second sample, Sample 2, was raw wastewater from the sedimentation process.

Sample 1 was "typically representative" of the final effluent ready for discharge to the receiving rivers, whilst Sample 2 was "a worst case scenario sample", as it had not been through the final sand and activated carbon filtration systems and hence contained a high amount of suspended particulate matter. The second sample was provided to illustrate the consequences of a failure within treatment process. Initially Sample 1 was analysed using the on-line manifold.

Samples 1 and 2 were evaluated on the laboratory system using the bromination method outlined in section 3.2.3.5 in order to obtain a target value. The value obtained for Sample 1 was $0.8 \pm 0.1 \text{ ng ml}^{-1}$ with spike recoveries of 97% and 98% for 1 and 2 ng ml^{-1} additions respectively. The value obtained for Sample 2 was $33.4 \pm 0.2 \text{ ng ml}^{-1}$, with spike recoveries of 95% and 101% for 5 and 10 ng ml^{-1} additions respectively.

3.4.2. Experimental

The next stage in development was to transfer the bromination chemistry to the on-line manifold. The on-line system has been specifically designed to determine mercury in liquid samples with full process and data control via an IBM

compatible computer. A full description of the on-line manifold is given in Chapter 2. The standard manifold was used to evaluate the incineration wastewater sample, a schematic diagram of the manifold configured for the bromination technique is shown in Figure 3.3.

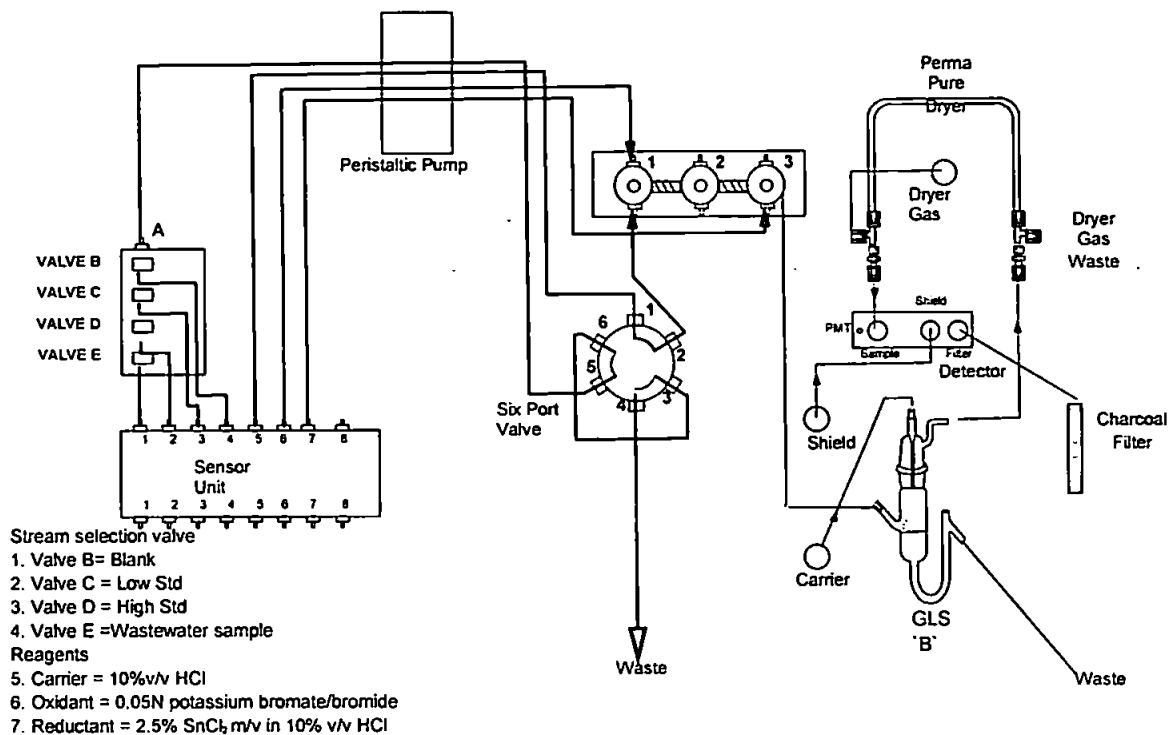


Figure 3.3. Standard on-line manifold configured for bromination chemistry

3.3.1.1 On-line manifold

With the standard instrument set up the stream selection valve was fitted with four valves, only one of which could be selected at any one time. The sample/standard was pumped to a six-port flow injection valve where a fixed volume of the sample was introduced to the mixing manifold. Line 5 in Figure 3.3 shows the carrier stream of dilute HCl in the standby mode; here the carrier is flowing in to the six-port valve through port 1 and exiting via port 2. The carrier then entered the mixing manifold (Line 5), where it was butt-mixed with a solution of potassium bromate/bromide (Line 6). The resulting acid bromate then oxidised

bromide to bromine that in turn oxidised any mercury present to the divalent Hg^{+2} state as HgBr_4^{2-} . The oxidised standard/sample was then further mixed through the coil to ensure complete oxidation.

The oxidised sample was then mixed with an acidic solution of tin (II) chloride through the reducing coil (Line 7). Here, the divalent mercury (HgBr_4^{2-}) and the excess bromate was reduced to mercury Hg^0 and Br_2 respectively. The resulting solution/gas was then passed through the mixing coil and to the gas/liquid separator (GLS) for purging. The carrier gas purged the mercury Hg^0 out of solution and through the Perma Pure[®] membrane dryer tube at a rate of 300 ml min^{-1} . Here the damp sample was continuously de-solvated as it passed through the Nafion[®] membrane. The dry sample then arrived at the detector for fluorescence detection. The transient signal was converted in binary coded decimal (BCD code) and forwarded to the computers digital input/output (DIO) card for interpretation by the software.

3.3.1.2 Reagents

The bromination reagents used for the on-line manifold were the same as those utilised during the off-line laboratory method development evaluations. The only modification was the omission of the hydroxylamine hydrochloride solution as the pre-reductant. The pre-reductant can be omitted and replaced with higher strength SnCl_2 reductant solution to fully reduce the excess oxidant in the sample/standard.

Since reagent addition was fully automated on a continuous flow basis the reagent concentrations were altered accordingly. The numbers below indicate the line position of each reagent displayed in Figure 3.3.

Line 4 - the sample was a fresh batch of the undiluted incineration wastewater, (previously collected at the same time as the laboratory method development sample and stored in the refrigerator). The sample was continuously stirred using a magnetic stirring unit (Stuart Scientific, Bedford UK). Standards were prepared from the appropriate dilution of a 1000 µg l⁻¹ Hg solution (SpectrosoL®, Merck).

Line 5 - carrier stream of 10% v/v HCl (AnalaR®, Merck, Pool, UK) in DDW (Elga Option 3, High Wycombe, UK).

Line 6 - oxidant of 0.05M potassium bromate/potassium bromide solution (ConVol®, Merck) in DDW.

Line 7 - reductant of 2.5% m/v Tin (II) Chloride (Aldrich, Gillingham UK) in 10% v/v HCl (AnalaR®, Merck) in DDW.

3.3.1.3 Instrument settings

Fit type = Least squares straight line.

Measurement = Peak Height %

Gain = 1000 X 3.0 Filter = 4 Autozero = On

Carrier gas = 300 ml min⁻¹ Dryer gas = 2.5l min⁻¹

Sheath gas = 300 ml min⁻¹ Delay = 120 sec

Measure = 120 sec Memory = 100 sec

Runs per determination = 1. Timer = Off Loop size = 400µl

Red/red Tygon® pump tubing for all lines at 0.8 ml min⁻¹

3.3.1.4 Analysis program

The analysis program used for the initial evaluations on Sample 1 is shown in Table 3.3.

Table 3.3. On-line analysis program used for initial evaluation

Line Number	Valve Position	Reference
1	B	Blank
2	C	2 ng ml ⁻¹ std
3	D	5 ng ml ⁻¹ std
4	E	Sample
5 Through to 15	E	Sample
16	C	Chk low std (2 ng ml ⁻¹)

3.3.2 Results and Discussion

3.3.2.1 Sample with low particulates (Sample 1)

The results for Sample 1 are shown in Figure 3.4. The standard instrument manifold was calibrated with standards of 0, 2 and 5 ng ml⁻¹ Hg and then set to analyse the sample 10 times on a continuous basis before performing a check standard of 2 ng ml⁻¹.

The mean result over ten runs for Sample 1 was found to be 0.35 ± 0.02 ng ml⁻¹ with a precision of 5%, the check standard of 2 ng ml⁻¹ produced a value of 1.95 ng ml⁻¹. The low value obtained in comparison to the laboratory value of 0.81 ng ml⁻¹ suggests a recovery of only 43%. This would indicate that the oxidation stage was insufficient in fully converting all the available mercury from within the sample. Although the check standard was already in the divalent form, its accuracy serves to confirm that the poor recovery was not due to a function of drift within the detector but due to incomplete oxidation of the sample.

One possible and relatively simple approach of improving the oxidation procedure to enable a total mercury result was to increase the length of the oxidation coil. Increasing the length serves to extend the duration of contact time with the oxidant. One must remember that off-line the contact time for the sample

and the oxidation reagents is approximately 10 minutes before being analysed whilst here the contact time is little more than a tenth of that value.

Hence, the manifold was modified by increasing the length of the oxidation coil from 150 cm to 250 cm (0.5mm id. PTFE). To account for the increased oxidation retention the overall measurement cycle was increased to from 340 sec to 400 sec per a determination. Figure 3.4 shows the effects of extending the length of the oxidation coil from 150 cm to 250 cm, or from 60 to 100 seconds.

Figure 3.4 shows the results obtained plotted directly against those of the standard length oxidation coil. Extending the length of the coil clearly showed a marked improvement on the efficiency of oxidation. The mean result of the sample increased from 0.35 ng ml⁻¹ to 0.60 ± 0.05 ng ml⁻¹ (RSD = 8%) or by 70% when using the longer length coil. Although the result was higher it was still low in comparison to the off-line laboratory value of 0.81 ng ml⁻¹ equating to an overall recovery of only 74%.

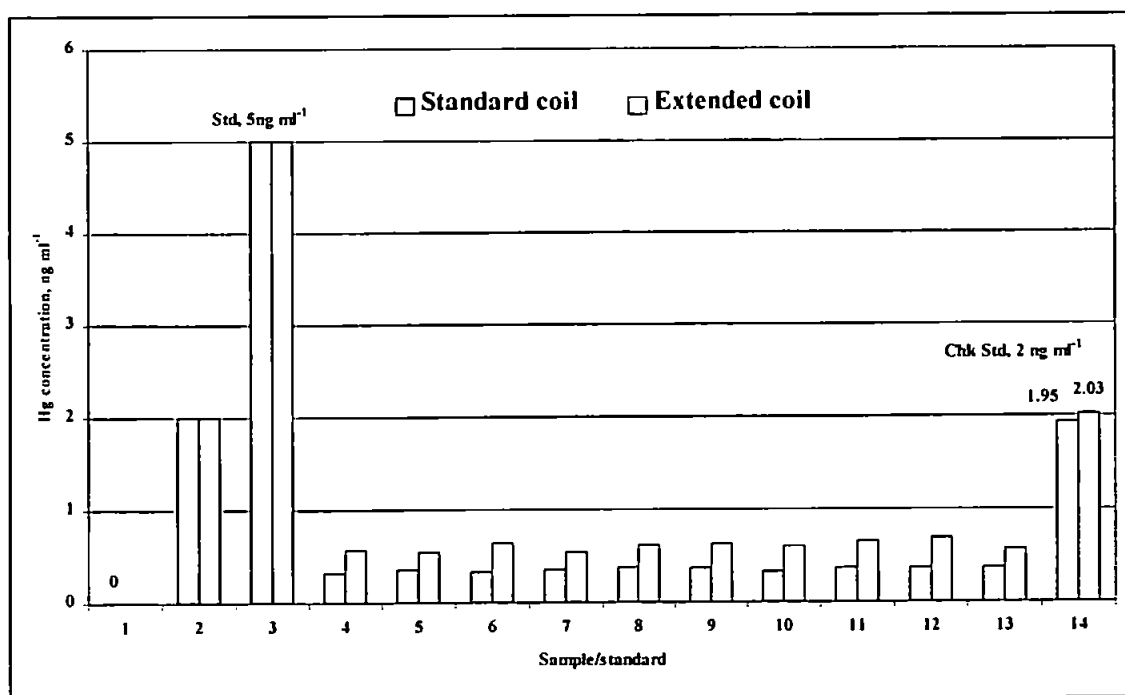


Figure 3.4. Standard (150cm) and extended (250cm) length oxidation coils

3.3.2.1.1 Effect of heating coil

In order to improve the oxidation efficiency the length of the oxidation coil could be increased further, however this would serve to increase the analysis time to over ten minutes per a determination, making the analysis frequency unfavourable. An alternative approach was to heat the oxidation manifold to increase the rate of oxidation taking place within the coil.

The oxidation manifold was further modified by incorporation of a heating coil around the oxidation manifold. The standard length coil (150 cm) was wrapped in a thermally insulated heating jacket of 7.5 cm ID. and 50 cm long (Model UDA Z11001, Briskheat Corporation, Ohio, USA) and the temperature maintained at 85°C. Control was performed by an automatic temperature modulator (Cal 9900, Series 1, Cal Controls Ltd, Hitchin, UK).

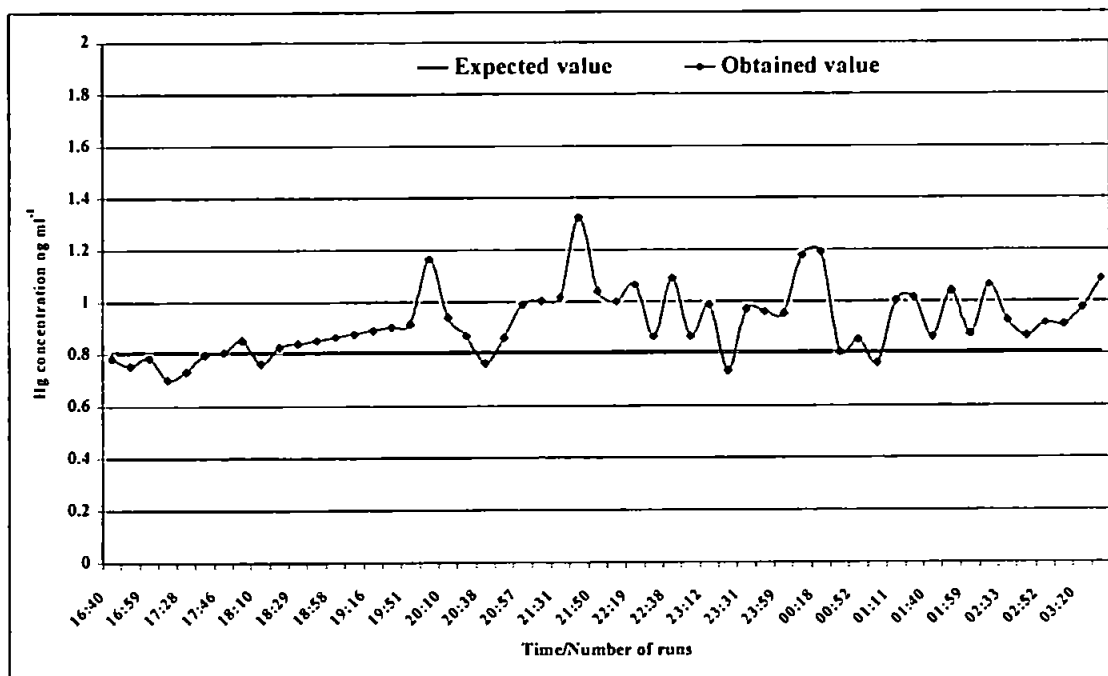


Figure 3.5. Heated oxidation coil (150 cm) at 85°C

The results of the heated coil are shown in Figure 3.5. The graph shows a marked improvement to the oxidation efficiency when observing the first ten runs where heating was applied to the oxidation coil. The mean value obtained over

the first ten runs was now $0.78 \pm 0.04 \text{ ng ml}^{-1}$ with precision of 6 %, resulting in a 96% recovery of the laboratory value (0.81 ng ml^{-1}).

3.3.2.1.2 Short-term stability

Wastewater Sample 1 was analysed repeatedly using the batch operation of the on-line instrument. The analysis program and reagents used were the same as those shown in Table 3.3 and section 3.3.1.4 respectively. After calibration the sample was analysed repeatedly in batch mode for approximately 12 hours.

Figure 3.5 shows the results of the short-term stability study. The results showed positive drift over the test period with the mean result rising from $0.78 \pm 0.04 \text{ ng ml}^{-1}$ ($n = 10$, $t = 1.5 \text{ hrs}$) to $0.92 \pm 0.12 \text{ ng ml}^{-1}$ ($n = 53$, $t = 11 \text{ hrs}$). The graph clearly shows the results progressively increasing with time up to a point where instability was observed; the precision over the whole test period was 13%.

This instability was attributed to condensation formation within the gas liquid separator. Large liquid droplets were clearly visible in the connection tubing from the gas/liquid separator to the membrane dryer unit. It would appear that these droplets were causing solvation of the mercury vapour and gradually being carried through the hygroscopic membrane dryer unit leading to instability. The cause of this excessive water vapour formation was due to the continuous addition of hot solution from the heated oxidation coil to the cooler gas/ liquid separator. Eventually the separator became warm promoting the formation of further condensation droplets.

3.3.2.1.3 Stability test with heating manifold and cooling chamber

The manifold was again modified to account for the success of the heated oxidation stage. A cylindrical heating unit (KKR0505 'K' type, Watlow Heaters)

was fitted around the standard oxidation manifold. Temperature control was again performed using the temperature modulator. The heating unit was also fitted with a safety cut-out thermostat to prevent over-heating of the internal PTFE mixing coil. The temperature of the coil was initially set at 85°C.

As a consequence of the condensation produced in the gas liquid separator during the short-term stability test, the modified heated manifold was fitted with a cooling chamber. The cooling chamber was fitted at the point of reductant addition. A borosilicate chamber was designed to enable the hot oxidised solution to pass along a 50 cm PTFE coil within a condenser type arrangement. Cold tap water was continuously pumped through the base of the cooling manifold using the existing peristaltic pump at a flow rate of 0.8 ml min⁻¹. The cooling water then circulates upwards to the exit of the chamber and out to waste. This also enabled the reduction process to take place during the cooling chamber. The cooled reduced solution then enters the gas liquid separator. A diagram of the heated oxidation stage coupled to the cooling chamber is shown in Figure 3.6.

Wastewater Sample 1 was analysed repeatedly in batch mode to assess the short-term stability over a twenty hour period. The analysis program and reagents used were the same as those in the previous section.

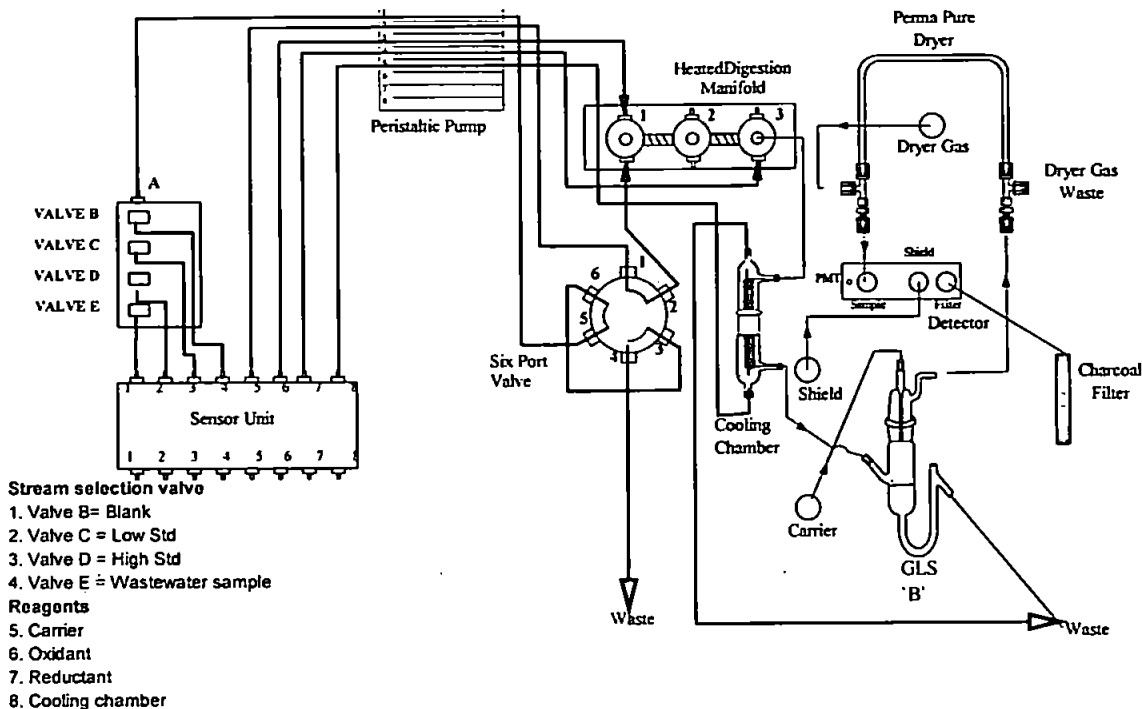


Figure 3.6. On-line wet section incorporating cylindrical heater and cooling chamber

The results of the test are shown in Figure 3.7. The results obtained over the test period of 20 hours show a mean result of $0.76 \pm 0.03 \text{ ng ml}^{-1}$. The precision over this test was only 4% with 132 measurements being performed. The expected value of 0.81 ng ml^{-1} was also plotted on the graph as a comparison; although the overall mean of 0.76 ng ml^{-1} was slightly lower than the expected value (0.81 ng ml^{-1}) this was equivalent to an overall recovery of 93%. The installation of the cylindrical heating unit coupled to the cooling coil chamber was clearly successful in improving the oxidation efficiency and minimising condensation effects.

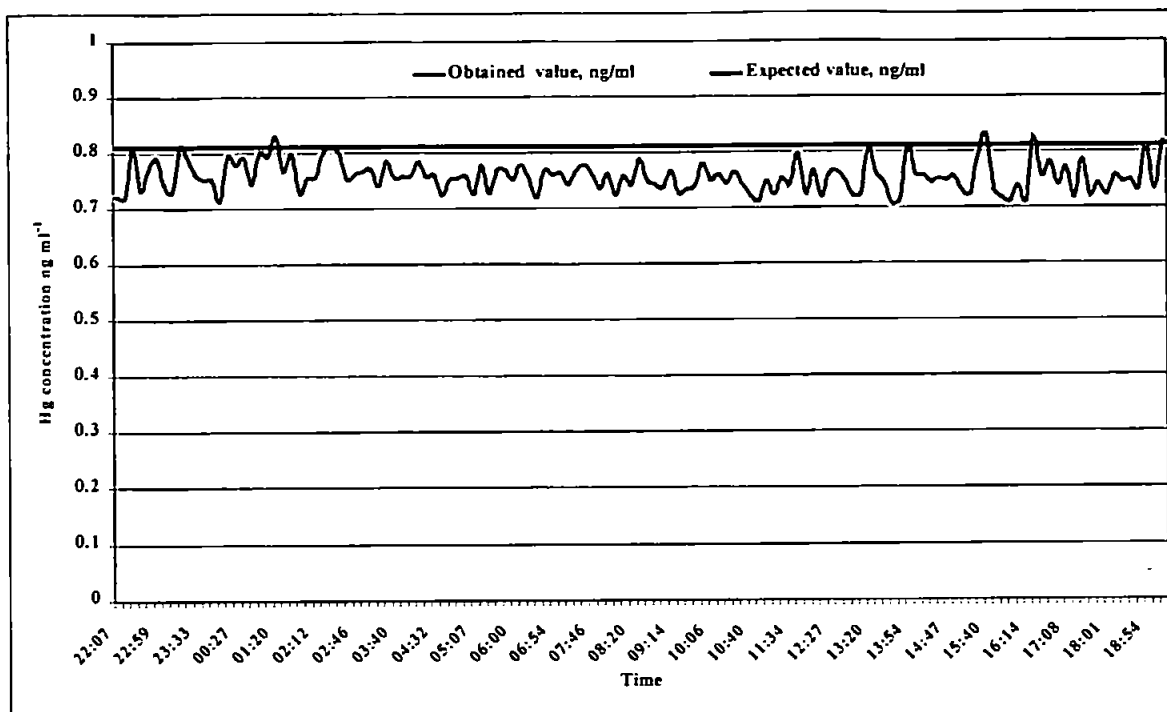


Figure 3.7. Short-term stability test incorporating the cylindrical heater and cooling chamber

3.3.2.1.4 Spiking of sample 1 with inorganic and organomercury compounds

The next stage of evaluations was to assess the efficiency of the heated oxidation manifold. Wastewater Sample 1 was spiked with inorganic and organic mercury compounds. Aliquots of Sample 1 were spiked with 1 and 2 ng ml⁻¹ of Hg(NO₃)₂ from the appropriate dilution of a 1000 mg l⁻¹ mercury stock solution (SpectrosoL[®], Merck). An organomercury stock solution was prepared by dissolving the appropriate quantity of solid CH₃HgCl (Strem Chemicals Inc, Newburyport, MA, USA). A working stock of 100 ng ml⁻¹ was prepared by the appropriate dilution of the stock solution; from this 1 and 2 ng ml⁻¹ additions were made to the sample. The results from the spiking experiments are shown in Figure 3.8. The mean result of the un-spiked wastewater sample was found to be 0.77 ± 0.07 ng ml⁻¹ over 25 runs with a precision of 9%. When spiked with 1 ng ml⁻¹ the obtained value was found to be 1.77 ± 0.15 ng ml⁻¹ resulting in a recovery 100%. When spiked with 2 ng ml⁻¹ the obtained value was 2.83 ± 0.06 ng ml⁻¹

resulting in a recovery of 98%. Although the sample was spiked with divalent mercury, which did not require oxidising, the good recoveries obtained suggest that no sample matrix effects were experienced.

The addition of 1 ng ml^{-1} and 2 ng ml^{-1} methylmercury chloride (CH_3HgCl) to the sample produced values of $1.8 \pm 0.06 \text{ ng ml}^{-1}$ and $2.68 \pm 0.07 \text{ ng ml}^{-1}$ respectively, resulting in recoveries of 101% and 98% respectively. Thus, it can clearly be seen that the oxidation manifold was fully capable of breaking down organomercury species which could be present in the wastewater sample as TMT mercury compounds.

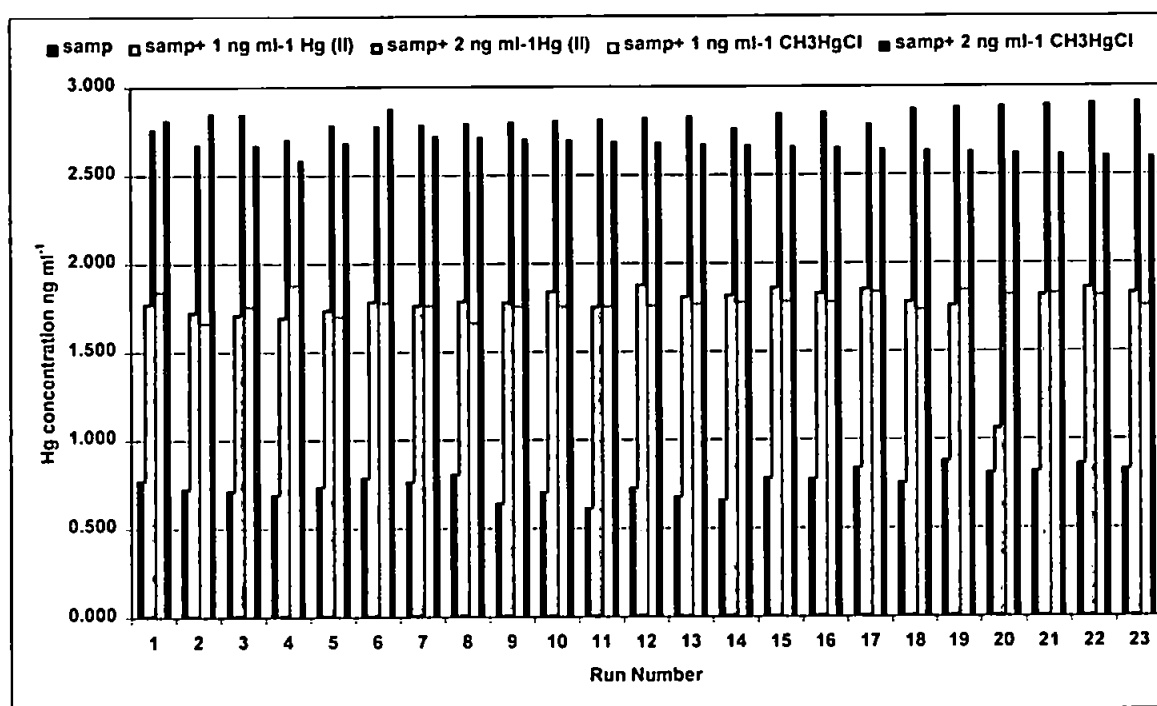


Figure 3.8. Spiking of wastewater sample with inorganic and organomercury compounds

3.3.2.1.5 Long-term stability

The final evaluation of Sample 1 was to obtain some long term stability data, i.e. over 100 hours of uninterrupted analysis. Ten litres of each reagent was prepared and stored in HDPE bottles, this would ensure enough reagent was present during over the 100-hour test period.

The instrument was modified slightly in order to perform this test; the standard four-channel stream selection valve was upgraded to 8 streams. This would therefore allow a greater number of calibration standards or sample streams to be analysed on-site at the incineration plant. Consequently, the instrument was now programmed to perform a three point calibration using mercury standards of 0, 5 and 10 ng ml⁻¹ before analysing the wastewater sample three times and performing three runs on a 5 ng ml⁻¹ check standard. The instrument was tested using the continuous re-calibration procedure so that the calibration and analysis cycles were continually repeated. The results of over 100 hours on continuous testing are shown in Figure 3.9

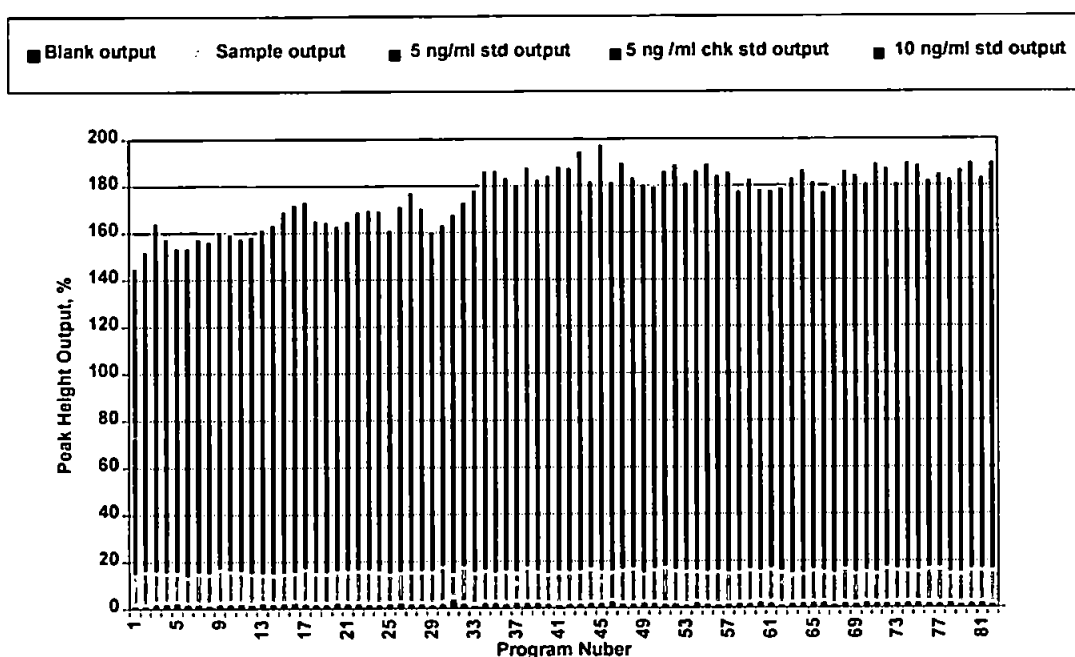


Figure 3.9. Peak height (%) data showing long-term stability test for Sample 1, (t = 100 hours)

From Figure 3.9 the process of continual re-calibration and analysis can clearly be seen. It should be noted that these values represented in Figure 3.9 are based on the peak height output % of the AFS detector (full scale deflection was set to 200% arbitrary units). Over the test period the instrument performed a

total of 82 analysis cycles resulting in precision's of 28% for the blank (mean = 1.45% \pm 0.41), 7.1% for the 5 ng ml⁻¹ standard (mean = 87.86% \pm 6.25) and 7% for the 10 ng ml⁻¹ standard (mean = 176.21% \pm 11.82).

After each calibration the instrument then performed three runs on wastewater Sample 1 followed by three runs on a 5 ng ml⁻¹ check standard. The obtained values were 0.78 \pm 0.07 ng ml⁻¹ and 4.78 \pm 0.16 ng ml⁻¹ for the sample and check standard respectively. Precisions over the 100-hour test were 9% for the sample and 3% for the check standard. The results of both the sample and check standard are shown in Figure 3.10

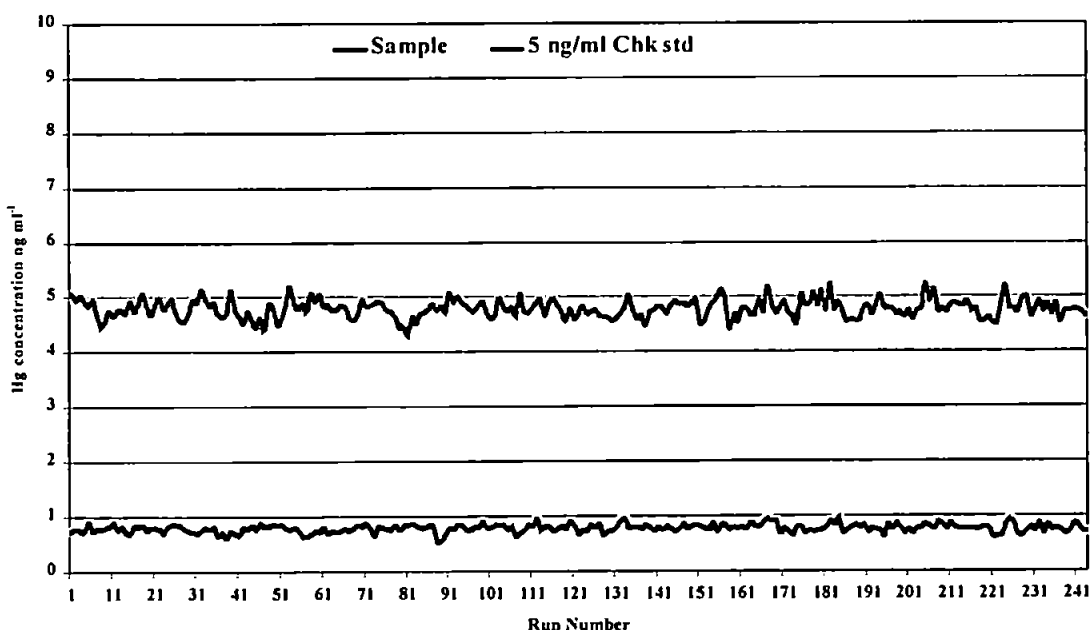


Figure 3.10. Long-term stability test showing the variation in concentration for Sample 1 and a 5ng ml⁻¹ check standard. (t = 100 hours)

3.3.2.2 Sample with high particulates (Sample 2)

Sample 2, which was also sent for evaluation, was briefly analysed on the on-line system. As a consequence of the higher concentration sample (off-line laboratory value = 33.4 \pm 0.23ng ml⁻¹), the system was calibrated over a wider range of 0-60 ng ml⁻¹ Hg. The sample was analysed in batch mode on the 8-

channel stream selection valve instrument. Initially a 'settled solution' of sample was analysed whereby the particulate matter within the sample was left to settle out and form a sludge, this resulted in the analysis being performed on a 'supernatant sample'.

After analysing the 'supernatant sample' the sample was then analysed by agitating the settled solution, this was simply done by using a PTFE coated magnetic stirring rod to re-suspend the settled particulate matter.

Figure 3.11 shows the results of analysing both the supernatant and stirred solutions of Sample 2. When analysing the supernatant or settled solution the mean concentration was found to be $7.9 \pm 1.0 \text{ ng ml}^{-1}$, with a precision of 12.65% over the test period of 6 hours. The obtained value was low in relation to the off-line laboratory result of 33.40 ng ml^{-1} , resulting in a recovery of only 24%. A low value was expected, as the majority of mercury within the sample would be bound to the particulate flakes of flocculent material. The poor precision of the settled solution could also be attributed to the occasional passage of particulate matter through the flow injection loop.

When analysing the stirred sample a dramatic difference in results was observed, as can be seen from Figure 3.11. Agitating the sample re-suspended the settled particulate matter to produce a solution of widely varying particle size distribution. When this solution was analysed there were dramatic variations in the concentration observed, as can be seen from Figure 3.11.

The mean result of the stirred solution was now $18.4 \pm 10.3 \text{ ng ml}^{-1}$ resulting in a precision of 56% over the test period. It would appear that the observed concentration was purely a function of the quantity of particulate matter passing through the flow injection loop at the time of activating the FI valve.

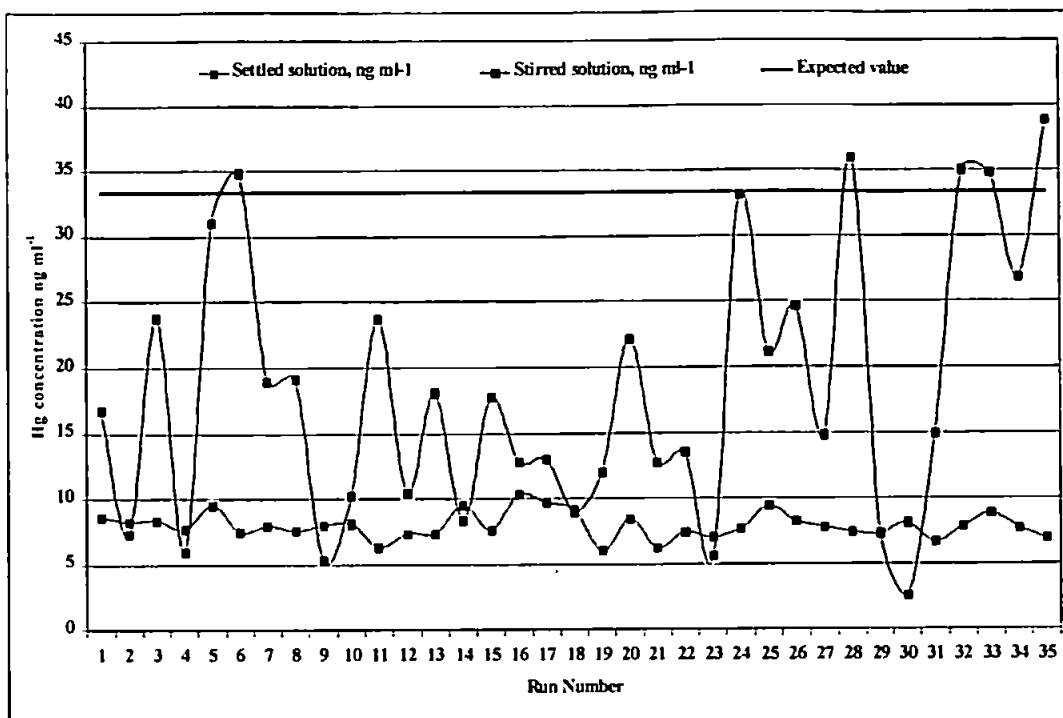


Figure 3.11. Variation of Sample 2 (high solids sample) when settled and stirred

On some occasions there would be a high amount of particulate material within the sample loop whilst at other times the loop would contain very little suspended matter. Thus, it became apparent that the instrument was not capable of analysing a sample with such a wide particle size distribution.

3.3.2.2.1 Pre-treatment techniques for breaking down particulate matter

In an attempt to breakdown the large size particulate matter the sample was homogenised by vortex mixing using a high speed PTFE magnetic stirring rod (Stuart Scientific). This agitated sample was then passed along an 1/8" PTFE heating coil maintained at 70°C. The resulting heated sample was then passed to an ultra-violet pre-treatment stage to breakdown the particulates further. A 200 cm 1/8" PTFE coil was wrapped around a 40W ultra-violet lamp (Heraceus, UV Technology, Cambridge, UK) prior to arrival at the instruments stream selection valve.

Figure 3.12 shows the effects of heat-treating the sample followed by subsequent passage along an ultra-violet coil. Although the mean observed concentration increased from 18.39 ng ml⁻¹ to 39.74 ng ml⁻¹ ± 14.16 the overall precision was still very poor, 35%. Thus, the addition of the heating coil and ultra-violet treatment did serve to increase the overall recovery however the observed variability was still too great in relation to the expected result.

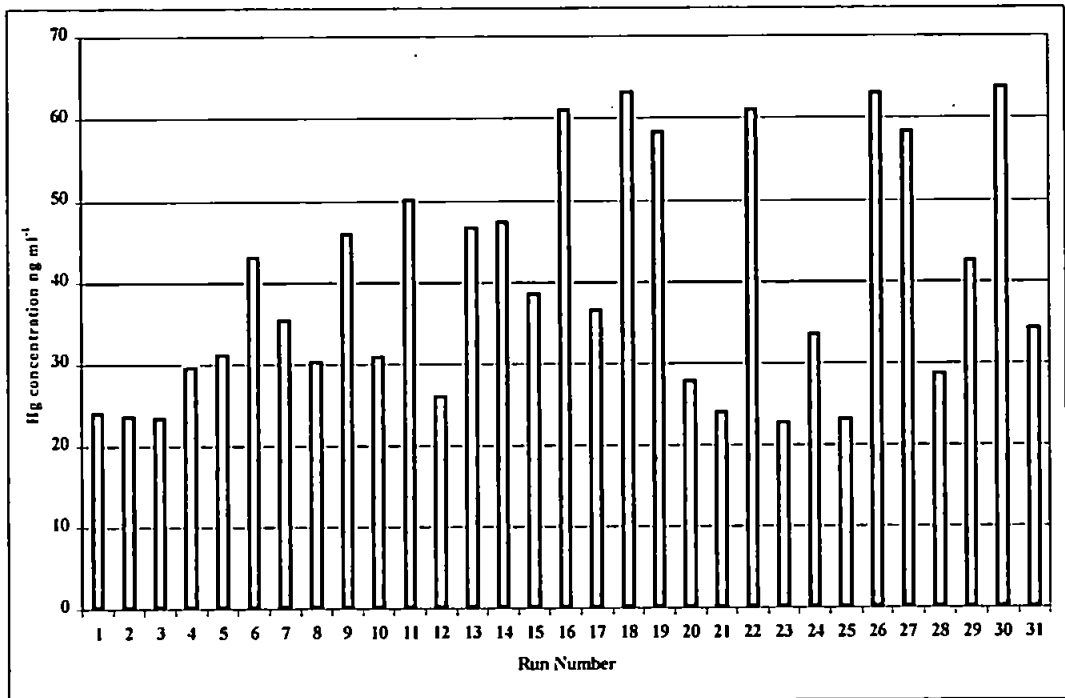


Figure 3.12. The effects of stirring Sample 2 followed by heating and subsequent u.v. irradiation to break down the particulate matter

3.3.3 Conclusions

The standard on-line manifold required significant modification when the off-line laboratory bromination technique was translated on-line. It became apparent that in order to replicate the off-line laboratory measurement a heated oxidation stage was required for similar results to be obtained. The addition of the heated oxidation stage then required subsequent cooling prior to detection otherwise condensation formation became significant leading to poor

reproducibility over longer time periods. A simple but effective cooling chamber was designed and added to the heated oxidation manifold, reducing condensation formation almost completely.

The oxidation manifold proved effective for the complete recovery of organic mercury compounds added to the sample matrix, with a mean recovery of 100% for methylmercury chloride additions. Mercury-TMT complexes within the sample were readily broken down by oxidation manifold releasing all the available mercury for subsequent determination.

Excellent long-term stability data was obtained with the low particulate sample (Sample 1), precisions of less than 9% were obtained for the sample and less than 3.5% for the check standard over the 100-hour test period. The excellent precision of the continuous re-calibration procedure over the long-term test also served to verify the stability of the instrument indicating that the need for such frequent calibration was unnecessary. This would therefore free-up the instrument to perform more measurements on the sample hence increasing the overall analysis frequency.

When the high particulate sample (Sample 2) was analysed poor reproducibility was obtained. This was later attributed to the degree of particle flux entering the sample loop at the time of activation. Attempts were made to reduce the distribution of particle sizes within the sample, both heating the sample and ultra-violet pre-treatment techniques during sample delivery proved generally unsuccessful.

It was concluded that the instrument was not capable of handling samples with a particulate content of more than 3% (total suspended solids, TSS of greater than 3000 mg l⁻¹). In fact, one must remember that the sample sent for evaluation

was the 'worst case scenario', which would only normally occur during wastewater treatment failure.

Despite the instrument not being able to cope with such high particulate samples the variability in observed results could be used as a tool for indicating wastewater treatment failure. When such variability in the results is observed this would indicate that there was likely to be sand filter-bed breakthrough in the treatment process, resulting in the plant operator taking the subsequent action. With successful on-line laboratory tests on the final discharge effluent (Sample 1), the instrument was finally installed on-site at the waste incineration plant to undergo further trials.

3.4 INSTALLATION AND TESTING AT AN INCINERATION PLANT

It became apparent at an early stage that the initial samples sent for laboratory evaluation were clearly "worst case scenarios" with high TMT solids content. The actual wastewater streams being monitored were in fact much "cleaner" and should be less challenging to the instrument than those studied during the laboratory trials. The second sample obtained for evaluation (on-line Sample 1) was more representative of what the instrument would be configured to analyse, i.e. had a low solids content and was in the region of less than 5 ng ml⁻¹ mercury.

3.4.1 Sample collection device and instrument housing

The instrument was located in a purpose built concrete analyser house located adjacent to main incineration plant. Figure 3.13 shows a photograph of the analyser house. The analyser house was air conditioned at a temperature of 25°C, had an electronic heater for cold periods and was airtight from the surrounding atmosphere.

Two sample streams were plumbed to the instrument in ½" stainless steel tubing. Each sample was delivered to a constant over-flow sampling system fitted with liquid level sensors. The first wastewater sample was called 'ABA 1' containing no visible particulate matter whilst the second was called 'ABA 2' containing small quantities of the TMT flocculent matter.

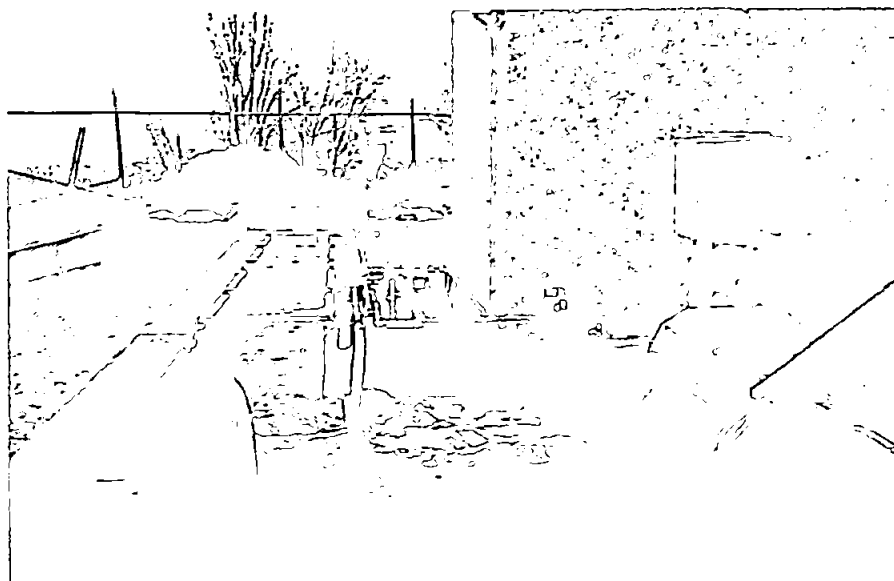


Figure 3.13. Sampling point at effluent discharge point

3.4.2 Reagents

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

All reagents were the same as those used during the on-line laboratory trials, 10.0 litres of each reagent were prepared this should result in at least 7 days unattended operation. Tap water was used for the cooling chamber.

The customers action level, the point at which the “contaminated” sample would be re-circulated to the wastewater treatment process for further polishing was 10 ng ml⁻¹. Hence mercury standards of 0, 5, 10 and 40 ng ml⁻¹ were prepared in the same matrix as the carrier solution, 0.5 litres of each standard were prepared and stored in HDPE bottles.

3.4.3 Experimental

3.4.3.1 Instrument settings

Due to the instrument running on nitrogen as the carrier gas the gain amplification of the AFS detector was increased to account for the effects of quenching.

Gain = 1000

Fine gain = 3.5

Delay period = 150 sec, Measure time = 200 sec Memory = 150 sec.

Autozero = On

Filter factor = 8.

Loop size = 500 μ l.

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

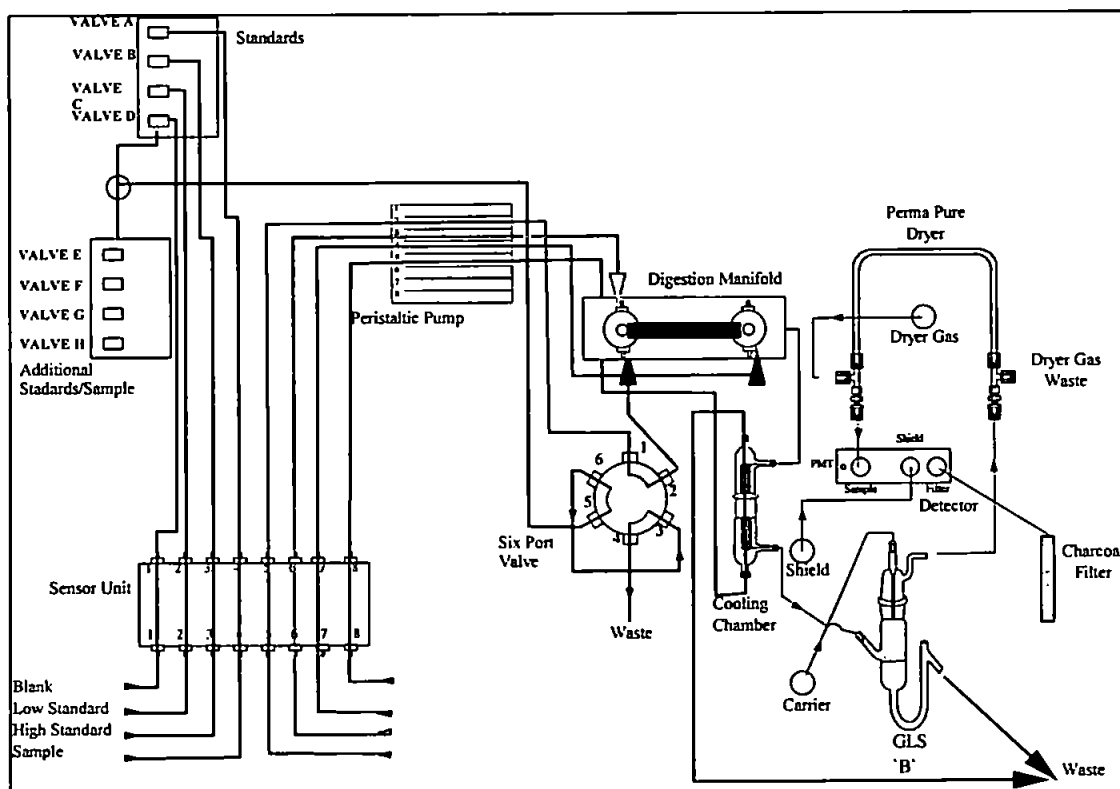


Figure 3.14. Schematic diagram of wet chemistry section used at incineration plant trials

3.4.3.2 Procedure

The system was set up with the above instrumental conditions and as shown in Figure 3.14. A simple analysis programme involving a four-point

calibration of 0, 5, 10 and 40 ng ml⁻¹ Hg was employed for the test period. Once calibrated the instrumental would automatically perform twenty determinations on the inlet sample followed by two check standards of 10 ng ml⁻¹ and finally another twenty determinations on the outlet sample. This analysis cycle was then continuously repeated over a 12-day period. The results from the instrument were then exported to the DCS via a two-channel 4-20 mA output. The results from the instrument are shown in Figure 3.15

3.4.4 Results and Discussion

3.4.4.1 Inter-calibration variation during test period

Table 3.4 shows the variation of the instruments stability with respect to calibration variation. Each of the calibrants peak height outputs has been grouped together so that inter-calibration variations can be compared.

Table 3.4. Variation of calibration peak height outputs (%)

Date	0, std	5 ppb	10ppb	40 ppb
07-Apr-09	1.616	13.22	27.86	113.8
07-Apr-09	1.871	17.51	30.23	113.2
08-Apr-09	0.387	14.26	28.88	115.3
08-Apr-09	0.443	15.09	30.25	114.5
09-Apr-09	0.667	13.8	28.99	111.5
09-Apr-09	0.486	15.93	31.67	118.8
10-Apr-09	0.454	13.96	28.48	112.7
10-Apr-09	0.513	14.74	29	110.2
11-Apr-09	1.519	16.52	29.86	112.6
12-Apr-09	0.678	13.64	26.2	102.5
12-Apr-09	0.394	14.87	29.14	110.3
13-Apr-09	3.23	14.66	27.8	105.3
13-Apr-09	0.94	12.81	26.64	104.7
14-Apr-09	0.573	15.52	30.61	109.8
15-Apr-09	0.352	16.14	30.12	111.9
15-Apr-09	0.599	15.65	31.28	114.5
17-Apr-09	0.701	14.58	27.87	103.6
17-Apr-09	1.086	12.78	27.27	103.3
18-Apr-09	0.848	11.09	24.06	95.42
19-Apr-09	0.776	11.03	22.95	95.62
19-Apr-09	0.121	13.22	28.57	102.6
Mean	0.916	14.90	29.22	110.01
Std Dev	0.78	1.54	1.46	5.43
RSD %	85.33	10.31	4.96	4.93

From Table 3.5 the variation of inter-calibration peak height outputs over the test period can be seen. The results show that the precision over the test period for both the 5 and 10 ng ml⁻¹ standards was less than 5%. Figure 3.15 shows the mean calibration graph obtained during the test period. Once again the reproducibility of the continuous re-calibration procedure was within 5%.

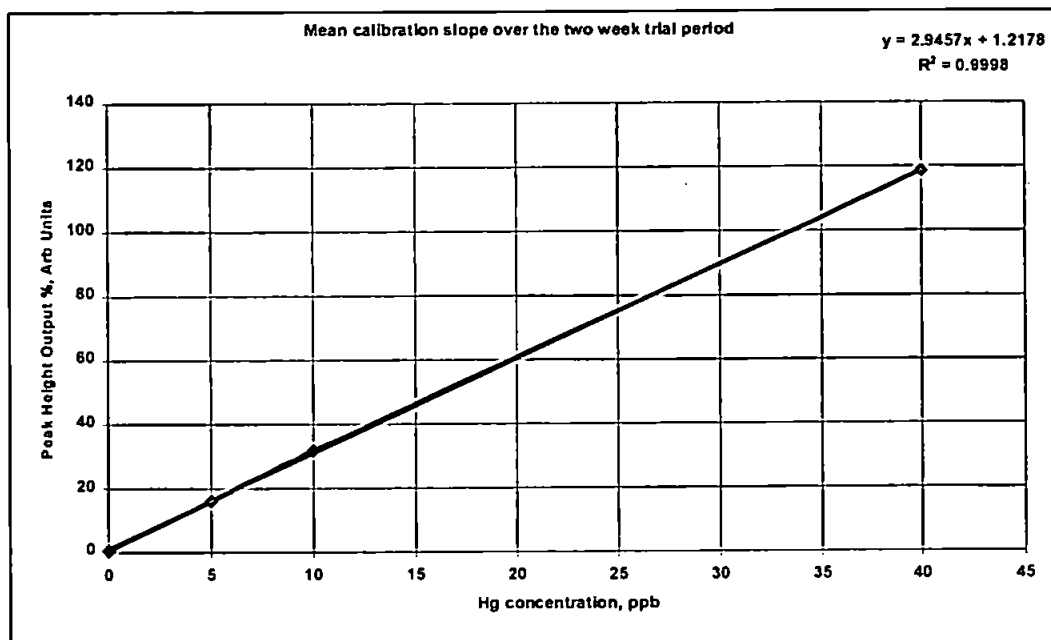


Figure 3.15. Mean calibration slope over the test period

The mean values for each calibrant have been used to calculate the overall mean calibration slope. Again the slope varied less than 5% over the test period.

3.4.4.2 Variation of internal check standard over the test period

Table 3.5 shows the value obtained for each check standard. Two check standards of 10 ng ml⁻¹ were performed between analysing the inlet and outlet of the carbon beds.

Table 3.5. Variation of 10 ng mt⁻¹ check standard over the test period

Date	Tag	Concentration ng/ml
08-Apr-1998	CHKSTD	9.268
08-Apr-1998	CHKSTD	9.646
09-Apr-1998	CHKSTD	10.13
10-Apr-1998	CHKSTD	9.076
10-Apr-1998	CHKSTD	10.01
11-Apr-1998	CHKSTD	10.32
11-Apr-1998	CHKSTD	9.892
12-Apr-1998	CHKSTD	10.9
14-Apr-1998	CHKSTD	10.05
14-Apr-1998	CHKSTD	9.351
15-Apr-1998	CHKSTD	9.132
15-Apr-1998	CHKSTD	9.151
17-Apr-1998	CHKSTD	9.708
18-Apr-1998	CHKSTD	9.223
18-Apr-1998	CHKSTD	9.581
19-Apr-1998	CHKSTD	9.408
	Mean	9.678
	Std Dev	0.510
	RSD%	5.275

3.4.4.3 Variation of inlet and outlet Hg concentration from carbon beds

Figure 3.16 below shows the variation of both the inlet and outlet mercury concentrations over the test period. The on-line monitoring system was set-up to export the results of each effluent stream to the control room where the appropriate action can be taken when discharge levels are exceeded. The results clearly show the efficiency of the carbon clean up system. With the rapid generation of results (every 7 minutes) the operators in the control room can take the necessary action and have a greater degree of confidence, control and compliance.

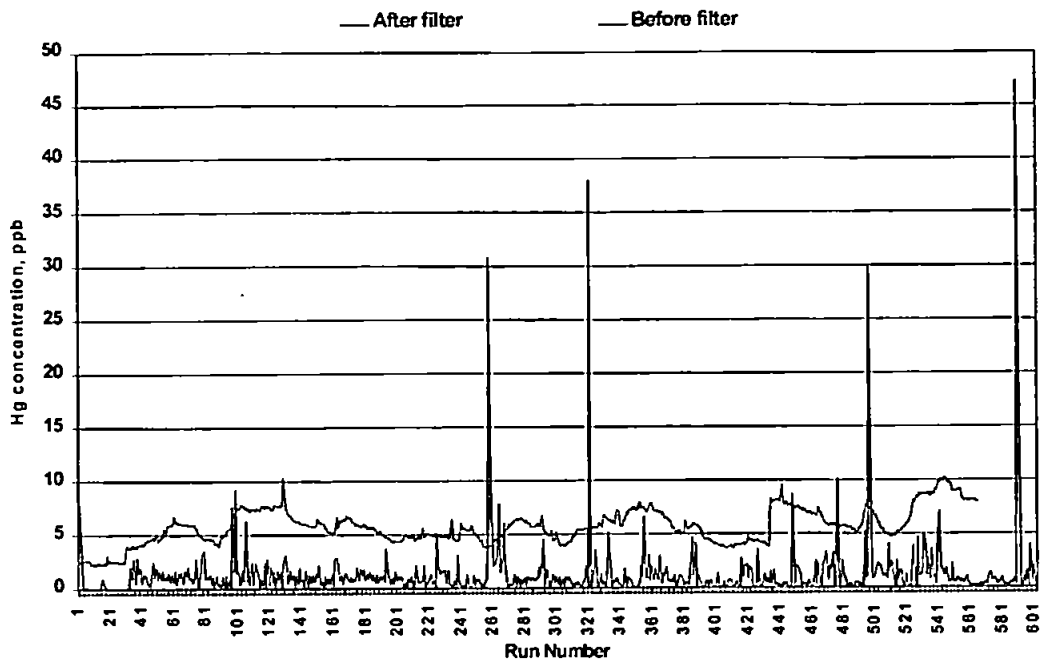


Figure 3.16. Variation of inlet and outlet Hg concentration from carbon beds

3.5 CONCLUSIONS

The presence of mercury in the incineration industry has been discussed. An on-line mercury detection system has been successfully configured for the determination of mercury in incineration wastewater. The system allows continuous monitoring, 24 hours a day, every day with minimal operator supervision. The off-line chemistries were successfully applied on-line. A robust oxidation method was developed to cater for all forms of mercury that may be present in the sample. Good agreement was obtained using two different oxidation techniques. The standards and reagents were proven to be effective and stable for more than 10 days. The reagent flow rates were adjusted for minimal consumption so the operator would only need to prepare the reagents once a week, thus minimising operator attention. The system is capable of sample collection, preparation, calibration, determination and report generation.

The system provides:

- Complete automation and rapid sampling frequency (every 6 mins) giving the operators a greater degree of confidence, control and compliance over their effluent stream.
- Helps prevent contamination of large batches of effluent.
- Follow trends in processes.
- Full data exporting via a 4-20 mA output to a DCS.
- Up to 16 process streams can be monitored sequentially.
- Automatic calibration and error monitoring system.
- System optimised for minimal gas and reagent consumption along with alarm outputs indicating gas and reagent failure.
- Reagent use kept low allowing weekly reagent preparation.

CHAPTER 4

ON-LINE DETERMINATION OF MERCURY IN SULPHURIC ACID PROCESS STREAMS

4 ON-LINE DETERMINATION OF MERCURY IN SULPHURIC ACID PROCESS STREAMS.

4.1 INTRODUCTION

Sulphuric acid is the world's most important industrial chemical; it is the cheapest bulk acid available in every country in the world. Today, almost all of the world's sulphuric acid is produced using the "Contact process" whereby SO₂ is oxidised to SO₃ by air in the presence of a vanadium (V) oxide catalyst on a silica support.

The SO₂ is obtained either by burning pure sulphur (Equation 4.1) or by roasting sulphide minerals such as iron pyrites or the ores of copper, nickel or zinc (Equation 4.4).



4.1.1 Mercury in sulphuric acid

The presence of mercury in sulphuric acid is due to the association of mercury (II) sulphide (cinnabar) with the sulphide bearing ores. When the sulphide ore is roasted the cinnabar decomposes at 600 °C to produce mercury vapour and sulphur dioxide:



In some production plants the roasted gas is purged through a solution of mercury (II) chloride to form mercury (I) chloride, which precipitates, thus removing the majority of the mercury from the gas.

One would expect that hot sulphuric acid would be strongly oxidising and convert all the available mercury in to mercuric (II) sulphate.

4.1.1.2 Sulphuric acid mercury quality

Sulphuric acid has many industrial applications ranging from fertilizer production to food processing. Acid containing less than 1 mg kg⁻¹ is a standard requirement, while less than 0.5 mg kg⁻¹ is mandatory for sulphuric acid designated for food processing, animal feed production and fertilizer manufacture [80]. In fact, low mercury acid (e.g. containing 0.1 mg kg⁻¹ Hg) often attracts a premium over typical merchant grade acid containing up to 0.5 mg kg⁻¹ mercury [81]. Consequently, acid customers have set stringent quality criteria specifically for mercury that need to be met by their acid suppliers [81].

At present acid process streams at smelting plants are monitored manually several times a day for mercury, whereby a grab sample is collected and analysed on a non-automated system in the laboratory. This is laborious, prone to contamination, and time consuming, the results of which can often take up to a day before the mercury content within the acid is known. In this time several hundred tonnes of acid may have been produced which does not meet the set criteria. In such situations this "contaminated acid" process stream is diverted from its normal storage tank to a poor quality acid storage tank.

Mercury levels in sulphuric acid vary according to the type and origin of the sulphide ore being roasted, however the greatest variation usually occurs after routine plant maintenance. During these shutdown or start up periods where reactor tanks and pipe-works are maintained, sludges and liquors are often disturbed. These disturbances inevitably increase mercury concentrations during

the various stages of the production process and ultimately result in contaminated product acid.

The action level of mercury in sulphuric acid is typically 1.0 mg kg^{-1} ; if the concentration increases above this level then the retail cost of the acid is significantly reduced. If the acid is highly contaminated the manufacturer may have to store the acid until a suitable customer is found, in severe cases the manufacturer will have to pay to have the acid removed.

4.1.1.3 Mercury removal from roast gas

In order to understand the removal process of mercury during the production of sulphuric acid one must first consider the equilibria of mercury (I) and (II). This equilibrium is dependent on an understanding of the redox potentials of the mercury (I) state:



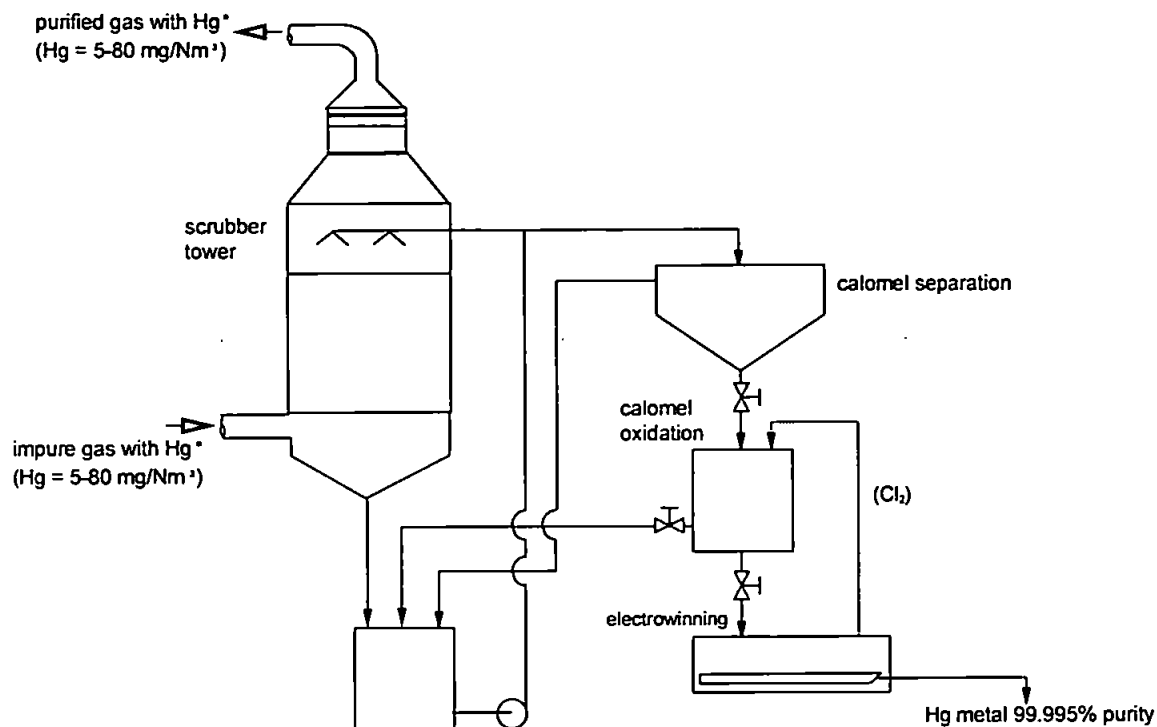
For the disproportion equilibrium:



It can be seen from equation 4.9 that Hg^0 is capable of reducing Hg^{2+} to Hg_2^{2+} , as the electrode potential favours the reverse reaction. However it should also be noted that any removal of Hg^{2+} by precipitation of insoluble Hg_2^{2+} compounds, or by out-gassing Hg^0 , would cause the reaction to proceed in the forward direction. This principle is sometimes used to remove mercury from the roast gas in the contact process. The SO_2 is bubbled through a solution of mercury (II) chloride to form calomel (mercury (I) chloride), which is then removed as a sludge. This process is often referred to as the Boliden Norzink mercury

removal process after the company that designed the process, a schematic diagram of the process is shown in Figure 4.1 [82].

FLWSHEET



WORKING PRINCIPLE

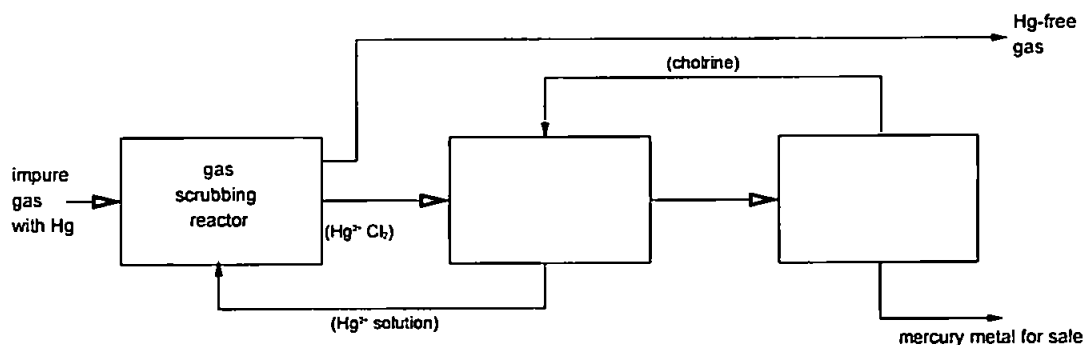


Figure 4.1. Boliden-Norzink removal system for Hg in SO₂ roast gas [82].

Prior to mercury removal by the Boliden Norzink process, the gas must be cleaned by electrostatic filters until visibly clear. The SO₃ mist must be less than 20 mg m⁻³ as SO₃ and the dust should be reduced to less than 1 mg m⁻³. The gas temperature at the entrance to the mercury scrubber should not exceed 40°C.

The scrubber (reaction tower) is installed in the plant directly after the last electrostatic precipitator stage. The gas scrubbing process is based upon the very fast and complete reaction that takes place when metallic mercury vapour comes into contact with mercuric chloride ions dissolved in solution in the gas scrubber.

During this reaction mercurous chloride is precipitated as an insoluble compound suspended in the liquid phase. In order to separate the precipitated calomel, part of the solution that would otherwise have circulated into the reaction scrubber is passed to a small thickener where it settles to the bottom as a heavy sludge. The clarified overflow solution is returned to the circulation unit, while the heavy calomel sludge is passed to a second thickener, together with a certain volume of solution that must be bled from the primary scrubber circuit. A small volume of calomel is removed for further processing. Calomel can be stored, disposed, further refined or converted into mercury metal. The rest of the calomel is passed to a chlorination vessel, where it is oxidised by the addition of chlorine gas to mercuric chloride:



The strong mercury chloride solution from the chlorination stage is transferred to a small feed tank, from which it is dosed into the scrubber reaction system to compensate for the consumption of mercuric ions. The scrubber is designed to clean the gas so that gas leaving the scrubber will have been reduced typically to 0.05-10 mg m⁻³. Although mercury removal rates of greater than 95% are obtained with such processes it is unavoidable that some mercury compounds (Hg⁰, Hg₂Cl₂, HgCl₂) are also transferred with the wet roast gas to the reaction chamber and are present in the final product acid.

4.2 EXPERIMENTAL

4.2.1 Instrumentation

4.2.1.1 *Basic features of at-line system*

An at-line system was specifically designed to determine mercury in liquid samples with full process and data control via an IBM compatible computer. The software allows the operator to fully customise the instrument to suit the application, automatic calibration and analysis protocols can be fully programmed within the software. The unit also employs an error monitoring system which checks for the flow of sample, reagents and gases, as well as for leaks within the system. Should any of the reagents or gases fail to be present an alarm will sound and the instrument shut down. The main components of the system are a stream selection valve, a peristaltic pump, a six port switching valve, a gas liquid separator, an atomic fluorescence spectrometer and a computer fitted with a 4-20 mA DAC output. The instrumental conditions typically used during at-line process analysis are shown in Table 4.1.

4.2.1.2 *Sample collection*

The sample was collected either via a fast loop principle from the flowing process stream or by sub-sampling a constantly replenished over-flow vessel (Figure 4.2). Hence, a fresh representative sample of the process stream was delivered to the instrument with minimum delay and no change in composition.

Table 4.1. Instrumental conditions for PSA 10.223 At-line mercury analyser

Carrier gas = 300ml min ⁻¹ argon Sheath gas = 300ml min ⁻¹ argon Dryer gas = 2500ml min ⁻¹ air
Autozero = On Timer = On Timer interval = 15.00 mins Filter factor (smoothing) = 4 Runs = 1 Fit type = Least squares straight line Gain = 1000 X 4.0 Delay = 120 secs Measure = 150secs Memory = 120secs
Loop size = 300 μ l Sample flow rate = 0.7 ml min ⁻¹ Reductant flow rate = 0.7 ml min ⁻¹

Britannia Zinc Sampling Manifold

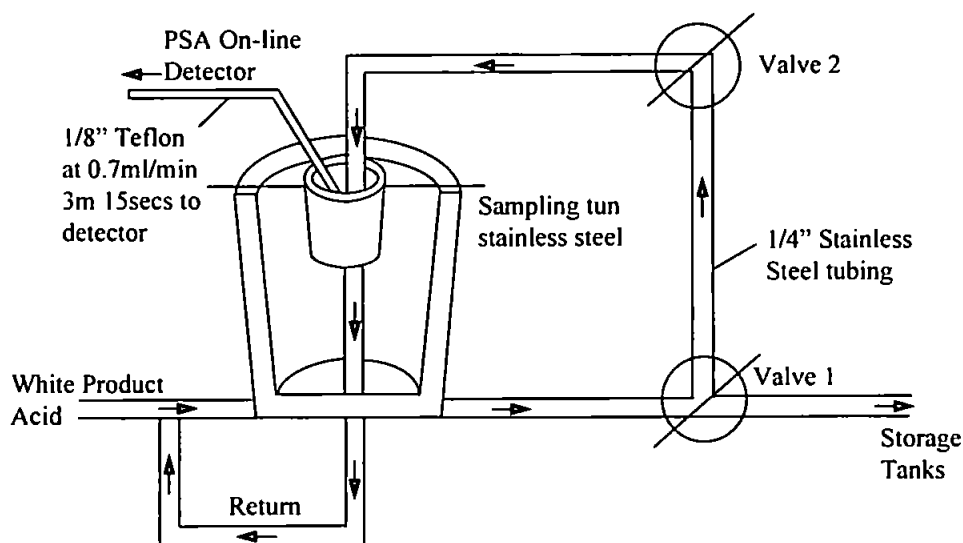


Figure 4.2. Sampling manifold for the collection of laboratory and on-line sulphuric acid samples.

4.2.1.3 *Sequence of events*

With the standard instrument set up shown in Figure 4.3 the stream selection device was fitted with four valves any one of which could be selected at a time. The sample/standard was pumped to a six port discrete injection valve where a fixed volume of the sample was introduced to the mixing manifold. At the mixing manifold chemical pre-treatment was performed whereby the sample was mixed first with an oxidant to convert all the available mercury into the divalent state, Hg^{2+} , then the mercury was reduced to the gaseous phase, $\text{Hg}(0)$ by reduction with tin (II) chloride. The mixing coils were 0.8 mm i.d. and 200 cm long and 150 cm long for the oxidation and reduction respectively, resulting in respective residence times of 86 s and 65 s. The gaseous mercury was stripped from solution using the gas/liquid separator in the presence of a carrier gas, and then passed through a hygroscopic membrane dryer (Nafion, Perma-Pure Products, Farmingdale, NJ, USA). The dried sample gas was then introduced to a fluorescence detector for determination. The detector returned a transient signal which was forwarded to the computer in BCD code, and then transmitted via a DAC output to the process control room through the systems Touchstone[®] software.

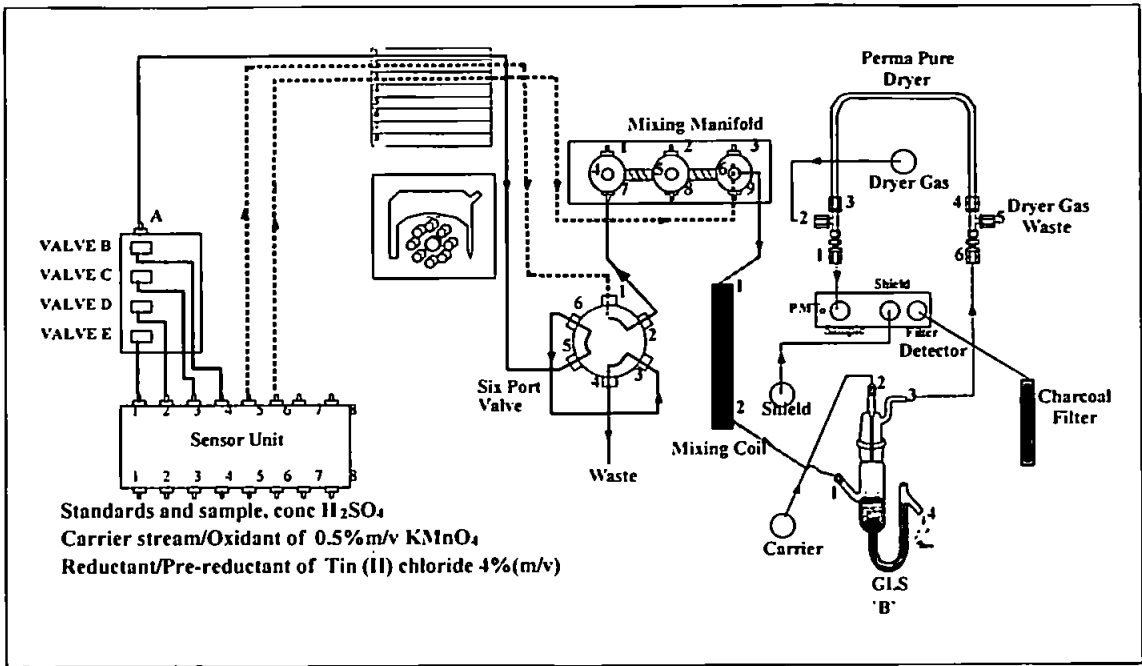


Figure 4.3. Schematic layout of the at-line atomic fluorescence instrument for the analysis of sulphuric acid.

4.2.1.4 Modes of operation

With an analysis program such as that shown in Table 4.2, the instrument can be configured into almost any analysis sequence. The at-line instrument has two modes of operation. The first is when the instrument performs one calibration daily and then analyses the sample repeatedly over the day against that single calibration, which is a feasible mode of operation given the excellent stability of the system, as demonstrated later. The second mode of operation is when the instrument continually re-calibrates itself between each sample.

Table 4.2. Analysis program used for laboratory trials using the bromination chemistry.

Line	Valve	Tag
1	B	Std 1, Blank 10 % (v/v) H ₂ SO ₄
2	C	Std 2, 10 mg ml ⁻¹ Hg "
3	D	Std 3, 50 mg ml ⁻¹ Hg "
4	E	Sample ???mg ml ⁻¹ (Sample, 10%v/v)
5	E	Sample ??? mg ml ⁻¹ (Sample, 10%v/v)
6	E	Sample ??? mg ml ⁻¹ (Sample, 10%v/v)
7	E	Sample ??? mg ml ⁻¹ (Sample, 10%v/v)
8	A(off)	Time-loop back to line 1

4.2.2 Reagents

Standards were prepared using a mercury (II) stock solution (SpectrosoL[®], BDH, Poole, UK) in both 10% (v/v) and concentrated sulphuric acid (AnalaR[®], BDH, Poole, UK). The reductant was prepared from tin (II) chloride dihydrate (AR, Aldrich, Gillingham, UK), a 4% m/v solution was prepared in 30% v/v HCl, (AR, Fisons, Loughborough, UK). The reductant was purged with argon (Pureshield[®], BOC, Guilford, UK) for approximately 20 minutes in order to remove any residual mercury vapour. The oxidant was either a 0.1M potassium bromate/potassium bromide solution (ConvoL[®], BDH, Poole, UK) or 5.0% m/v solution of potassium permanganate (SpectrosoL[®]- low in Hg, BDH, Poole, UK) in de-ionised water (Option 3, Elga, High Wycombe, UK).

4.2.3 Method Development

To determine the efficacy of various oxidation methods the following sample pre-treatments were performed:

- a) To analyse the sample at different dilutions, without any oxidation stage using the standard additions approach. Omitting the oxidation stage produces a Hg(0) and Hg(II) result only because Hg(I) will not be readily reduced to Hg(0).
- b) To analyse the sample using the proposed two oxidation methods, again with the standard additions approach (at 1 and 10% dilutions). Oxidising the sample will produce a total mercury result.

The acid sample was first analysed without any oxidation at a dilution of 1% and 10% v/v. Mercury standards were prepared in the same matrix at 20, 40 and 60 ng ml⁻¹ Hg. Next the sample was analysed using potassium bromate/bromide as the oxidant. To each acid cleaned 100ml volumetric flask 2ml of 0.1M potassium bromate/bromide solution was added. Standard additions was again employed at the same level as before (20, 40 and 60 ng ml⁻¹ Hg). Each flask was then diluted to the mark with either a 1% or 10% solution of the acid sample. The flasks were then left to stand for approximately 20 minutes. Prior to analysis each flask was pre-reduced with a few drops of hydroxylamine hydrochloride to convert the excess bromine to bromide. The samples were then analysed in the same manner as the un-oxidised sample. Instrumental conditions are shown in Tables 4.2 and 4.3.

Last, the samples and standards were prepared according to the same method as for bromination, except for the bromate/bromide was replaced with 5.0 ml of 5.0% m/v KMnO₄ solution as the oxidant.

Table 4.3 Instrument settings for PSA 10.023 Merlin detector and PSA 10.004 vapour generator used for laboratory analysis.

Carrier gas = 300 ml min ⁻¹ argon Sheath gas = 300 ml min ⁻¹ argon	Dryer gas = 2.5 l min ⁻¹ air Filter factor (smoothing) = 32
Sample/blank flow rate = 8.0ml/min Reductant flow rate = 4.0ml/min	Delay = 10secs Rise = 30 secs
Amplification = 1 X 7.5 = 7.5 (1-10,000)	Measure = 30secs Memory = 60secs

4.3 RESULTS AND DISCUSSION

4.3.1 Method Development

The results for the oxidised and un-oxidised sample are shown in Table 4.4. These results suggest that around 50% of the mercury in the sample is likely to be present as mercury (I). The 1% v/v dilution gave exactly the same value as that of the 10% v/v solution (10.5 µg ml⁻¹ Hg) suggesting that the sulphuric acid did not cause a matrix interference on the mercury determination.

The bromination pre-oxidation resulted in a mercury concentration of 17.6 µg ml⁻¹ Hg which was 92% of the manufacturers value (Table 4.4). This was probably due to the oxidation of Hg (I) to Hg (II), or by the removal of other interfering species by oxidation. The potassium permanganate pre-oxidation resulted in higher recoveries than those obtained without oxidation, with a mercury concentration of 18.1 µg ml⁻¹ (Table 4.4) being obtained, which was similar to that obtained by the bromination technique.

Table 4.4. Results of the comparison of oxidation sample pre-treatment methods

Oxidation pre-treatment method	Hg concentration in conc H ₂ SO ₄ (µg ml ⁻¹)		Recovery
	This work	Manufacturers value	
10% sample, no oxidation	10.4 ± 0.04	19.0 ± 1.0	54
1% sample, no oxidation	10.5 ± 0.05	19.0 ± 1.0	55
10% sample, Br ⁻ /BrO ₃ ⁻ oxidation	17.6 ± 0.06	19.0 ± 1.0	92
10% sample, KMnO ₄ oxidation	18.1 ± 0.03	19.0 ± 1.0	95

The results of the off-line investigations indicated that it was necessary to pre-oxidise the sulphuric acid sample in order to obtain close to 100% recovery for Hg. It is probable that pre-oxidation converted the Hg (I) species to the Hg²⁺ ion, which is readily reducible with an acidic solution of tin (II) chloride. It would appear that around 50% of the mercury present in the sulphuric acid sample was present as a Hg (I) salt, most probably Hg₂SO₄.

The next stage was to transfer the chemistries and the sample to the PSA 10.223 at-line mercury analyser for further development.

4.3.2 Laboratory Trial

The at-line monitoring system was initially tested in the laboratory using a grab sample of concentrated sulphuric acid from a zinc smelting plant which was diluted to 10% v/v. During this trial the tests were performed using an acidified solution of potassium bromate/bromide as the oxidant. Figure 4.4 shows the results of continual re-calibration and analysis. This resulted in a relative standard deviation (RSD) of 1.36% for the sample and less than 8.0% for the standards

over the test period of 36 hours. In three instances the sample peak height was greater than that of the top standard. The greatest variation appeared to be in the blank solution which was 10% v/v sulphuric acid, which may have been due to carry-over from the top standard.

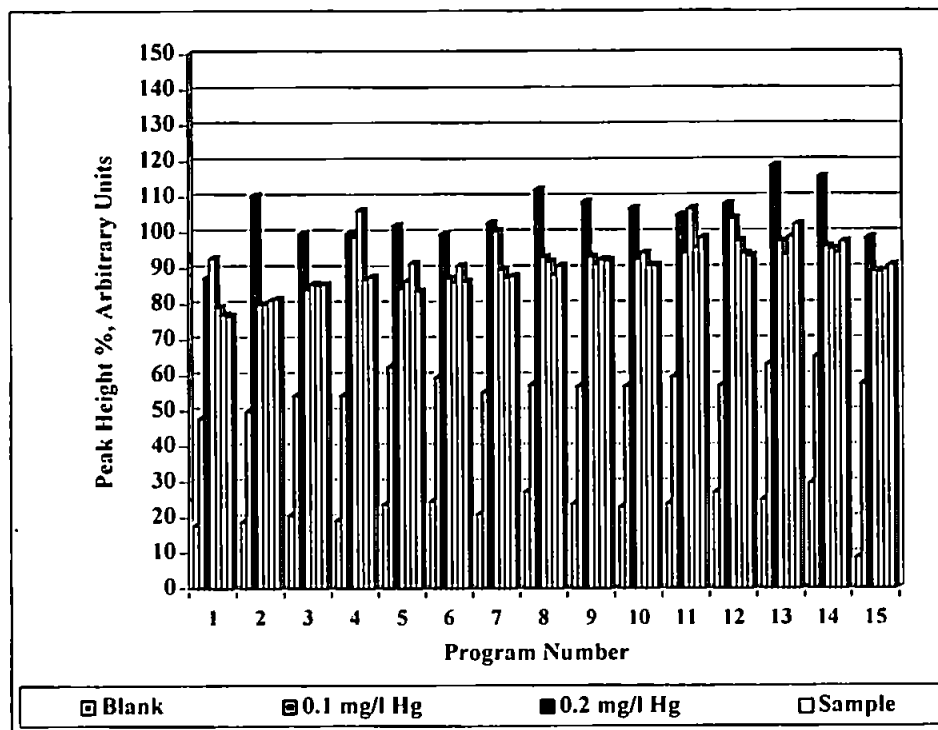


Figure 4.4. Graph showing the variation in peak height % in the continuous re-calibration mode.

It had previously been necessary to add hydroxylamine hydrochloride after the pre-oxidation stage in order to reduce excess oxidant, however, this was also eliminated by increasing the concentration of the tin (II) chloride solution from 2% to 4% m/v so that it was in excess. Sample dilution was further reduced by using the oxidant stream as the sample carrier stream. These changes also improved the signal to noise ratio. The bromination oxidation gave rise to a noisier signal than the permanganate oxidation, so it was decided to use the latter method for the site trials.

4.3.3 Off-line Site Trial

Having configured the system as described above, and using permanganate as the pre-oxidant, it was installed at a zinc smelting plant. Two separate production streams of sulphuric acid required monitoring for mercury, namely the final product 'white' acid, and the un-bleached 'black' acid, the black colour being caused by carbon in the sulphur dioxide gas used to produce the acid.

4.3.3.1 Continuous recalibration mode

A single sample of concentrated 'white' sulphuric acid was obtained from the production line and analysed continuously for 15 hours (36 analyses) using the at-line system operated in continuous recalibration mode, as shown in Figure 4.5. This sample was also analysed using laboratory based cold vapour atomic absorption spectrometry (CVAAS) for comparison. Mean results are shown in Table 4.5 and excellent agreement was obtained with the laboratory result. The standardisation procedure was also very stable with the $0.543 \mu\text{g g}^{-1}$ Hg and $1.358 \mu\text{g g}^{-1}$ Hg standards giving RSD's of 3.2% and 7.3% respectively. The instrument was calibrated ten times over the analysis period.

Table 4.5 Comparison of continuous mercury analysis with batch mode analysis for off-line site trial.

	Hg concentration ($\mu\text{g g}^{-1}$)	
	Continuous AFS	Laboratory CVAAS
Continuous recalibration	1.08 ± 0.1 (n= 36)	0.95
Daily calibration	1.11 ± 0.06 (n=77)	1.2

Hg concentration / $\mu\text{g g}^{-1}$

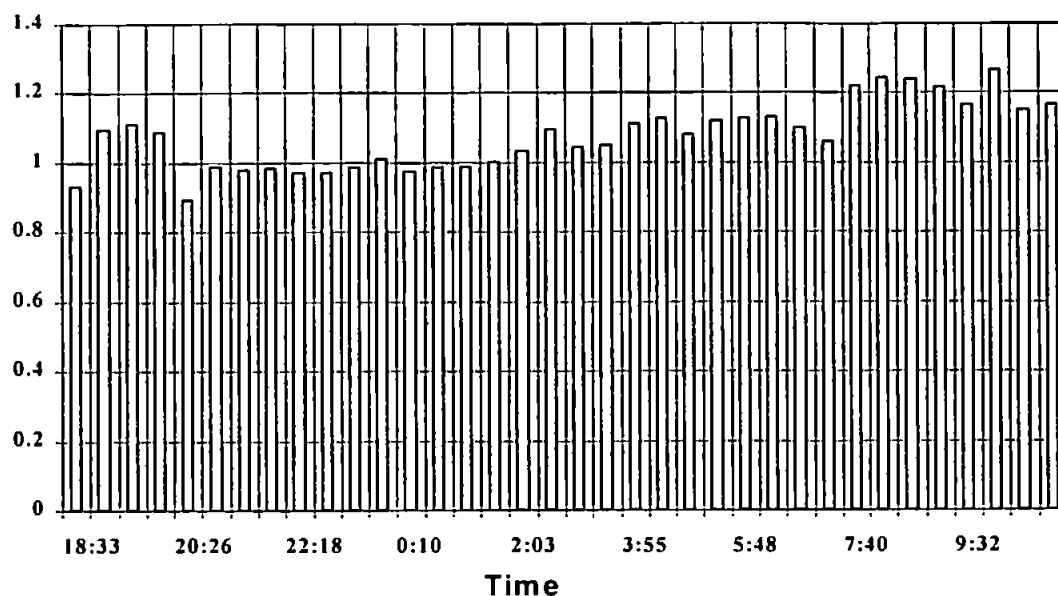


Figure 4.5 Results of off-line site trial for the determination of Hg in 'white' sulphuric acid showing the stability of the instrument when using the continuous re-calibration mode.

4.3.3.2 Daily Calibration Mode

The stability of the system was also tested by calibrating the unit once at the start of the day, then analysing a single sample of concentrated 'black' sulphuric acid repeatedly for 24 hours. Results of the continuous analysis are shown in Figure 4.6 and illustrate the excellent stability of the unit in this mode of operation. Mean results are shown in Table 4.5, and show that the sample concentration varied less than 6% over 24 hours and 77 repeat analyses. Also, excellent agreement between the continuous and laboratory systems was obtained.

Hg concentration / $\mu\text{g g}^{-1}$

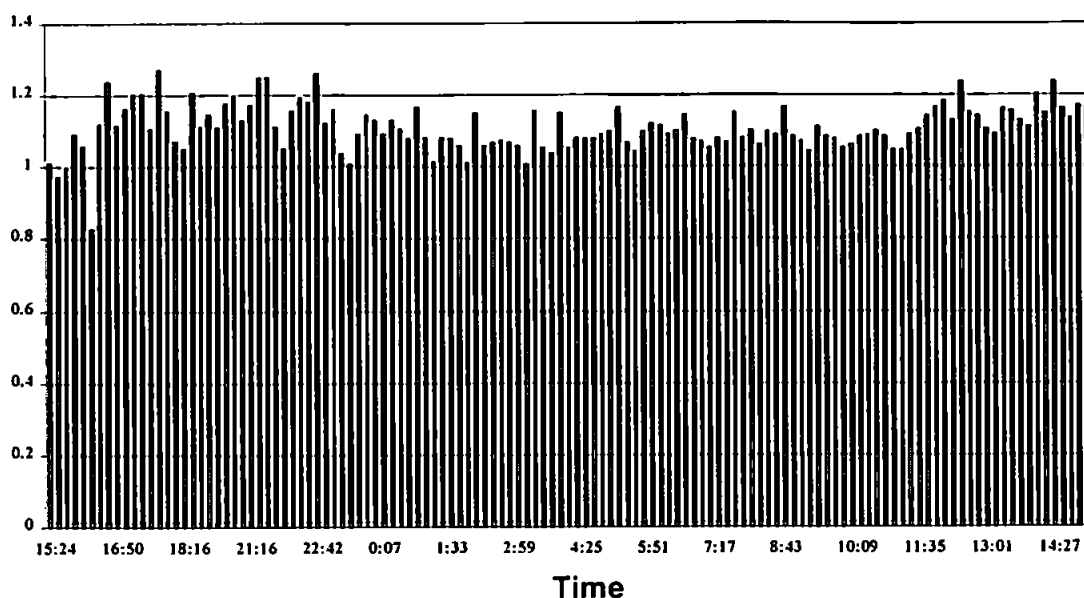


Figure 4.6. Results of off-line site trial for the determination of Hg in 'black' sulphuric acid using the daily calibration mode

4.3.4 At-line Site Trial

The system was now set up at-line, i.e. connected to the production stream for continuous monitoring and the concentration of Hg in both 'white' and 'black' acid production streams. The instrument was calibrated over a 50 minute period, then 5 determination of Hg concentration were made at 9 minute intervals, after which the cycle was repeated. Results for Hg concentration over a ten day period are shown in Figure 4.7. It is evident from the results that the concentration of Hg in both 'white' and 'black' acid streams followed a similar trend, with peaks in concentration occurring between runs 37-67 and 130-170 respectively. The regions of blank data between runs 67-70 and 60-62, for the 'white' and 'black' acids respectively, represent periods of plant shut-down.

During the ten day period only 8 laboratory analyses were performed for each of the production streams. These results are shown in Table 4.6 alongside the results obtained with the at-line monitoring system, and excellent agreement

was obtained. During the monitoring period the Hg concentration in the product acid rose above the 1 $\mu\text{g ml}^{-1}$ action limit during the peaks shown in Figure. 4.7. These peaks could be identified much earlier using the at-line monitoring system allowing the acid to be diverted to a low grade holding tank until the Hg concentration dropped back below the action level. This illustrates two of the major advantages of continuous at-line monitoring as follows:

1. It is possible to identify the trend in Hg concentration, thereby allowing action to be taken much earlier than if only single grab samples were analysed once every day.
2. Results were obtained in real time rather than the five-hour delay typical of laboratory analyses.

Table 4.6. Comparison of data for Hg concentration in white sulphuric acid, obtained with the at-line continuous monitoring system and data obtained by off-line laboratory batch analyses.

Sampling Time ^a	Hg concentration ($\mu\text{g g}^{-1}$)	
	At-line analysis	Off-line laboratory analysis
21/09/96	1.25	1.3
22/09/96	0.64	0.6
23/09/96	0.61	0.6
24/09/96	0.58	0.6
25/09/96	0.75	0.8
26/09/96	0.70	0.8
27/09/96	0.56	0.5
28/09/96	0.64	0.6

^a Off-line laboratory samples were taken at 6.30 am and at-line samples at either 6.20 am or 6.40 am.

Finally, Figure 4.8 shows longer term data obtained over a three-month period. Once again excellent agreement was obtained between laboratory and on-line measurements. The system was proved effective for the on-line

determination of mercury in concentrated sulphuric acid process streams, giving the process operators a greater degree of confidence and control over their production process.

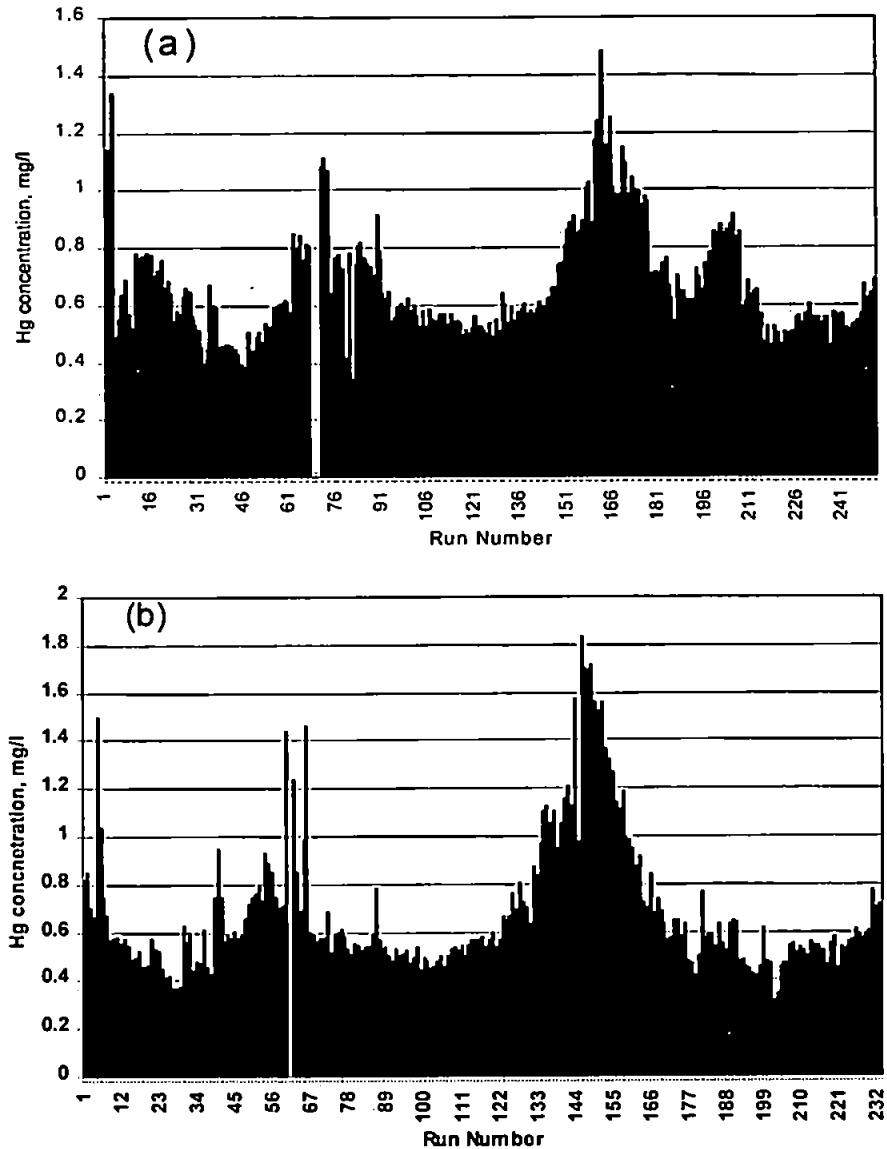


Figure 4.7 Results of at-line site trial with continuous monitoring of the sulphuric acid production stream showing the variation in the concentration of Hg in: (a) 'white' acid; (b) black acid; over a ten day period

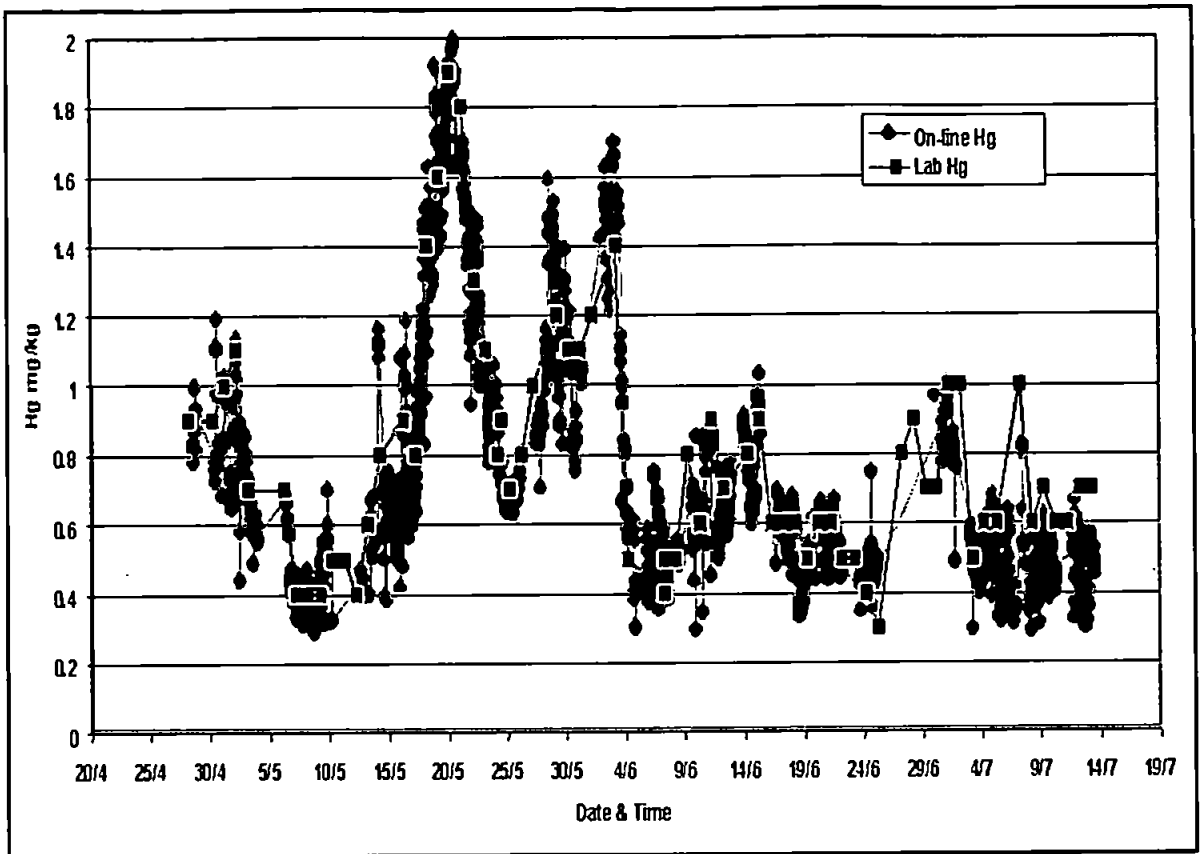


Figure 4.8. Longer-term data obtained over a three-month period from a U.K. zinc smelting plant. Green points indicate the mean of 120 on-line measurements whilst black points represent manual daily laboratory analysis

4.4 CONCLUSIONS

The at-line mercury detection system was successfully configured for the determination of mercury in concentrated sulphuric acid. The off-line chemistries were successfully applied at-line. A robust oxidation method was developed to cater for all forms of mercury which may be present in the acid. Good agreement was obtained using two different oxidation techniques. The permanganate technique was chosen over the bromination oxidation as it requires fewer reagents and minimises instrument signal noise.

The systems components proved resistant to attack from concentrated acids. The standards and reagents were proven to be effective and stable for more than 10 days. The reagent flow rates were adjusted for minimal

consumption so the operator would only need to prepare the reagents once a week, thus minimising operator attention.

The sample collection manifold also proved effective for the delivery of a fresh representative sample of hot sulphuric acid to the instrument. The extreme weather conditions experienced (-12°C) did not appear to effect the instruments performance in any way. Very good agreement with laboratory results utilising CVAAS was obtained from the at-line AFS system. The system was proved effective for the at-line determination of mercury in concentrated sulphuric acid process streams, giving the process operators a greater degree of control of their production process.

CHAPTER 5

THE DETERMINATION OF MERCURY IN NATURAL GAS PROCESS STREAMS

5 THE DETERMINATION OF MERCURY IN NATURAL GAS PROCESS STREAMS

5.1 INTRODUCTION

Natural gas and its liquid condensates are a primary feedstock for a variety of industrial processes. Consequently, the presence of mercury is not just of environmental concern but also has significant economic implications. Heavy financial losses can be incurred by mercury corrosion of aluminium surfaces and catalyst poisoning of steam cracking units [83].

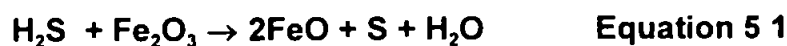
The determination of mercury in natural gas was not routinely performed before the 1980's. The costly consequences of undetected mercury led to several expensive plant shutdowns due to corrosion of aluminium cryogenic equipment. Examples can be found in Holland, Algeria, Indonesia, Malaysia, Thailand and the United States. In addition, the upgrading of natural gas condensates by steam cracking has led to severe mercury poisoning of downstream palladium olefin hydrogenation catalysts, especially in European and North African condensates [84].

The implication of the effects of mercury in natural gas were not reported until 1973, when catastrophic failures of aluminium heat exchangers occurred at the Skikda liquid natural gas (LNG) plant in Algeria [85]. Investigations revealed that mercury corrosion caused the failure, and that the mercury source was accidental, most probably from pressure testing instruments on site. After the Skikda failure, further tests in the Groningen field in Holland revealed similar corrosion in gas gathering systems, with mercury levels ranging from 10 ng m⁻³ to as high as 80 µg m⁻³.

5.1.1 Implications of mercury in natural gas

Mercury associated problems begin at each gas producing well. The investment required and the remote nature of well sites prohibit the installation of *in-situ* mercury removal systems. As a result, mercury is introduced into the well-bore and gathering systems simply by gas production. Mercury can also be introduced accidentally by pressure testing equipment incorporating mercury type bellows.

As mercury accumulates in the pipelines, its concentration in the natural gas is reduced due to chemisorption onto the steel pipe walls. Lepper [86] suggests the following reactions for the reduction of mercury levels in a pipeline:



Trace amounts of H₂S catalyse the reaction of mercury with the steel pipe. The mercurous sulphide precipitates and is adsorbed onto the pipe wall. Grotewold *et al.* [87] reported that for one 68-mile pipeline the mercury concentration decreased from 50 to 20 µg m⁻³ along the length of the pipe. Pipe wall smoothness and adhesive forces influenced its reduction. Similar reductions are also experienced in pipes and vessels at the refineries and processing plants.

Organomercury species can condense into the liquid phase of hydrocarbons and gas treating chemicals due to their higher solubility in higher molecular weight streams. In most gas processing installations there is a separation or dehydration stage. Grotewold *et al* [87] reported that some 50-60% of the inlet mercury accumulates at the bottom of the glycol absorber and that 15-20% is separated in the scrubbers, leaving 20-35% to enter the plant

and pass down into the stream processing equipment and/or transportation pipelines.

Mercury contamination is considered to be a “critical severity” risk with a “frequent to probable” probability of occurrence [88]. Safety management in the design and operation of gas, LNG, refinery and petrochemical facilities, which operate on mercury tainted feeds, strongly recommend the implementation of mercury removal systems to lower the risk factor. Two operational factors that favour mercury removal are catalyst poisoning and equipment corrosion.

5.1.1.1 Catalyst deactivation by mercury

Mercury has been found to be responsible for many cases of selective hydrogenation catalyst deactivation. Palladium based catalysts are commonly used for the selective hydrogenation of acetylenic species in the steam cracking of C₂ to C₄ cuts.

Low levels of mercury can be present in a wide range of boiling points in a steam cracker feed condensate. During the cracking process the mercury is concentrated into the lighter fractions of the cracker effluent. For example, one particular European petrochemical manufacturer using a North African condensate had the cycle length of the C₃ hydrogenation catalyst shortened from the expected lifetime of 1000 days down to just 30 days. The mercury content of the cracker feed was found to be less than 60 ng g⁻¹, which caused sintering of the palladium catalyst. The deactivation of the catalyst along with its shorter lifetime was also accompanied by the subsequent contamination of the catalyst regeneration gas [89].

5.1.1.2 Mercury Corrosion

Mercury is known to be the cause of corrosion problems with aluminium-based heat exchangers, rotors and condensers at natural gas refinery plants. Currently there are at least seven heat exchangers in service that are operating with mercury-induced leaks [90]. Heat exchanger replacement is a costly operation due to the capital investment of the exchanger itself and the plant downtime incurred for its replacement. Two types of mercury-induced corrosion are known: mercury induced stress cracking and mercury catalysed oxidation of aluminium by water.

5.1.1.2.1 Mercury induced stress cracking

Probably the most notorious case of mercury induced stress cracking occurred in 1987 at an ethylene plant in Alvin, Texas. Here the plant experienced a 20cm diameter piping rupture, attributed to liquid mercury embrittlement of the aluminium heat exchanger [90] (Figure 5.1).

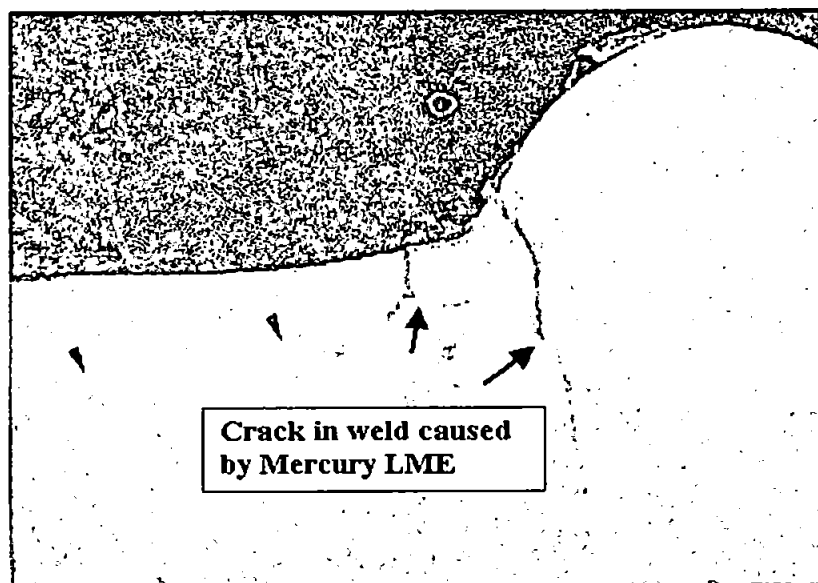
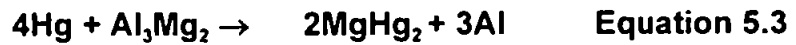


Figure 5.1 Photograph of a typical weld crack caused by liquid mercury embrittlement [89].

Aluminium is the predominant choice for cryogenic service due to its brazeability, excellent mechanical properties at low temperatures, and superior

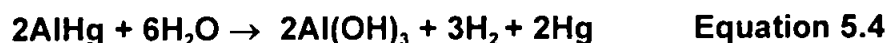
heat transfer characteristics. Brazed aluminium heat exchangers are composed of a magnesium-rich phase at the metal grain boundaries caused by precipitation during welding. When liquid mercury is brought into contact with this anodic phase, dissolution occurs by equation 5.3:



The dissolution of the grain boundary is rapidly accelerated if any stress is applied to the attacked region. Stress cracking occurs by the propagation of a crack from the point of mercury attack on the magnesium rich phase through the connecting grain boundaries. Laboratory testing can consistently produce liquid metal embrittlement in aluminium 5083 welds with as little as 47 mg of mercury [90]. Figure 5.1 shows a photograph of a typical weld crack caused by liquid mercury embrittlement; this is the most common type of mercury corrosion and does not require the presence of water.

5.1.1.2.2 Mercury catalysed oxidation of aluminium by water

The oxidation of aluminium by water is a highly exothermic process. However, this reaction does not normally proceed due to the formation of a protective layer of aluminium oxide on the external surface of aluminium. Small fissures in this protective layer render the clean metal surface susceptible to local oxidation by water. When metallic mercury is present on the clean metal surface, aluminium diffuses from the mercury aluminium interface into the mercury droplets and is rapidly converted to Al_2O_3 on the outer surface of the droplets. By this mechanism, metallic mercury bores holes into the aluminium surface leaving "whiskers" of grey Al_2O_3 .



Operating conditions conducive to corrosion of cryogenic aluminium heat exchangers include derimming and shutdown. Derimming is a heat cycle

process on the exchangers that removes “frost” (ice, hydrates and solid CO₂) build-up from exchanger internals. To melt the frost the exchanger is normally taken off-line and hot dry gas passed through the unit. The hot gas melts the frost and purges out moisture and impurities. Derimming is periodically necessary in order to improve exchanger efficiencies due to frost accumulation.

Shutdown occurs when no gas is passed through the system, heat exchange can no longer take place and the exchanger is warmed to ambient temperatures. The metal corrosion rate can be reduced if the temperature is maintained below the melting point of mercury, -39 °C [91].

Derimming and shutdown frequency should be kept as low as possible in order to minimise the potential for a corrosive environment. Liquid water can be present during both of these operations. When the thaw gas is passed through the exchanger or when operations are resumed, gas containing trace amounts of mercury are allowed into contact with the aluminium in an aqueous environment so that mercury induced stress cracking can take place.

Although elemental mercury has a very high boiling point compared to that of its organometallic species, mercury present in natural gas is believed to be almost exclusively in the metallic form, although some more volatile organomercury compounds such as dimethylmercury may be present (Table 5.1).

Table 5.1 Boiling points of various mercury species [92]

Species	Boiling Point °C
Hg	357
(CH ₃) ₂ Hg	96
(iC ₃ H ₇) ₂ Hg	170
(C ₃ H ₇) ₂ Hg	190
(C ₄ H ₉) ₂ Hg	206

5.1.1.3 Nature of mercury species in condensates.

By contrast, mercury present in condensates associated with the natural gas may be in various forms, (elemental, organometallic, organohalide and inorganic salts) depending on the origin of the condensates [91].

Sarrazin *et al.* [91] showed that after steam cracking, mercury is redistributed into all of the hydrocarbon cuts, the C₃ and C₄ cut having the highest contamination with approximately 90-95% of the total mercury exiting the distillation column, as shown in Figure 5.2. About 75% of the mercury entering a steam cracker unit is not found in the hydrocarbon products, but rather contaminates the internal walls of the unit. When this mercury comes into contact with a clean mercury-free feedstock, the product will be rendered mercury rich. Furthermore, when the raw mercury containing feedstock or one of its cuts are transported to another site the transport vessel will inevitably become a source of mercury contamination.

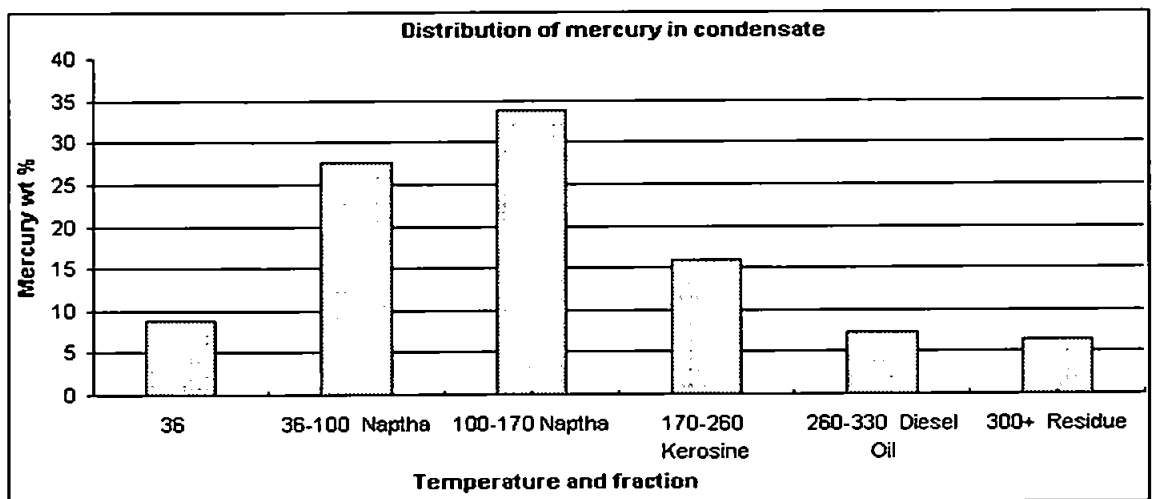


Figure 5.2. The distribution of mercury in a SE Asian condensate [91].

5.1.1.4 Mercury removal systems

Although significant amounts of mercury are removed from natural gas by surface adsorption or by condensation, concentrations should be reduced

further before the gas enters cryogenic process equipment. There are a variety of methods utilised for mercury removal from natural gas. For efficient mercury removal the medium must have a high capacity for active binding of mercury in a form in which it can be safely disposed of or regenerated. The media must be capable of operating at the high temperatures and pressures of natural gas streams, must have reasonable investment and operating costs and finally be readily available.

Mercury removed by sulphur-impregnated activated carbon has been commercially used since the 1970's. This is probably the most effective and economical method for treating high volume gas streams. Muchilis [93] reports mercury reductions from $200 \mu\text{g m}^{-3}$ in the inlet gas of the removal beds down to less than $1.0 \mu\text{g m}^{-3}$ in the outlet gas.

Sulphur impregnated carbon has a minimum sulphur content of 10%. The beds can obtain a full mercury loading of 0.625 Kg per Kg of adsorbent, although saturation of this level is not normally experienced in the field. Changes in system pressure or inlet mercury concentration have little effect on bed performance, but increases in gas pressure can decrease bed-scrubbing efficiency. Frequent monitoring of the removal beds is therefore an essential requirement in order to prevent breakthrough and subsequent damage to downstream plant equipment.

5.1.2 Mercury sampling techniques

Sampling of gas streams for the determination of mercury has traditionally been performed in one of three ways:

1. The gas sample is collected in a sample bomb for later analysis,
2. The gas stream can be pressure regulated to pass into a trapping solution,

3. The gas stream can be pressure regulated to pass directly over a sample collection trap.

In each case the sampling point should be representative of the gas being analysed, this should therefore consider Joule-Thompson effects of adiabatic gas expansion and temperature inversion.

5.1.2.1 Joule -Thompson Effects

A typical pressure-temperature phase envelope for a dry natural gas sample is shown in Figure 5.3. Phase diagrams are frequently used to predict the temperature required to keep the natural gas above the dew point and prevent 'heavy' hydrocarbon condensation.

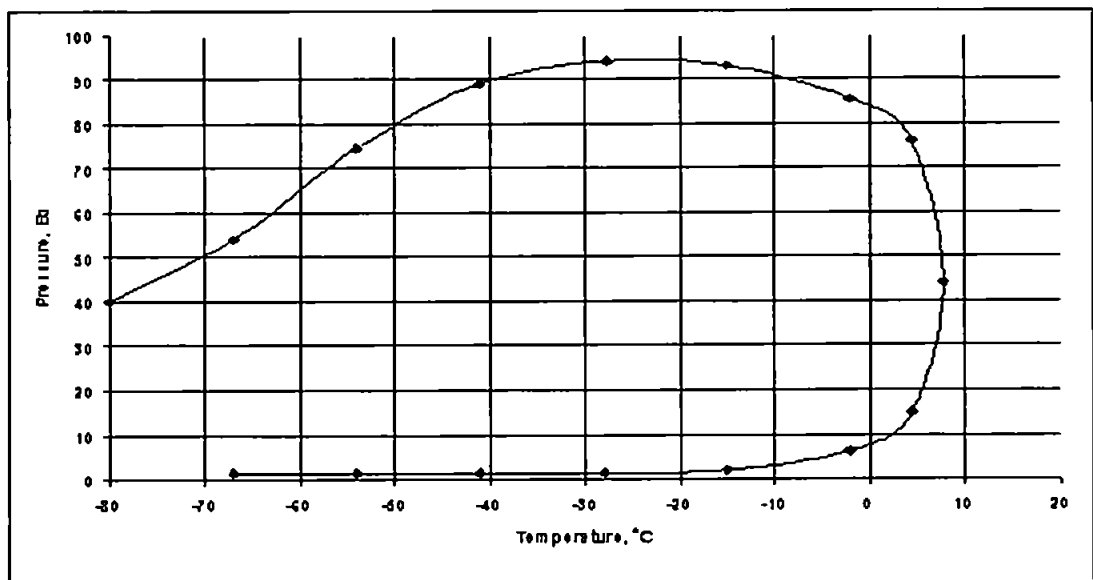


Figure 5.3. Phase envelope diagram for a typical export North Sea natural gas sample.

From Figure 5.3 it can be seen that on upon decreasing the pressure from approximately 100 bar to 1 bar, the associated adiabatic temperature drop leaves the gas at a temperature of -30°C . This is below the dew point of the heavier hydrocarbon fractions that may be present in the natural gas sample.

As the pressure is decreased heavy hydrocarbon cuts are released from the vapour phase and condense as a liquid. Section 5.1.1.1. has already

highlighted the higher affinity of mercury in the heavier hydrocarbon cuts. Thus, the gas sample subsequently collected would not be representative of the sample gas, as it now contains additional mercury which was initially present in the heavier hydrocarbon cuts, thus giving rise to apparently high mercury concentrations within the sample gas.

To obtain a representative sample of natural gas from a high-pressure gas stream, the use of heated regulators, needle valves and sample transfer lines is normally necessary during the pressure letdown stage. Heating elements are used to supply additional heat to compensate for the adiabatic temperature expansions experienced during this Joule-Thompson effect [94]. Using this technique the sample gas at ambient pressures will have the same composition as that at the higher line pressure and will be representative of the natural gas process stream.

5.1.2.2 Sample bombs

The use of pressurised gas cylinders or "sample bombs" is a commonly used technique for collection of natural gas samples. However, caution should be applied to samples collected in bombs. Bombs should be specifically dedicated and clearly labelled for mercury analysis. Only PTFE coated stainless steel bombs stored under positive nitrogen pressure should be used for the collection of mercury samples.

Loss of mercury by surface adsorption on container and cylinder walls can greatly effect results. The larger the transfer vessel (bomb), the larger the ratio of liquid volume to internal wall surface area, thereby reducing the "wall effects" of the cylinder. The transfer vessel should be transferred to the laboratory and analysed as soon as possible after the samples are collected due to rapid sample degradation.

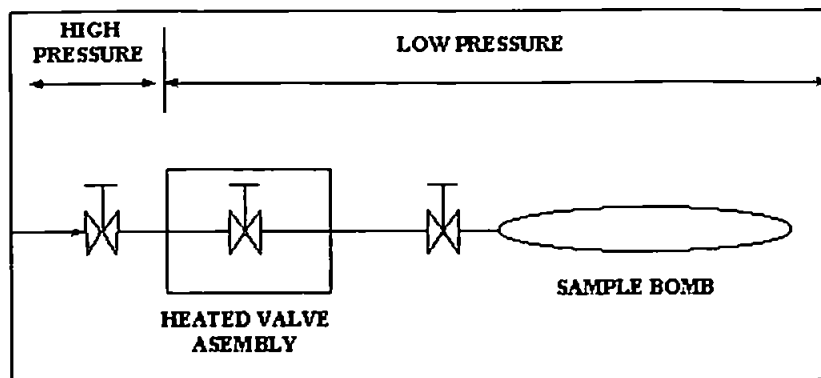


Figure 5.4. Sample collection procedure when using gas cylinders (bombs).

The main problem associated with sampling from cylinders is the poor reproducibility obtained. Mercury concentrations have been found to vary significantly when sampling from bombs. This variability can be attributed to pressure decreases within the cylinder as the gas is released, this in-turn promotes surface adsorption and condensation of heavy hydrocarbons on the walls of the vessel. As high mercury concentrations are often associated with heavier hydrocarbons, apparently high gas concentrations are often encountered. This Joule-Thompson effect can again be minimised by placing the sample cylinder in a heated water bath set at the same temperature at which the sample gas was collected and also using a heated pressure letdown stage. Sampling in this manner from a heated cylinder is already a common technique for hydrocarbon composition analysis and leads to more reproducible results [95]. Other problems associated with sample bombs are their difficulty to transport and also ensuring the bomb is not contaminated from previous samples.

5.1.2.3 Pressure regulated sample streams

The second approach is to regulate the sample stream from its line pressure down to atmospheric pressure, typically from 120 bar to 1 bar. The use of a heated pressure regulator, needle valves and transfer lines will also be

necessary to prevent liquid condensation and/or hydrate formation depending on the gas composition. Once depressurised, the sample is either passed through a Dreschel bottle filled with a trapping solution or over a solid phase trap as shown in Figures 5.5 and 5.6 respectively.

When using such arrangements it is critical that all gas connections and sample lines are made from high quality stainless steel or preferably PTFE, and that the equipment is thoroughly cleaned with dilute nitric acid, flushed with water and then purged with nitrogen prior to sampling.

Sampling equipment should be completely purged of all dead space. A continuous gas purge through the collection equipment should be conducted to ensure fresh representative sampling. Gas samples should always be taken from the top of piping to minimise liquid effects, which can accumulate at the base of pipe bends.

Such sampling points are frequently used for on-line H₂S and chromatography instruments. These sample lines are well pre-conditioned to the sample gas, the sample gas delivered to these instruments is typically fed via a fast loop, heated above the dew point of the gas, is free of moisture and condensates, and is usually located within a temperature controlled environment. Such sampling arrangements are usually located at the last point of gas production, *i.e.* at gas metering skids. At the metering skids total volumetric flow of the "export or sales gas" is performed, thus providing an ideally representative sampling point for mercury analysis.

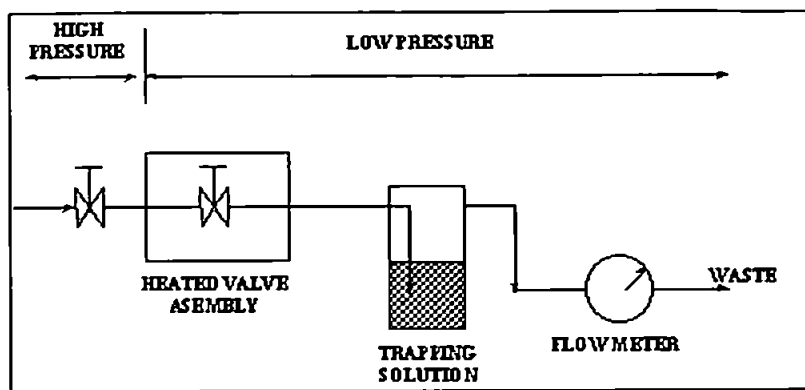


Figure 5.5 Depressurised sample passed through a Dreschel bottle filled with trapping solution.

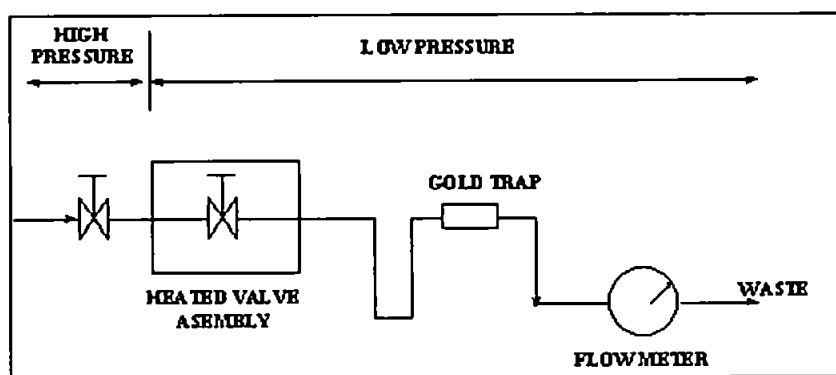


Figure 5.6 Depressurised sample passed over a solid phase trap.

5.1.3 Analysis techniques

5.1.3.1 Atomic absorption spectrometry techniques

The use of AAS detection for mercury in natural gas is an international norm, (ISO 6978:1992) [96]. This method describes two techniques, A and B, for the determination of total mercury in natural gas. The methods are based on two different approaches.

In method A, the sample is passed through a Dreschel bottle filled with an acidic oxidising solution of potassium permanganate (Figure 5.5). The solution traps mercury through the formation of mercury (II) ions prior to determination by cold vapour atomic absorption spectrometry. Methods based on mercury trapping solutions are robust and normally all the mercury present

in the gaseous stream will be collected. The main limitation with this approach is the blank contribution from the reagents used. High blank values are frequently found in the oxidation and reduction solutions. The use of strongly oxidising and acidic solutions also makes this procedure tedious and dangerous in the field.

High reagent blank values [108] and long sample collection times give high detection limits, the lowest detection limit is $0.5 \mu\text{g m}^{-3}$ with a sampling time of 2 hours. These, coupled with the fact that the trapping solution still needs to be analysed in a laboratory resulting in long turn-around times makes this approach unsuitable for frequent mercury monitoring.

In the second approach, method B, the gaseous sample is passed through a quartz tube containing a solid medium to amalgamate and trap the mercury (Figure 5.6). After sampling, the mercury is released by thermal desorption at around $600\text{-}800 \text{ }^\circ\text{C}$ and quantified using AAS detection. The sample tubes can then be easily packaged and sent to the laboratory where the analysis can then be performed.

Since this method is based on the specific absorption of light by atomic mercury at 253.7 nm , signal interference is unlikely. However, organic compounds, water, particulate matter and acidic gases can cause molecular absorption, resulting in abnormally high apparent mercury concentrations [109]. Although such instruments can achieve the required detection levels they are not particularly well suited for field analysis due to their size, weight, power and gas consumption.

5.1.3.2 Atomic fluorescence spectrometry.

The analysis of low-level mercury by atomic fluorescence spectrometry has become a well documented and often more powerful technique than AAS.

The application of AFS for the direct determination of mercury in natural gas however is almost impossible, due to the quenching effects of the fluorescence signal from nitrogen, air and other gases in the sample. However, the effects of quenching can be overcome by preconcentration amalgamation of the mercury onto gold traps as in ISO method B. By trapping the mercury from the sample gas and then releasing it into an inert carrier gas the effects of quenching can be overcome.

The sample gas is passed over a gold trap at a constant flow rate; the total volume passed over the trap is measured by a wet gas flow meter and a stopwatch (Figure 5.6). The remote sample tube is then connected to a thermal desorption module that releases the trapped mercury into a carrier stream of argon. The carrier gas containing the mercury is then delivered to second amalgamation unit that releases the mercury into the atomic fluorescence detector for measurement.

The main advantages of the AFS-preconcentration approach are the ease in which the remote sample tubes can be collected and transported. The traps are also relatively simple to clean and can be used repeatedly. The sample gas matrix also does not enter the AFS detection unit therefore preventing contamination from other species in the gas. The AFS approach also offers excellent accuracy, precision and sensitivity. The main limitation with this technique is the ease in which the trapping media can be contaminated by ambient air.

5.1.3.3 Mercury trapping devices

For the pre-concentration of mercury on solid media, various materials are available, e.g., silver, gold, platinum or a mixture of these with chromatographic packing materials. The noble metals are the most attractive.

Noble metals will amalgamate metallic, Hg^0 and other gaseous and organic forms of mercury such as CH_3HgCl or HgCl_2 [97]. The main problems associated with the amalgamation technique are memory effects. Memory effects are caused by mercury diffusing into the inner layer of the collector material from which it then only slowly desorbs during thermal desorption. These effects are enhanced when the collected sample is not analysed immediately, *i.e.* within hours of the sample collection. In order to reduce these memory effects and also increase the surface area of the collector, traps with noble metals attached to support materials such as silica are frequently used .

The collection and thermal desorption efficiencies of activated charcoal and silver coated and gold coated sand were investigated for the determination of volatile mercury compounds by Dumarey *et al.* [99]. These studies revealed that activated charcoal and silver-coated sand could not be recommended for mercury trapping. Their collection was not quantitative and depended on the sampling flow rate, sampling duration, ageing time of the collector, nature of mercury species and the simultaneous collection of interfering substances. Moreover, the thermal desorption of activated charcoal is not quantitative and memory effects are pronounced. As a consequence, Dumarey suggested that results in the literature using activated charcoal or silver should be regarded with some scepticism.

Gold impregnated silica on the contrary shows a quantitative collection for all volatile mercury species when using a sampling flow rate up to $5.0 \text{ litre min}^{-1}$ (Table 5.2). Dumarey *et al.* [100] has also optimised the composition and the quantity of the packing material to minimise memory effects and optimise peak symmetry for detection using CVAAS. The gold impregnated silica is now

commercially available under the trade name of Amasil™. The material has been packed into specially designed quartz tubes and is also commercially available [101].

The noble metal or support material can be prone to poisoning from concomitant species present in the sample gas, leading to losses of mercury or a reduction in amalgamation efficiency [102]. This is especially true for natural gas, where heavy hydrocarbon condensates condense out of the gas phase during pressure letdown. With the adiabatic expansion of the cold natural gas and the subsequent temperature drop, the dew point of the gas is lowered resulting in condensation of the heavier fractions on the surface of the collector. Condensation and the subsequent deposition on the surface of the collector reduce trapping efficiency and prevent complete thermal desorption. Provided that adequate precautions are taken to prevent condensation, the gold-sand amalgamation technique is the most favourable approach for gaseous mercury preconcentration.

Table 5.2. Collection efficiencies of various mercury vapour compounds at varying flow rates using gold-impregnated sand [102].

Collection efficiencies for mercury compounds on gold impregnated sand, %						
Flow Rate l min ⁻¹	Hg ⁰	HgCl ₂	(CH ₃) ₂ Hg	CH ₃ HgCl	(C ₂ H ₅) ₂ Hg	C ₂ H ₅ HgCl
1.0	99.8 ± 0.3	99.3 ± 0.4	98.9 ± 0.7	99.9 ± 0.4	99.7 ± 0.4	98.8 ± 0.6
2.5	101.0 ± 0.6	99.7 ± 0.6	99.7 ± 0.5	99.1 ± 0.6	100.3 ± 0.6	99.1 ± 0.7
5.0	99.9 ± 0.5	99.8 ± 0.4	99.5 ± 0.4	100.7 ± 0.8	99.9 ± 0.4	99.9 ± 0.3

5.2 DESIGN, OPTIMISATION AND EVALUATION OF THERMAL DESORPTION TRAP

The sensitivity of the fluorescence approach is such that it is possible to directly measure mercury levels in air as they are passed through the system. However, for many applications, where mercury levels are very low some means of pre-concentration prior to detection is necessary to avoid the quenching effects experienced by AFS.

Commercially there are several mercury preconcentration units available. However, until recently their application has been mainly limited to the low-level determination of mercury in natural waters. Instrumentation has been developed allowing the automation of a mercury amalgamation device with a thermal desorption module coupled to an AFS detection system [101]. This system has been commercially used for the sensitive determination of mercury in natural waters and is ideally suited for gaseous mercury monitoring.

The combination of such a preconcentration device with a thermal desorption unit and a sensitive fluorescence detector are the necessary building blocks for a reliable, robust and sensitive instrument to measure mercury in natural gas. The device described here automates the sample collection and thermal desorption stages, along with the replacement of the sample gas with an inert carrier stream of argon to avoid quenching effects. Coupling to a specific atomic fluorescence detector offered increased sensitivity and a more rapid sample collection and analysis response.

The integration of these modular devices is presented. A new approach to both the on and off-line monitoring of mercury in wet natural gas has been developed, along with its application at a gas processing facility.

5.2.1. Trap Design

Temmerman *et al.* [102] designed a trapping system for the collection and preconcentration of mercury prior to measurement by atomic absorption. This provided a simple purge and trap system to remove mercury from the surrounding gas and to transfer it, upon heating, into a carrier gas stream and to the analytical detector. A schematic diagram of a similar device is shown in Figure 5.7.

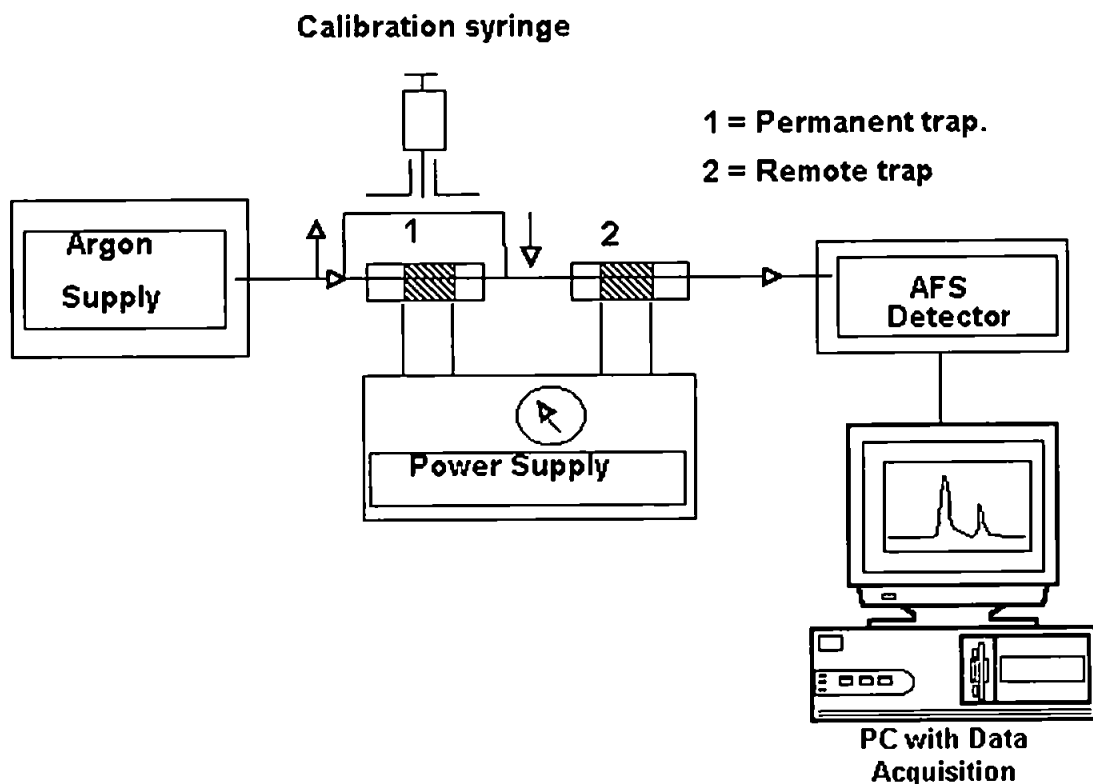


Figure 5.7. Schematic diagram of the basic stages of the analytical set-up.

An absolute calibration procedure developed by Dumarey *et al.* [100] based on the vapour pressure of mercury at a set temperature is used as the basis of calibration. Fixed volumes of mercury vapour are injected onto a permanent amalgamation device for calibration. Upon accurately knowing the temperature and the injection volume a definable quantity of mercury is adsorbed onto the gold-sand trap. The trapped mercury is then re-vaporised

into an AFS detector where a transient signal is recorded either by peak height or peak area, the signal is then integrated and forwarded to a computer in either BCD or RS232 code.

A diagram of the thermal desorption unit is shown in Figure 5.8. Gold-sand traps were constructed from quartz and based on the design of Dumarey *et al.* [100]. At 60 mm from each end two indentations are made in the quartz, at both ends of the indentations a silanised glass wool filter was used to retain approximately 30 mg of gold impregnated sand, (Amasil™, Phase Separations, Cambridge, UK). A length of 10 Ω Nichrome wire was wrapped around outside of the quartz tube where the packaging material was placed. The Nichrome heating wire was connected to a variable transformer, by altering the duration of current the temperature could be varied from 200-700°C allowing the thermal desorption of mercury into the carrier gas and to the detector.

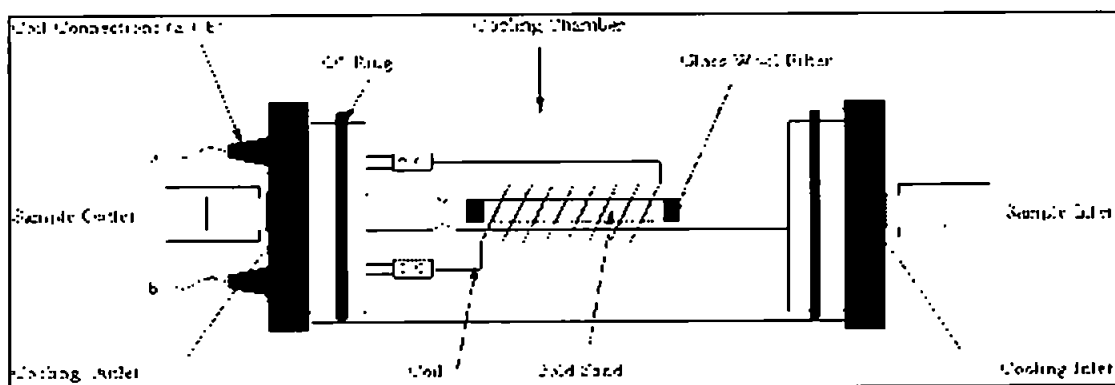


Figure 5.8 Thermal desorption trap

5.2.2. Trap Optimisation

The first experiment performed was to optimise the thermal desorption module; *i.e.* to investigate the temperature at which the adsorbed mercury was released from the amalgam and transferred to the AFS detector to produce a transient signal.

The procedure involved the injection of fixed quantities of mercury vapour into a carrier stream of argon by using a gas tight syringe. The gas was then passed directly over the fixed desorption trap so as to amalgamate the mercury vapour. Once trapped the duration of current across the 10Ω Nichrome wire was varied until a transient mercury signal was observed at the AFS detector. The peak maximum was then recorded as the signal was observed in the fluorescence detector. Figure 5.9 shows each stage of the thermal desorption process.

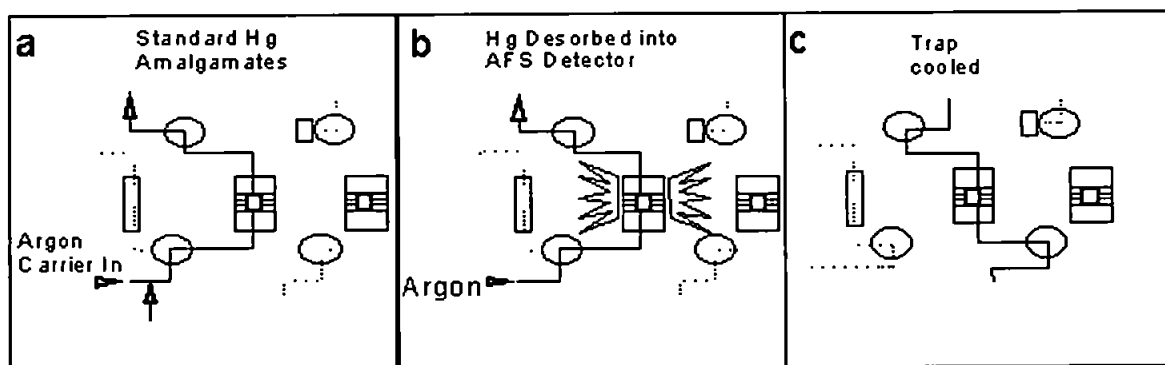


Figure 5.9 Stages of the thermal desorption process

A delay period of 30 seconds was allowed in order to ensure complete retention by the trapping media and also to flush out any residual gases that may be left within the system. When the mercury vapour was injected into the argon carrier stream no breakthrough of the sample was observed, indicating complete amalgamation of the mercury vapour with the gold of the Amasil. If breakthrough occurred this would have been evident at the detector as a signal would be observed.

After the 30 second delay a current was applied across the Nichrome wire. After ~15 seconds of heating the Nichrome wire was at 'red heat' - ~450°C. The results from Figure 5.10 show that the maximum peak height signal was observed after approximately 17 seconds of current being applied,

resulting in a temperature of approximately 540°C before the trapped mercury was released.

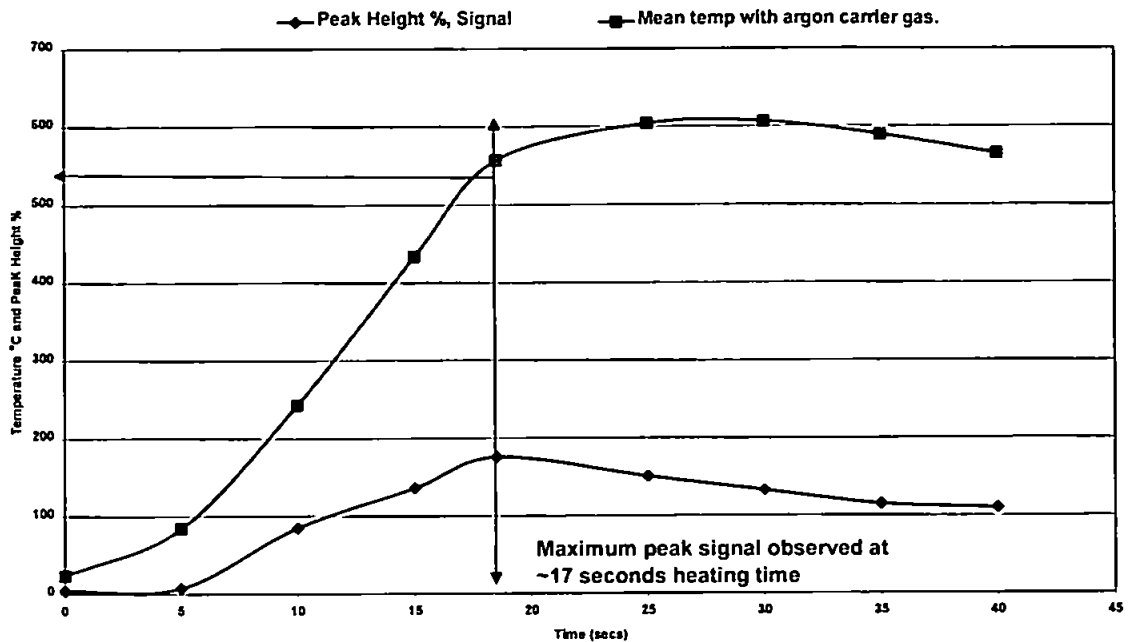


Figure 5.10. The variation of thermal desorption temperature with time as a function of signal peak height.

Heating the trap for more than 20 seconds resulted in elongated peak profiles, with a second 'hump' on the tail of the main peak. These broader signals observed with the longer heating times were attributed to mercury release from within the quartz tube itself. It would appear that the surface bound monolayer of mercury atoms from the sample gas are released rapidly up to ~17 seconds (540°C). At higher temperatures (longer heating times) mercury atoms from the quartz migrate through and along the tube and into the heating zone of the trap. This consequently leads to secondary Hg atoms producing 'tailing' on the main sample peak; this second peak or tail is not representative of the trapped mercury from the sample gas. Excessive heating can also damage the uniformity of the packing material, small pathways can

develop after prolonged heating allowing the sample gas to pass directly through the trap without amalgamation resulting in breakthrough.

The optimal heating time was found to be 17 seconds with an argon carrier gas flow rate of 0.35 l min^{-1} . At heating times between 15-17 seconds the peak profiles were almost symmetrical allowing optimal measurement of both peak height and peak area. Furthermore, after the 15 second heating stage the trap could be rapidly cooled by a stream of compressed air allowing the next sample to be loaded on to the trap.

A typical peak profile for a 14 pg sample of Hg is shown in Figure 5.11. Here a delay time (T1) of 30 seconds was utilised, the baseline during this time period remained flat, indicating complete trapping by the Amasil material i.e. no breakthrough. After the 30 second delay/amalgamation time heating was applied across the trap for 15 seconds (T2). The adsorbed mercury began to release after 12 seconds of heating with the peak maximum occurring at 15 seconds. After the heating stage the cooling gas of compressed air was activated and the trap cooled for 90 seconds by blowing air over the Nichrome wire (T3). The peak shown in Figure 5.11 illustrates the speed at which a remotely collected sample or calibration standard can be desorbed into the AFS detector for measurement.

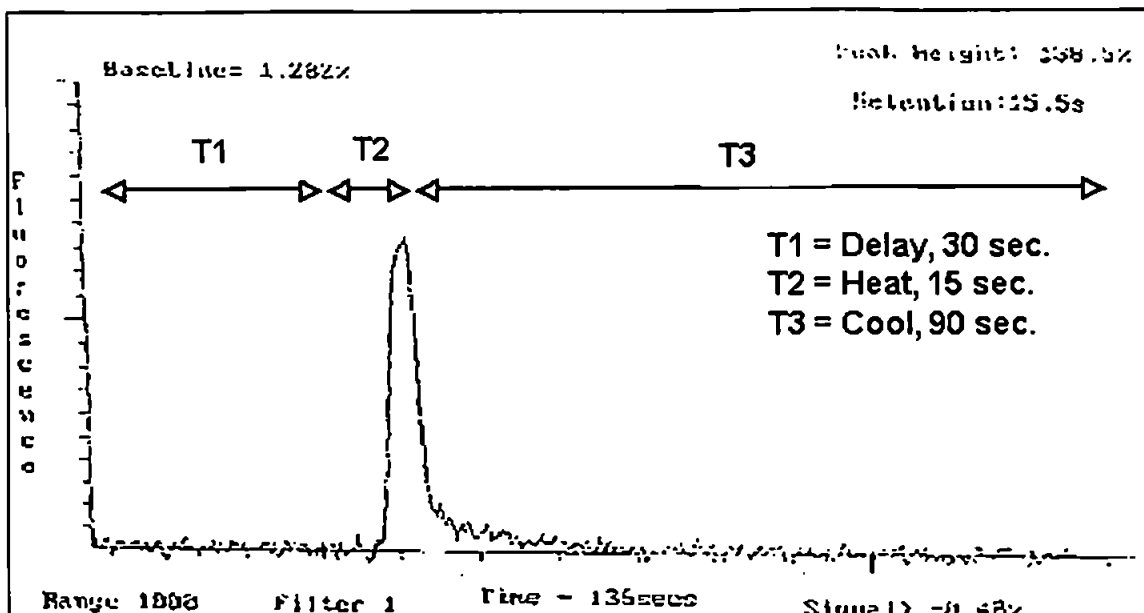


Figure 5.11 Typical peak profile for a 15 second thermal desorption stage

5.2.3. Calibration

5.2.3.1. Design of calibration vessel

For such a system to be readily useful it should have a simple calibration routine. Such a procedure has been developed based on the work of Dumarey *et al* [100]. This provides an absolute calibration method, which has been integrated into the control software. It involves the injection of mercury vapour at a set temperature onto the gold trap using a gas tight syringe. This is a simple, but effective, means of providing a primary standard that is more effective than alternative diffusion tube approaches and is also considerably more economical.

Elemental mercury was used as the primary standard and was contained in a specially designed glass vessel at atmospheric pressure as shown in Figure 5.12. The volume of the vessel was approximately 350 ml, which is assumed to ensure complete saturation of the air above the mercury. The inner pressure was kept at atmospheric pressure by means of a sidearm

capillary that was open to the atmosphere. The temperature was maintained by immersing the vessel in a water bath.

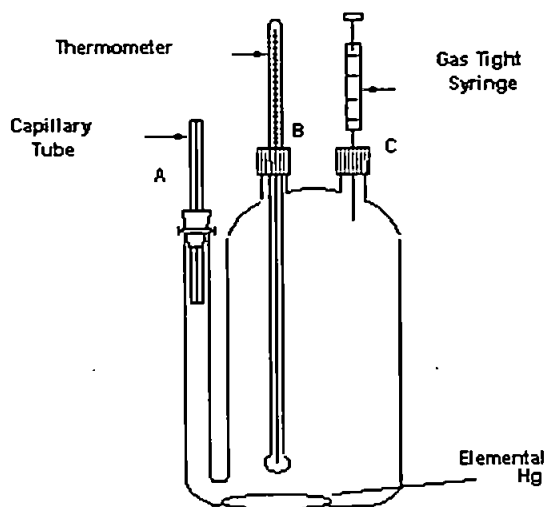


Figure 5.12. Calibration vessel for the mercury vapour injection technique.

The partial pressure of mercury, and hence the saturation concentration, was calculated using the data of Weast [92] and using the formula below:

$$C = \frac{3216522,61}{T} \times 10^{-(A + (B/T))}$$

Where C denotes the mercury concentration in the air in ng ml⁻¹; A = constant equal to -8.134459741, B is a constant equal to 3240.871534, and T is the absolute temperature in Kelvin. Table 5.3 shows the variation of mercury vapour concentration at different temperatures. It is important to keep the temperature of the vessel below ambient temperatures. Dumarey *et al.* [99] showed that large differences in temperature between the water bath and the ambient air can lead to deviations from the theoretical vapour concentration, this can be attributed to condensation of the mercury vapour on the inner-walls of the gas syringe.

Table 5.3. Variation of mercury vapour concentration at different temperatures, (concentration in ngmt¹)[103].

Temp° C	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
24	18.310	18.459	18.610	18.761	18.914	19.067	19.222	19.378	19.535	19.693
25	19.853	20.013	20.175	20.338	20.502	20.667	20.834	21.002	21.171	21.341
26	21.513	21.686	21.860	22.035	22.212	22.390	22.569	22.749	22.931	23.115
27	23.299	23.485	23.672	23.861	24.051	24.242	24.435	24.629	24.825	25.022
28	25.220	25.420	25.621	25.824	26.028	26.234	26.441	26.650	26.860	27.072
29	27.285	27.500	27.716	27.934	28.153	28.374	28.597	28.821	29.047	29.274

Partial mercury adsorption also takes place on the walls of the gas syringe leading to initial poor reproducibility. After 3-5 injections the syringe becomes pre-conditioned and reproducible results obtained. It is recommended to pre-condition new gas syringes before use, by simply pulling the maximum volume of saturated air into the syringe and leaving the vapour trapped in the syringe for at least 10 minutes.

A fixed volume of saturated mercury air can be drawn into a pre-conditioned gas tight syringe and injected directly into a stream of carrier gas via a Teflon injection port. The mercury vapour then passes over the thermal desorption trap where it amalgamates with the gold-sand.

The re-establishment of the equilibrium between liquid and gaseous mercury depends upon the cleanliness of the mercury pool surface. After some time the mercury at the surface becomes oxidised by atmospheric oxygen and the rate of mercury vaporisation may be reduced, hence elemental mercury should be replaced when the surface becomes tarnished.

Care should be taken when withdrawing large volumes (greater than 5.0 ml) from the calibration vessel. Several minutes are required to re-establish

the saturated vapour pressure equilibrium before the next large volume is collected.

5.2.3.2. Evaluation of calibration method

It is assumed from the work of Dumarey *et al.* [100] that approximately 15.0g of elemental mercury is sufficient to ensure full saturation of the air within the calibration vessel. Thus, the aim of this experiment was to vary the quantity of mercury within the calibration vessel and observe the effects (if any) on the slope of the calibration graph, resulting in a minimal, safe and accurate mass of mercury for calibration of the instrument.

A fixed quantity of elemental mercury was accurately weighed into an empty calibration vessel and the side-arm capillary fitted. The vessel was left to equilibrate at room temperature with each quantity of mercury for approximately 30 minutes prior to calibration.

The instrument was calibrated with a 1000 μ l gas syringe. Initially only a 2 point calibration was performed, the remaining points were added to construct the final calibration curve, in this way temperature drift during the injection procedure can be eliminated. The final calibration curve consisted of 0, 100, 300, 500, 700 and 1000 μ l injections.

For the 5.2g addition a small droplet of mercury formed around the bottom of the vessel, but with 163g a large pool formed completely covering the base of the vessel and blocking the side arm. With such a large quantity of mercury in the calibration vessel its effect was to close the vessel off to atmosphere resulting in a closed system.

The variation in each calibration slope is shown in Table 5.4 from which it can be clearly seen that there was a negligible effect on the slope of calibration regardless of the mass of mercury. This confirms that the

recommended quantity of mercury (15.0g) was more than sufficient to fully saturate the air within the calibration vessel and that any quantity more than 10.0 g would be unnecessary. Quantities of mercury lower than 5.0g were not evaluated.

If one considers that the average volume of a calibration vessel is 320 ml, then 5 g of Hg would only occupy 0.1% of the total vessel's volume. Similarly, 163 g of Hg in the calibration vessel occupies 4% of the total vessel volume. There was negligible difference when elemental mercury occupied between 0.1% and 4% of the total internal volume of the calibration vessel.

Table 5.4. Variation of calibration slopes with varying quantities of elemental Hg in calibration vessel.

Amount of Hg, g	Slope of calibration graph	Correlation coefficient, R²
5.2	0.04014	1.000
10.3	0.04184	0.9998
25.2	0.04094	0.9993
40.5	0.04010	0.9999
91.2	0.04338	0.9999
163.0	0.04385	0.9998

Mean calibration slope = 0.041708, Std Dev = 0.001615, RSD = 3.87%

The results clearly show that very little difference was observed upon the slope of calibration when varying the quantities of elemental mercury between 5 and 163g. It can be concluded that the recommended value of 15.0 g would ensure complete saturation of the air within the vessel, in fact this quantity could be reduced to as little as 5.0 g which corresponds to a volume of only 0.4 ml and still achieve saturation.

5.2.4. Analysis of remote samples

Samples of gas not in the immediate vicinity of the instrument could be easily analysed using specially designed, removable Amasil traps. Samples were first collected onto these traps using the methods previously described in sections 5.1.2.3, and analysed as soon as possible.

Upon analysis the trap was placed into the heating module, where it was flushed with argon to ensure that no traces of air or sample gas remained. The heating module heated the remote chamber for approximately 60 seconds, which was sufficient to fully vaporise the mercury. The adsorbed mercury was released and carried by a stream of argon over the permanent trap where it was adsorbed. Figure 5.13. shows the various stages of the dual thermal desorption process. The permanent Amasil trap goes through its heating cycle where the mercury was revaporised into the fluorescence detector and a signal produced, to ensure that consistent results were obtained when using the permanent Amasil trap for calibration.

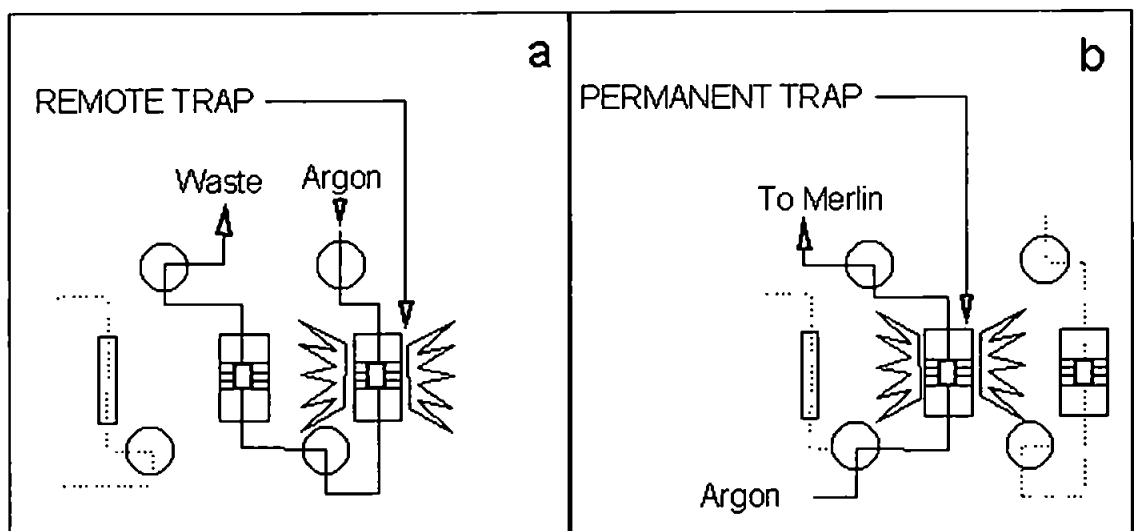


Figure 5.13. Stage A shows the transfer of the remotely collected sample to the permanent Amasil trap. Stage B shows the thermal desorption into the detector.

5.2.5. Sample Tube Trapping Efficiency

In order to determine the trapping efficiency of the trap the instrument was first calibrated. Once calibrated, a remote sample tube was inserted into the thermal desorption unit and the blank value measured. The blank mercury concentration was calculated in absolute terms against the constructed calibration. Several runs were necessary before a reproducible blank was obtained.

The results from Table 5.5 show that the reproducibility of the fixed desorption trap was better than 2% with a mean blank concentration of 32.81pg. The remote sample trap progressively cleaned up to produce a reproducible blank value of 38.51 pg (if one ignores the initial blank of 240.3 pg Hg). Five measurements were again performed on each trap. Upon attaining reproducible blank values for both the fixed and remote sample tubes a 100 μ l of saturated mercury vapour from the calibration vessel was injected onto each trap. Upon attaining a blank value a fixed volume of mercury was introduced onto the remote trap from the calibration vessel via a PTFE injection port identical to that used for injecting the calibration standards. With a carrier gas stream of argon, air saturated with mercury was injected (100 μ l) onto the sampling tube. Five consecutive measurements were performed on both the fixed amalgamation trap and on the remote sampling trap. The schematic arrangement used for spiking the traps is similar to that shown in Figure 5.13.

Table 5.6. shows the trapping efficiency using the manual injection technique, this not only shows trapping efficiency but also reflects injection precision. The outputs for 100 μ l spike additions to the fixed trap and remote traps are shown in Table 5.6, the mean results for the fixed and remote traps were 885.83 pg and 882.50 pg Hg respectively.

Table 5.5 Variation of fixed and remote sampling tube blank values.

Run Number	Calibration trap (pg of Hg)	Remote trap (pg of Hg)
1	32.54	240.3
2	33.42	41.21
3	32.10	36.45
4	33.45	38.41
5	32.54	37.98
Mean =	32.81	38.51
Std Dev =	0.60	1.98
RSD % =	1.82	5.15

Table 5.6 Variation of fixed and remote sampling tube spike values.

Run Number	Calibration spike (pg Hg)	Remote spike (pg Hg)
1	885.40	879.68
2	890.41	882.45
3	887.61	887.12
4	884.27	876.29
5	881.45	886.98
Mean =	885.83	882.50
Std Dev =	3.39	4.69
RSD % =	0.38	0.53

In order to calculate the trapping efficiency the spike results must first be blank corrected to account for the residual mercury that was already present on each trap before the spike was added. The formula below shows the calculation for assessing the trapping efficiency of the remote trap relative to the fixed calibration trap.

For example:

% Sample Tube

$$\begin{aligned}\text{Efficiency} &= \frac{(\text{Sample tube output} - \text{Sample blank output}) \times 100\%}{(\text{Calibration tube output} - \text{Calibration blank output})} \\ &= \frac{(882.50 - 38.51) \times 100\%}{(885.83 - 32.81)} \\ &= \frac{843.99}{853.02} \times 100\% = 98.94\% \\ &= 98.94\%\end{aligned}$$

Hence, the results show a trapping efficiency of 98.94% relative to the fixed trap was obtained. Upon attaining trap efficiencies of 95-105% the trap was deemed suitable for field analysis. The cleaned trap was sealed at both ends with PTFE tape and rubber caps and then stored in a gas-tight container until required for field analysis.

5.2.6. Comparison with ISO Method 6978B

The AFS Amasil mercury technique was compared with the ISO 6978 method (method A in section 5.1.3.1.) for validation. In the ISO method the natural gas sample is passed through a gas-washing bottle filled with an acidic oxidising solution. The mercury was retained within the solution and subsequently analysed in the laboratory by CVAAS. The sample was a dry natural gas from a North Sea offshore gas processing facility; with composition shown in Table 5.7. The samples were collected using a regulated gas stream as described in section 5.1.3.1.

Table 5.7. Gas composition from offshore North Sea gas facility

Gas Composition	% v/v
CH ₄	83.94
C ₂ H ₆	7.46
C ₃ H ₈	3.09
C ₄	0.98
C ₅	0.87
C ₆	0.23
C ₇	0.15
C ₈	0.01
CO ₂	2.37
N ₂	1.12
H ₂ S	0.001
Density	0.9 kg m ⁻³

5.2.6.1. Experimental

Atomic absorption spectrometry (AAS) was performed using a Varian Techtron AA-6 spectrometer complete with a deuterium lamp for background correction. The instrument was equipped with a Varian Tectron mercury hollow cathode lamp operated at 253.7 nm. A Tecmar Labmaster 12 bit ADC was used to interface the spectrometer with an Ericsson 486 PC. The AFS instrumentation consisted of the thermal desorption module and AFS detector along with pre-cleaned Amasil sample collection traps.

All reagents were of analytical grade unless otherwise stated. Stannous chloride solution, 12% m/v was prepared by dissolving 12 g of SnCl₂·2H₂O (Merck) in 30ml of 37% v/v HCl (Merck) and diluted to 100 ml with deionised water. Once prepared the solution was purged with argon (99.999% argon, Norse Hydro, Norway) to remove any residual mercury vapour. Standard solutions were prepared from a 1000 mg l⁻¹ mercury (II) nitrate stock solution

(Spectrosol[®], Merck). Dilute mercury solutions were prepared by dilution of the appropriate volume of stock solution in 1% KMnO₄ and 25% v/v H₂SO₄ analytical grade (Merck, UK).

Sample collection was performed using an existing sampling point on a North Sea gas-processing platform using "quick fit" fittings compatible with the sampling point on the process stream (Swagelock[™], South London Valve and Fitting Company Ltd, Burgess Hill, East Sussex, UK) and a gas valve compatible with the operating pressure of the plant, (Whitey[™], South London Valve and Fitting Company Ltd, Burgess Hill, East Sussex, UK). A pressure gauge limited to plant operating pressures. The flow rate was set according to adjustment of the needle valve (Whitey[™]). The sample line was regularly used for collection of composition samples and hence was pre-conditioned, nevertheless, the sample line was purged for approximately one hour at the sampling flow rate. The volume of gas collected was measured by a wet gas flow meter and the flow rate calculated by use of a wet gas flow meter (Alexander Wright, London) and a stopwatch. Once the flow rate was established the gas sample was delivered either to Dreschel bottles (acid cleaned Dreschel bottles filled with a solution of 1% KMnO₄ and 25% v/v H₂SO₄ analytical grade (AnalaR[®], Merck)), or a gold collection trap (gold Amasil traps PSA) at a flow rate of 0.5 l min⁻¹. After an appropriate volume was collected (0-70 litres) the gold tubes were sealed and stored in a gas-tight container until analysis. The trapping solutions were transferred to acid pre-cleaned polyethylene bottles after each collection. The solutions and traps were rapidly (5 days) transported back to the laboratory for subsequent analysis either by CVAAS or AFS.

5.2.6.2. Results

Table 5.8. AFS Amasil Method

Sample	Volume of gas (litres)	Sampling time, (mins)	Mercury concentration $\mu\text{g m}^{-3}$	Mercury concentration, ppm
1	0.513	1	118.6	0.014
2	0.997	2	78.1	0.010
3	4.747	5	37.5	0.005

Table 5.9. AAS ISO Method

Sample	Volume of gas (litres)	Sampling time, (mins)	Mercury concentration $\mu\text{g m}^{-3}$	Mercury concentration, ppm
1	24.4	30	108.7	0.013
2	47.6	60	71.9	0.009
3	71.9	90	*	*

*Trapping solution over saturated with mercury.

The results shown in Tables 5.8 and 5.9 indicate that the two methods performed similarly. A further advantage of the AFS approach is that much shorter sampling times were required compared with the ISO method. The reduction in sampling time allows a greater number of samples to be collected. Additional advantages include: the procedure avoids the use of hazardous reagents offshore, lower blank values were obtained with the Amasil traps compared to the trapping solution, smaller gas volumes could be collected allowing the safer dispersion of the waste natural gas. It is now possible to perform the measurements in-situ offshore due to the portability of the AFS equipment.

5.3 DEVELOPMENT OF THE SAMPLING INTERFACE

In order to obtain a representative sample of natural gas from a high-pressure gas stream, the use of heated regulators, needle valves and sample transfer lines are normally necessary during the pressure letdown stage. Heating elements are used to supply additional heat to compensate for the adiabatic temperature expansions experienced during this Joule-Thompson effect. Using this technique the sample gas at ambient pressures will have the same composition as that at the higher line pressure and will be representative of the natural gas process stream.

In order to design an on-line system for continuous mercury monitoring of natural gas process streams it was necessary to:

1. assess the reproducibility of thermal desorption by performing repeat adsorption and desorption cycles.
2. repeat the trapping efficiency and reproducibility tests at the higher temperatures likely to be necessary for overcoming Joule-Thompson effect.
3. assess the contributions from the use of heated regulators and heated sample transfer lines.
4. couple the components together to provide an off-line system.
5. translation of the off-line unit into an automated and safety compliant online monitoring system.

5.3.1. Reproducibility of trapping at room temperature

The instrument was calibrated according to the procedure outlined in sections 5.2.3. The system was calibrated between 0 -10.0 $\mu\text{g m}^{-3}$ Hg by taking variable gas volumes from the calibration vessel.

In order to supply a known amount of mercury to the traps a permeation system was used. The permeation source provides a constant stream of air that is mixed with a stream of saturated mercury vapour producing a stable mercury concentration source. The mercury concentration from the source could be varied by either altering the temperature within the permeation oven or by changing the flow rate of the diluent gas.

5.3.1.1. Procedure

In the first experiment the permanent desorption trap was tested to establish the trapping efficiency and reproducibility. One meter of 1/4" i.d. PTFE tubing, connecting the permeation outlet with the fixed desorption trap, was first preconditioned prior to connection to the fixed thermal desorption module. Preconditioning involved connection to the permeation source and passing permeation gas through the tube for 1 hour at a flow rate of 1.0 l min⁻¹.

The thermal desorption module was held at approximately 25°C, and a stable flow of permeation gas was passed over the permanent desorption trap for a fixed time period. After the sampling period the permeation gas was diverted to waste and the fixed desorption cycle activated. The absorbed mercury vapour from the permeation source was released from the Amasil and into the argon carrier gas during thermal desorption and delivered to the detector; where a signal was observed. The total analysis time including sample collection was 3 minutes 15 seconds.

5.3.1.2. Results

The results shown in Figure 5.14. show the excellent reproducibility obtained with the Amasil thermal desorption traps at room temperature for 25 successive absorptions/desorptions. The mean result over the 90 minute sampling period was $4.456 \pm 0.068 \mu\text{g m}^{-3} \text{ Hg}$ with a precision of 1.5%. These

results also show the stability of the permeation chamber as a source of mercury vapour – making it suitable as an on-line calibration source for an automated monitoring system.

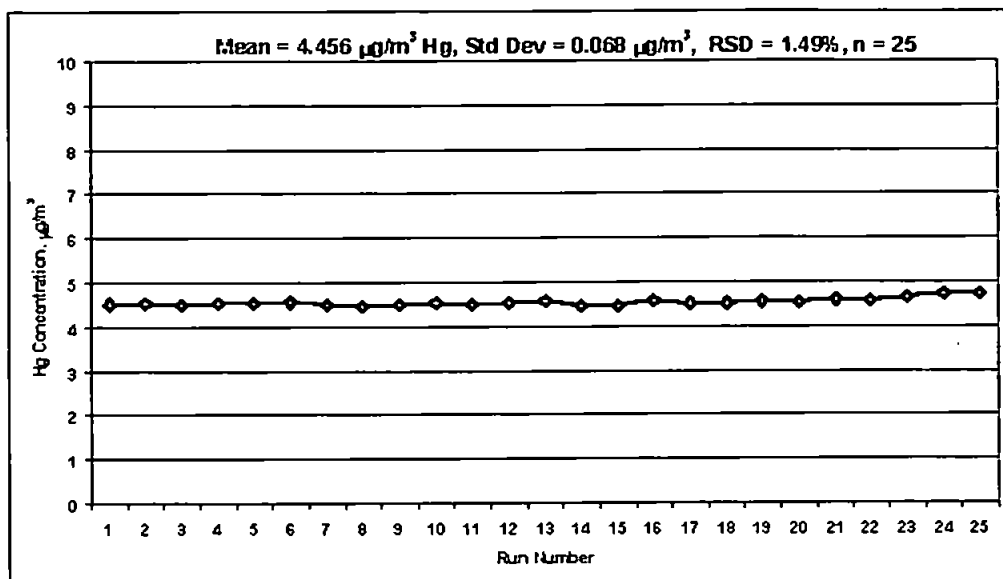


Figure 5.14. Variation of 1.0 litre sample batches from permeation source.

Inspection of the trap after successive use revealed no damage to the Amasil packaging material or the Nichrome wire coil. After the successive analyses the blank values of the permanent traps were measured and no significant memory effects were observed. After performing the memory test a check standard of the instruments calibration was performed by injecting a fixed volume of mercury from the calibration vessel. The injection fell directly on the calibration line and indicated a calibration drift of only 0.08% over the test period of 90 minutes.

5.3.2. Reproducibility of trapping at elevated temperatures

Prior to evaluating the heated regulators it was necessary to establish the trapping efficiency of the gold Amasil tubes at elevated temperatures. The temperature of the heated regulators would ultimately depend on the dew point and composition of the gas.

5.3.2.1. Procedure

A specially made thermal desorption module was designed to fit into an electrically heated oven which was variable from 0 to 220 °C. The mercury permeation device was connected to the input and the thermal desorption module was connected externally to the permanent calibration trap of the instrument. The transfer line between the oven and instrument was made of pre-cleaned 1/8" o.d. PTFE tubing. Mercury from the permeation device was absorbed onto the tube within the oven, and upon activation, the absorbed mercury was thermally transferred to the permanent tube for secondary desorption into the AFS detector as shown in Figure 5.15.

The temperature of the oven was varied from room temperature up to the maximum oven setting of 210 °C. At each temperature-rise the oven was given approximately 30 minutes to equilibrate before sampling started. At each of the temperature the permeation gas was introduced and analysed for 5 measurements.

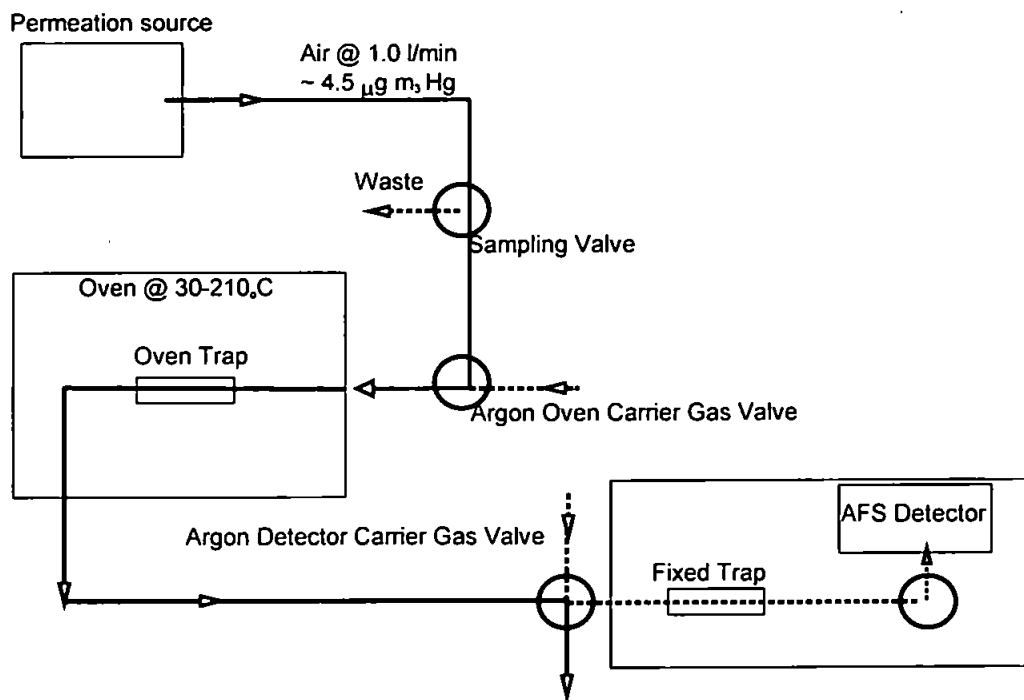


Figure 5.15. Schematic diagram of the basic stage of the transfer of a remote sample through the heated oven sample trap and delivery to the fixed detector trap.

The cycle began by first opening the sample valve which allowed a fixed flow rate of 1.0 l min⁻¹ of permeation gas to pass directly over the oven sample trap and out to atmosphere (waste). After the 1-minute sample collection/preconcentration period the permeation gas was diverted to waste and argon carrier gas swept over the oven trap at a flow rate of 350 ml min⁻¹. A flush period of 30 seconds was allowed to sweep out any remaining permeation gas and after this flush/purge period, the thermal desorption cycle started and 15 seconds of heating was applied across the 10 Ω Nichrome wire of the oven sample trap. The trapped mercury was thermally released and carried out of the oven in a stream of argon and re-trapped on the fixed thermal desorption trap in the instrument. Thereafter, the normal sequence of events took place and the mercury from the permanent trap was delivered to the AFS detector for measurement.

Unlike the permanent desorption trap the oven sample trap was not cooled down with compressed air prior to the next loading stage. The total analysis cycle was the sum of each of the collection, transfer and detection stages i.e.

Oven sample trap

- 60 seconds sample loading from permeation source
- 30 seconds flush/purge over oven trap
- 15 seconds thermal desorption of oven trap
- 60 seconds flush/purge of oven trap

Permanent sample trap

- 30 seconds flush/purge over fixed trap
- 17 seconds thermal desorption of fixed trap
- 60 seconds cool of fixed trap

The time period between each vaporisation was sufficiently long enough to allow the Amasil material to cool down and collect the next sample without releasing trapped mercury. As the purpose of this trap was to transfer the mercury from the sample gas and deliver it to the permanent adsorber trap a slightly higher heating time was used in order to ensure complete transfer. The vaporisation time used for the oven trap was 17 seconds. Additionally, when the oven trap is maintained at temperatures at which heated regulators operate (120-190°C) the trap will reach the mercury release temperature more rapidly. This combined effect of additional heating time ensures the complete transfer of mercury from the sample gas to the instrument trap.

5.3.2.2. Results

The results shown in Table 5.10 indicate that, after heating the thermal desorption trap from room temperature to 210°C, no breakthrough of mercury was observed and 100% of the permeation mercury was trapped and successfully transferred to the instrument. The mean concentration of mercury determined directly at the permanent desorption trap was $4.456 \pm 0.068 \mu\text{g m}^{-3}$ whilst the mean concentration found with the heated trap (210°C) attached was $4.51 \pm 0.01 \mu\text{g m}^{-3}$, resulting in a recovery of 101%.

Table 5.10. Trapping efficiency of Hg⁰ from the permeation source at various temperatures. (Mean values based upon 5 measurements).

Oven Temp, °C	30	50	70	90	110	130	150	170	190	210	Mean trap value
Mean	4.54	4.47	4.5	4.6	4.52	4.56	4.55	4.55	4.47	4.51	4.53
Std Dev	0.03	0.05	0.04	0.05	0.03	0.02	0.03	0.05	0.04	0.01	0.04
RSD %	0.74	1.17	1.09	1.09	0.75	0.54	0.74	1.28	0.9	0.35	0.91
Recovery, %	101.89	100.31	100.99	103.23	101.44	102.33	102.11	102.11	100.31	101.21	101.59

5.3.3. Evaluation of heated regulators

The next stage of the sampling interface was to evaluate methods of reducing the process gas pressure down to ambient pressures for delivery of the sample gas to the Amasil amalgamation trap. Natural gas is normally at high process pressures of ~100 bar, and when the pressure is reduced to ambient levels condensation of the liquid hydrocarbons contained within the sample gas occurs. Hydrocarbons from the liquid phase eventually accumulate and poison the Amasil trap preventing further amalgamation and thermal desorption.

The obvious choice for obtaining a low-pressure sample of heated natural gas would be to use a heated pressure regulator, which can be used to heat the sample gas above its dew point and prevent condensation during pressure let-down

Heated pressure regulators are commercially available and frequently used in petrochemical gas monitoring systems. Stringent safety requirements have to be met by regulator manufacturers to ensure compliance with intrinsically safe explosive gas application, the apparatus should conform to industry-approved standards of ExDIIc T3 and Cenelec [102], which effectively means that the equipment can be used in hazardous Zone 1 areas. The heating element can be either electrical or steam powered depending upon the constraints of the application. Regulators can be used individually or combined in series to produce the required outlet gas pressure.

Ultimately the system would be configured for monitoring natural gas applications at process gas pressures, however, recreating such a system in the laboratory is almost impossible due the various safety constraints necessary with explosive gases. Consequently, all further development had to be

performed using an inert gas at high pressure, such as argon or compressed air. While this would not simulate the matrix of raw natural gas, it would provide the opportunity to evaluate mercury adsorption characteristics of the heated regulators at high pressures and temperatures.

5.3.3.1. Procedure

A commercially available heated regulator system was used (Go Regulators Inc.). The regulator was constructed in 316 Stainless steel (316 SS), the body and head of the diaphragm cavity were specially electro-polished to minimise surface adsorption effects of mercury. The inlet pressure range of the regulator was from 10-3000 psi and the temperature variable from 120-196°C. The regulator was electrically powered at 110 Volts.

The first experiment was to evaluate mercury adsorption characteristics over a single heated regulator. Injections of mercury vapour were performed into the gas line before and after the regulator, and compared to a spike injection of the same concentration performed directly at the instrument. A schematic diagram of the sampling arrangement is shown in Figure 5.16.

The regulator was set to a temperature of 146°C and an argon gas supply of 65 psig was connected to the inlet port via a ¼" female 316 SS NPT fitting. The outlet pressure of the regulator was set at 12 psig. A Teflon injection port was inserted in line with the inlet and outlet gas flows. Pressure gauges were connected to the inlet and outlet ports of the regulator. A digital thermometer was used to measure the temperature of the regulator. All inter-connecting gas lines were made of pre-cleaned 1/8 " 316 SS tubing or PTFE.

A period of 45 minutes was required in order for the regulator to reach the set point of 145°C. Upon attaining temperature, argon was passed through

the regulator for approximately 2 hours in order to pre-condition the stainless steel tubing and internal components.

The fixed thermal desorption unit and AFS detector were calibrated according to section 5.2.1. The sampling arrangement was connected directly to the front sampling port of the instrument, in that the gas which had been passed through the regulators was sampled continuously in batch mode (similar to Figure 5.15). One-minute batches of argon at a flow rate of 1.0 l min^{-1} were collected over the fixed desorption trap from the sampling arrangement and continuously transferred to the AFS detector.

A gas tight syringe was used for mercury vapour injections both at the instrument and at either side of the regulator. In each case $1000 \mu\text{l}$ of air saturated with mercury at a temperature of 22.0°C , was withdrawn from the calibration vessel. Five injections were performed at each point illustrated in Figure 5.16.

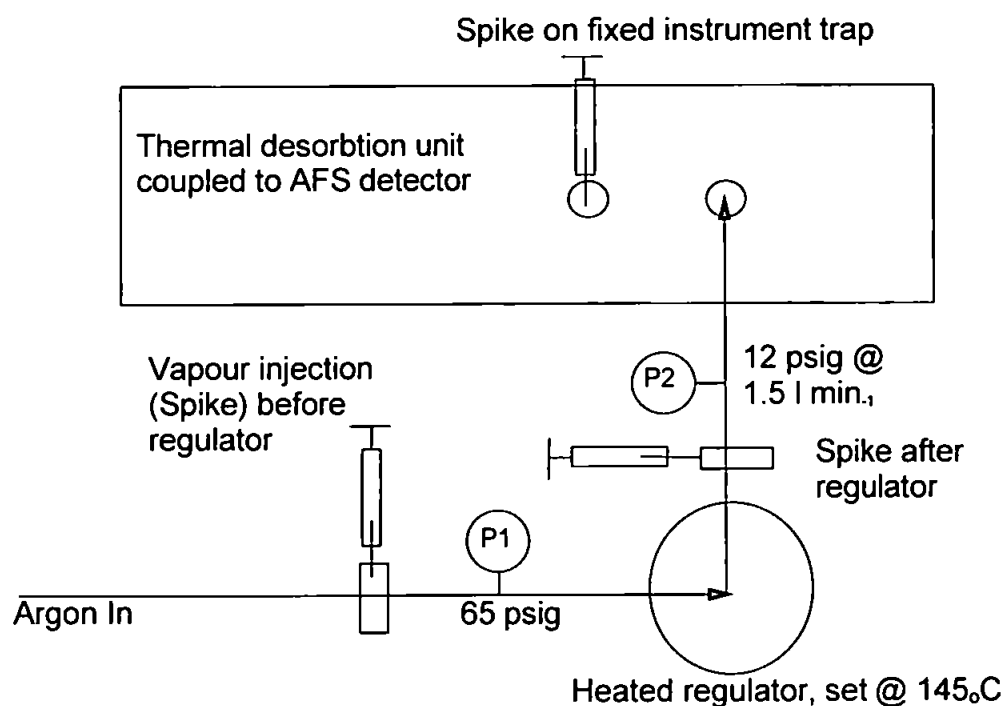


Figure 5.16. Schematic arrangement for the evaluation of heated regulator

5.3.3.2. Results

Prior to performing any vapour injections on the sample gas, it was first necessary to evaluate the mean concentration obtained when injecting mercury vapour directly on to the fixed trap in the instrument. The mean result obtained for five consecutive 1000 μ l injections onto the instruments trap was 825.38 ± 23.57 ng m⁻³ Hg with a precision of 2.85%.

Next, the blank contribution from the sampling arrangement was evaluated. After attaining operating temperature the blank measurement of the regulator was performed 20 times in batch mode. The mean blank value obtained from the outlet of the regulator was found to be 0.926 ng m⁻³ \pm 0.078 ng m⁻³ Hg (n=20), with a precision of 8.43%. The blank value was then subtracted from each spike measurement performed for the regulator.

The mean spike value after the regulator was found to be 814 ± 48 ng m⁻³ Hg with a precision of 4.3% (n=5). Blank correcting this result produced a value of 805 ng m⁻³ Hg which corresponded to a spike recovery of 97.57% relative to the fixed instrument trap.

The result obtained for the addition of mercury vapour before the regulator was blank corrected and found to be 797 ng m⁻³ Hg which corresponded to a recovery of 96.60% relative to the fixed trap.

Argon gas at pressure of 65 psi was passed through a single stage heated regulator, the outlet pressure of the regulator was set to 12 psig and a corresponding gas flow of 1.5 l min⁻¹ was obtained. The temperature of the regulator was maintained at 145°C. Upon comparing the results of mercury vapour injection in both the high and low-pressure phases it can be concluded that negligible losses were observed within the system. It would appear that the electro polishing process of the stainless steel components proved effective

in the minimisation of mercury adsorption effects. The negligible losses observed could be improved by replacing the inter-connecting stainless steel tubing with PTFE tubing. However, the blank value obtained from the heated regulator could prove to be a limiting factor when very low level gas monitoring applications are required.

The regulator was evaluated using the maximum line pressure available within the test laboratory, 65 psi. Ultimately, the regulator would be used in the field at process line pressures of around 3000 psi. As it was not possible to reproduce process line conditions (3000 psi) within the laboratory the efficiency of the pressure reduction stage will have to be evaluated by repeating the spike additions of mercury vapour at line operating pressures.

5.3.4. Design and Evaluation of the Complete Sample Interface

5.3.4.1. Final design

The excellent recovery of mercury vapour additions at 65 psig indicated that the sample collection arrangement would be an ideal method for delivery of a natural gas sample to a heated Amasil trap assembly. By combining a heated pressure reduction stage with a heated trap assembly it would be possible to collect a representative sample of natural gas and trap mercury present within the gas. The mercury could be collected onto a removable Amasil trap and then inserted directly into a thermal desorption module. This arrangement would provide an effective off-line sampling interface for the collection of samples that could then be transferred back to the laboratory for later analysis. Basic components within the system are shown in Figure 5.17.

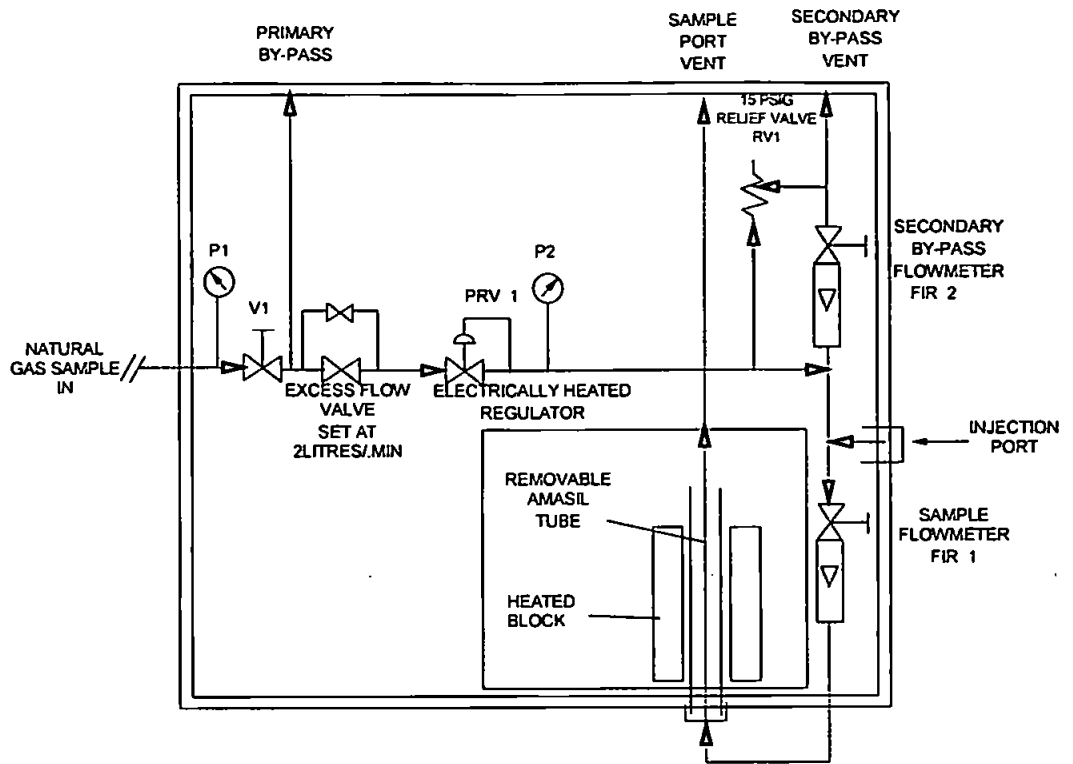


Figure 5.17. Detailed schematic diagram of the off-line sampling interface.

The gas pressure in the natural gas pipeline was first reduced in one stage using an electrically heated regulator with a typical pressure drop is typically from 2500 psig to 14 psig. A controlled flowrate of gas was then passed over the Amasil sampling tube, which was maintained at an elevated temperature of 145°C, the volume of gas passed over the trap was measured using a flowmeter. Once the sample gas had been collected the remote tube was inserted into a thermal desorbtion module and measured using the principles outlined in sections 5.2.1

5.3.4.2. Principle of operation

A detailed schematic diagram for the sampling interface is shown in Figure 5.17. The bold black arrows indicate the main direction of gas flow and the dashed blue lines indicate the fast loop by-pass for the sample. The red box indicates the location of the heated Amasil collection trap.

The sample gas first enters an isolation valve V1, and then passes through an excess flow check valve fitted with a by-pass reset valve. The flow check valve prevents any sample gas escaping within the enclosure if there is an excessive backpressure on downstream-pressurised components. The sample pressure is then reduced using the electrically heated regulator, labelled PRV1. The regulator reduces the sample pressure to a safe working level for the Amasil adsorber tube, injection port and measuring flow control system. Pressure indication on the inlet and outlet sides of the regulator is provided by pressure gauges P1 and P2 mounted on the front panel of the system. A relief valve, RV1 provides further over-pressure protection. In the event of over pressure this valve relieves to the secondary by-pass vent for protection of the systems components.

A flow meter labelled FIR2 (mounted on the front panel) is connected to the sample outlet port of PRV1 and can be used to provide a fast loop by-pass through the secondary by-pass vent located on the enclosure back panel. Maximum by-pass flow and flow through the Amasil trap should not exceed a total flow of 2 l/min. The front panel layout of the sampling interface is shown in Figure 5.18. Sample gas from PRV1 then passes through an injection port system. The injection port system is designed to allow a spike injection using a gas tight syringe directly into the sample gas flow and over the adsorber tube.

From the injection port the sample flows through a shut off valve and inlet to the Amasil tube housing seal. The Amasil tube is heated above the sample dew point in the heated block to prevent condensing of high boiling point components in the sample. The shut-off valve prevents leakage of sample gas when the removable Amasil adsorber tube is being changed.

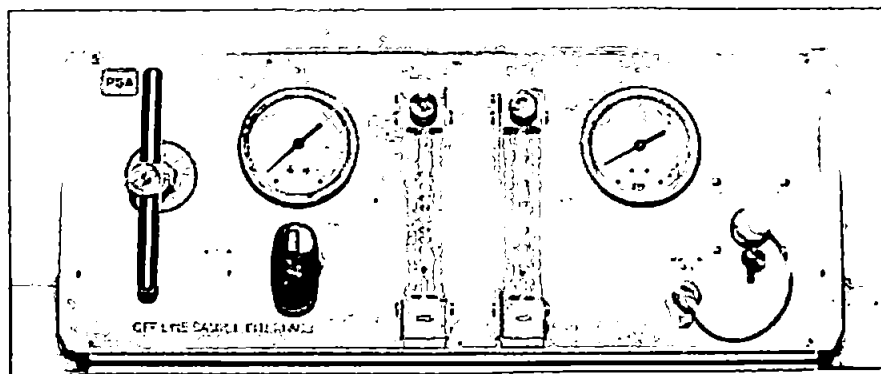


Figure 5.18. Front panel of the off-line sampling interface.

Flow through the adsorber tube exits via a Teflon compression fitting which seals and holds the Amasil tube in place using a spring release locking device to a removable flexible tube which is connected to a bulkhead fitting (labelled "Sample In FIR1"). This fitting is connected to the inlet of sample flowmeter FIR1, the sample gas then exits from flowmeter FIR1 through the sample-port vent located on the rear panel.

FIR1 is used to control the flow through the adsorber tube. This is not an accurate indication of the actual flow but is used as a flow indicator to set an accurate flow volume. A mass flowmeter or wet gas flowmeter is connected in series with the sample port vent connection located on the rear panel to accurately measure the volume of gas sampled. On completion of sampling the Amasil adsorber tube is removed, the sample volume is measured and the tube sealed and stored until analysis. The remote tube is then inserted into the thermal desorption unit for analysis using the procedure outlined in sections 5.2.1.

5.3.4.3. Evaluation

The off-line sampling interface was first tested in the laboratory using argon as the sample gas. Argon at a pressure of 65 psig was connected to the rear of the sampling interface via a ¼" SS 316 NPT fitting. The gas pressure

was reduced from 65 psig to 14 psig across PRV1, indicated on P1 and P2 respectively. The primary by-pass flow rate was set to deliver gas at a flowrate of 2.0 lmin⁻¹ using FIR2 to regulate flow. FIR 1 controls the sample gas flow rate through the fast loop from the primary by-pass flow; the flow over the Amasil collection trap was set to 1.5 l min⁻¹. The actual volume of gas passed over the trap was measured by placing a wet gas flowmeter after the sample port vent on the rear panel of the instrument in combination with a stopwatch to measure sampling duration.

The system was evaluated by comparing mercury vapour injections at the sampling interface with those directly at the thermal desorbtion module. The experiment was essentially the same as that performed during the evaluation of the heated regulator, (section 5.3.3). The trapping efficiency of the off-line sampling interface was evaluated using 1000 μ l volumes of mercury vapour. Injections were compared from the heated trap assembly with those directly at the manifold for the same amount of mercury.

Two hours was necessary for the heated components to reach temperature of approximately 145°C. During this time the system was pre-conditioned with the argon sample gas. Initially, five consecutive mercury vapour injections were performed directly on the fixed thermal desorbtion trap.

A new Amasil tube was taken for the analysis, prior to analysis the blank value was calculated. Four cycles of thermal desorbtion were necessary before a reproducible blank measurement was obtained. The cleaned Amasil tube was then inserted into the sampling interface and 5 litres of argon sampled over the tube at a flow rate of 1.5 lmin⁻¹. After the sampling time the Amasil tube was removed and inserted directly into the thermal desorbtion unit and analysed. This entire procedure was repeated three times for volumes of

5,10, 20 and 50 litre samples of argon. The tubes blank mercury value was deducted from each of the sampling-interface blanks. Table 5.11 shows the mean corrected blank measurements for each sample volume collected.

Table 5.11 Blank values for different gas volumes through the sampling interface.

Volume of gas sampled (litres)	Hg Concentration ng m ⁻³				
	Run 1	Run 2	Run 3	Mean	Std Dev
50	0.87	0.95	1.1	0.97	0.12
20	0.54	0.87	0.48	0.63	0.21
10	0.38	0.25	0.58	0.40	0.17
5	0.25	0.37	0.42	0.35	0.09

The results were as expected, indicating that the highest blank values were obtained from the largest sample volumes. The apparatus had been pre-conditioned for two hours prior to the each sample being collected. However, when collecting a 50-litre sample, the blank value was only four times higher than the value of the 5.0 litre sample, indicating that the blank emanated from either the Amasil collection trap or the equipment was still conditioning. The mean blank contribution from the sampling interface was 0.58 ± 0.15 ng m⁻³ for sample volumes between 5 and 50.0 litres.

1000 ^{Hg} mercury vapour injections were performed directly into the sample gas and passed over the removable Amasil tube. Samples were collected at a flowrate of 1.5 l min⁻¹. Five replicate injections were performed on 20 litre sample volumes, the spikes were performed midway during each sampling period.

The same volume mercury injection was also performed directly on the fixed thermal desorbtion trap. The mean result obtained directly at the

instrument was $885 \pm 29 \text{ ng m}^{-3} \text{ Hg}$ with a precision of 3.33% (n=5), whilst the mean result obtained from the sampling interface was 857 ± 44 with a precision of 5.22%, (n=5). Recovery of the mercury vapour spike relative to the fixed instrument trap was calculated to be 96.83%, indicating almost complete mercury transfer from the sampling interface to the instrument.

5.3.4.4. Conclusion

An off-line sampling interface has been specifically designed to sample natural gas for mercury determination. The components of the system have been combined within an instrument enclosure allowing use in Zone 1 hazardous areas utilising electrical components conforming to Cenelec EExd IIC T3. All components within the system were made from either SS 316 or PTFE where possible.

Mercury vapour injections were performed during sampling of argon gas and recoveries of over 95% were obtained relative to the fixed desorbition trap of the instrument. Although the sampling interface was evaluated using argon, the ability to perform spike additions into the sample matrix would provide an ideal method of checking the integrity of the sampling system.

The system has been designed to accommodate removable Amasil collection tubes. The tubes are easily inserted into the sampling interface allowing a natural gas sample to be collected. After collection the tube can be easily sealed and stored until analysis. Alternatively, the tube can be easily transported to the laboratory for measurement. In this way, samples can be collected from remote offshore locations and analysed rapidly in the laboratory, avoiding expensive instrumentation and transportation costs and providing the plant operator with an accurate, rapid, reliable and safe method of determining mercury in natural gas.

5.4 MERCURY ANALYSIS AT A NATURAL GAS PROCESSING FACILITY.

Evaluation of the off-line sampling interface have been restricted to testing with inert argon gas at relatively low pressures obtainable within the laboratory. In order to fully evaluate the efficiency and accuracy of the system it was necessary to analyse a real natural gas sample, so a natural gas processing facility was approached in order to do this. The facility processes gas from the several North Sea gas platforms, and the plant operators were in the process of commissioning a mercury removal system to protect downstream gas processing equipment. The operators were particularly interested to measure the mercury concentration exiting the mercury removal towers (Figure 5.19).

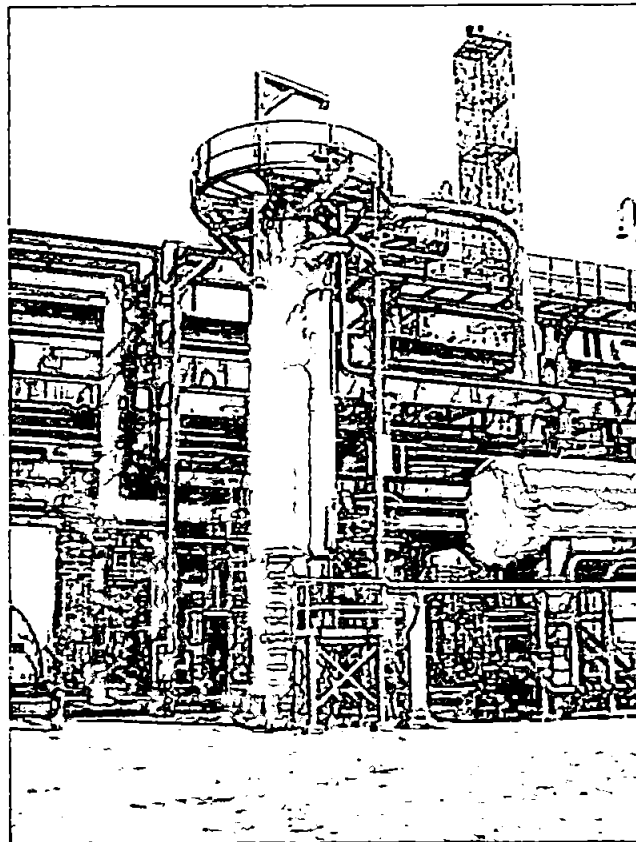


Figure 5.19. Mercury removal towers at a gas processing facility.

5.4.1. Procedure

Prior to connection to the pipeline the sampling interface was powered up for 1 hour in order to ensure that all internal components within the interface were pre- heated to a temperature of approximately 150°C. After reaching temperature, the off-line sampling interface was connected to an established sampling point on the exit of the mercury removal tower. This sampling point was frequently used for gas composition measurements and hence was already preconditioned. The gas composition at this sampling point had been previously analysed, results of which are shown in Table 5.7.

A photograph of the system connected to the main outlet pipe is shown in Figure 5.20, and a schematic diagram is shown in Figure 5.21. The interface was connected *via* 12 feet of ½ " 316 stainless steel tubing. The pressure of the natural gas sample within the main outlet pipe was indicated on pressure gauge P1 to be 1680 psig.



Figure 5.20. Connection of the sampling interface to the outlet pipeline of the mercury removal tower

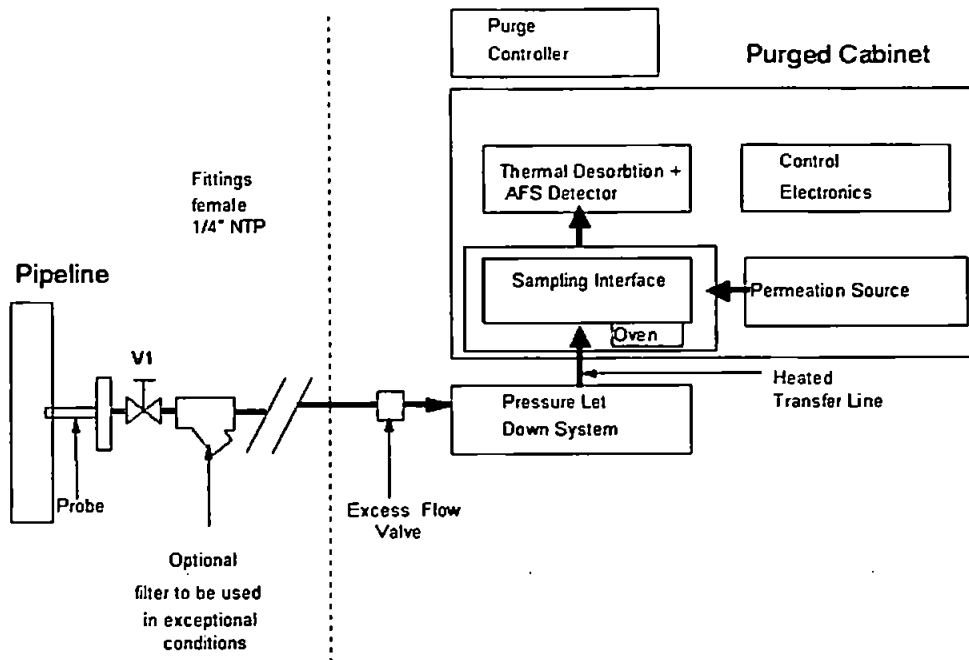


Figure 5.21. Block diagram of a fully automated on-line natural gas monitoring system.

Prior to collection of a sample, the off-line sampling interface required pre-conditioning with the sample gas. The sampling interface was set-up with a dummy tube in order to establish the sampling flow-rate before any real measurements could take place. Initially, the primary bypass flow was set to deliver gas at a rate of $20.0 \text{ litre min}^{-1}$ through the components of the interface by adjusting FIR2. The pressure measured after pressure reduction was shown on pressure gauge P2 and was measured to be 14 psig.

A secondary sampling flow rate of $1.0 \text{ litre min}^{-1}$ was then passed over a dummy sample tube by adjusting flowmeter FIR1. A wet gas flow meter was connected to the rear of the sampling interface. The waste gas was vented from the rear of the interface to atmosphere. The unit was located within a well-ventilated area allowing rapid dispersion of the vented gas.

The system was left to precondition at this flowrate for approximately 8 hours, after which 4800 litres of natural gas had passed through the sampling system components, and 480 litres of gas over the dummy sample tube. While

the sampling interface was preconditioning the AFS thermal desorbtion system was calibrated and several Amasil sample tubes pre-cleaned ready for analysis. The instrumentation was located in the on-site laboratory where power, carrier and cooling gases were available. The instrumental conditions for the AFS detector and dual thermal desorbtion system are shown in Table 5.12.

Table 5.12 Instrumental conditions for AFS detector and thermal desorbtion unit.

Amplification/ Gain	100	Carrier Gas	Argon, 300 ml min ⁻¹
Measurement Mode	Sample Volume	Remote Transfer Delay	60 secs
Autozero	Off	Remote Flush	30 secs
Flush	30 secs	Remote Vaporise	60 secs
Vaporise	15 secs	Remote Cool	120 secs
Coolant	120 secs, Air 50 psig		

5.4.2. Results and discussion

The system was calibrated and the calibration line equation was $y = 2.56391x + 9$, $r^2 = 0.9997$. Two labelled Amasil tubes (A and B) were dedicated for the analysis. Each tube was inserted in to the thermal desorbtion unit and its blank value measured. Three runs were required with Tube A to obtain a reproducible blank:

After cleaning, the tube was immediately sealed at transported to the sampling point. The dummy tube was removed and the clean Amasil tube inserted into the sampling interface's heated trap enclosure. A record of the collection time, sampling volume and sample flow rate was made using the wet gas flowmeter and stopwatch. The sample gas temperature was also measured through the wet gas flowmeter in order to account for volume correction. Sample information is summarised in Table 5.13.

After collection, the sample tube was sealed and returned to the laboratory for immediate analysis. The tube showed no visible signs of condensate deposition on the Amasil collection material, indicating that the sample gas was successfully maintained above its dew point and that the trapping material retained all mercury within the sample.

Table 5.13. Sampling information for mercury removal tower.

Sample Reference (Location)	Outlet Gas
Date of Sampling	28-5-99
Time Interval	18:45 - 19:58
Tube Identification	Tube A
Corrected Sample volume	64 litres
Mean Sample Flow Rate	0.84 litres min ⁻¹
Gas temperature of flow meter	11°C, Conversion factor = 1.049

*Rotameters calibrated for air at 25°C, specific density of sample gas was 0.84, H₂S ≈ 1 ppm. Volume measurements were taken from the wet gas flow meter.

After sampling 64.0 litres of natural gas the sample tube was removed and analysed immediately. After the first desorbtion to the permanent amalgamation trap 32.37 pg of Hg was measured, after blank deduction this equated to a concentration of 0.387 ng m⁻³ Hg. However, a second run on the sample trap produced a further 16.83 pg of Hg which was not transferred during the first desorbtion, this additional mercury was not present in the sample tube before the sample was collected and therefore could only have originated from the sample gas. Further desorbtions indicated that the tube returned a similar blank concentration (5.7pg) to that before any sample was collected. Consequently, both desorbtion runs were summed together in order to produce a total mercury concentration. After additional blank correction the combined total for natural gas exiting the mercury removal tower was measured to be 0.65 ng m⁻³ Hg.

A second sample was collected from the same point using Tube B, and this time 58.22 litres of gas were sampled. The first desorbition into the detector produced 26.82 pg of Hg, a second desorbition showed that no residual mercury was observed and that the trap had returned to its original blank value of around 10 pg Hg. Hence, the mercury concentration for this sample was calculated using the first thermal desorbition run alone and was calculated to be 0.46 ng m⁻³ Hg.

A much larger sample volume was then collected in order to assess volume effects. Tube A was pre-cleaned and inserted into the sampling interface. The flow rate was set, and the tube left to sample the outlet gas overnight so that 646 litres of gas were sampled by the tube over a sampling period lasting almost 13 hours. Inspection of the sample trap revealed that even with collection of such a large sample volume no condensates were deposited on the Amasil collection material. The trap was analysed on the thermal desorbition unit and once again additional mercury was left on the trap after the first desorbition (88.9 pg), even though this mercury was not present on the trap prior to sample collection. Summation of both desorbitions produced a total mercury concentration of 0.65 ng m⁻³ Hg. A fourth sample of 146 l was taken in order to establish an average sample concentration from the mercury removal towers.

Table 5.14 shows the results obtained for the gas exiting the mercury removal towers over the 2-day study. The mean mercury concentration over the four samples collected was found to be 0.593 ± 0.09 ng m⁻³.

Table 5.14. Mercury concentrations exiting the mercury removal towers

Date	Time Interval	Sample Volume (l)	Concentration (ngm ⁻³)
28-5-1999	18:45 - 19:58	64.0	0.65
28-5-1999	20:00 - 21:00	58.2	0.46
28/29-5-1999	21:10 - 10:15	646.2	0.65
29-5-1998	10:15 - 13:04	146.0	0.61

Now that a mean sample concentration was obtained the next stage was to test the efficiency of the sampling system by spiking the sample stream with mercury vapour from the calibration vessel. A 200 μ l injection of mercury vapour was made into the sample stream midway during sample collection, corresponding to 1952.5 pg of Hg, via the septum connection on the side of the sampling interface. The spike recovery was 92%, indicating that the sampling interface was effective in obtaining a representative sample of natural gas from the main process pipeline and that no matrix effects were observed from the sample. Ideally, the spike should contain a similar mass of Hg in the sample, however, the practical constraints of injecting micro litre volumes of air saturated with mercury in the field are extremely difficult.

The Method Detection Limit (MDL) for a 58.2 litre sample of argon gas indicating that the sample concentrations determined at the mercury removal towers were well within the scope of the instruments capability.

The desorbition efficiency on transferring mercury from the sampling tube was evaluated by adding a known quantity of mercury to a sampling tube with a stream of argon gas. The sampling tube was then analysed in a conventional manner (section 5.2.4.) and compared to a calibration output of the same quantity of mercury, or the transfer efficiency could be calculated as follows:

Sample tube A blank output	=	20.46 ± 2.65% (n = 16)
Sample tube A spiked with 50 µl Hg vapour	=	1131 ± 35.0% (n = 2)
Calibration blank output	=	6.032 ± 1.37% (n = 3)
Calibration tube spiked with 50 µl Hg vapour	=	1173 ± 16.0% (n = 2)

$$\text{Remote Transfer Efficiency} = \frac{(\text{Sample Tube Spike} - \text{Sample Tube Blank})}{(\text{Calibration Tube Spike} - \text{Calibration Tube Blank})} \times 100\%$$

$$= \frac{(1131 \pm 35) - (20.46 \pm 2.65)}{(1173 \pm 16) - (6.032 \pm 1.37)} \times 100\%$$

$$\frac{(1110.54 \pm 37.65)}{(1166.97 \pm 17.37)} \times 100\%$$

$$\text{Transfer Efficiency} = 95.16 \pm 4.5\%$$

The remote transfer efficiency of the thermal desorbition system was established to be over 95% indicating that almost all of the mercury contained on the remote sample tube was quantitatively transferred to the fixed desorbition trap for analysis.

5.5 ON-LINE NATURAL GAS MONITORING

Although the off-line sampling interface provides an effective technique for sample collection, the procedure is still a manual process, the operator has to remove and insert the sample tube into a thermal desorption instrument. This entire process can be automated further by the introduction of switching valves, electronics and software.

A prototype system was designed, which contained the same components as the off-line system which is shown in Figure 5.21., except that in this case the analysis by AFS was performed automatically.

The system is shown in block diagram form and is housed in a purged enclosure. The system complies with area classification EExp-IIB T3 and is built in conformance to Cenelec EN50016/Exp II SRA 3009 [103].

The heart of the interface is a pneumatically controlled 10 port-rotary sample valve combined with two heated Amasil traps. These were contained within the oven enclosure and maintained at around 150°C. The sample tubes sequentially adsorb mercury from the sample stream, then desorb the amalgamated mercury into a stream of carrier gas which delivers the gaseous mercury into the thermal desorption system and AFS detector located, in the same cabinet. The function of the valve is to allow sampling and desorption at the same time, thus providing an arrangement for continuous sampling. Figure 5.22. shows the direction of flow through the 10-port rotary sampling valve and Figure 5.23 shows a photograph of the rotary valve located within the oven enclosure and connected to the two Amasil sampling tubes.

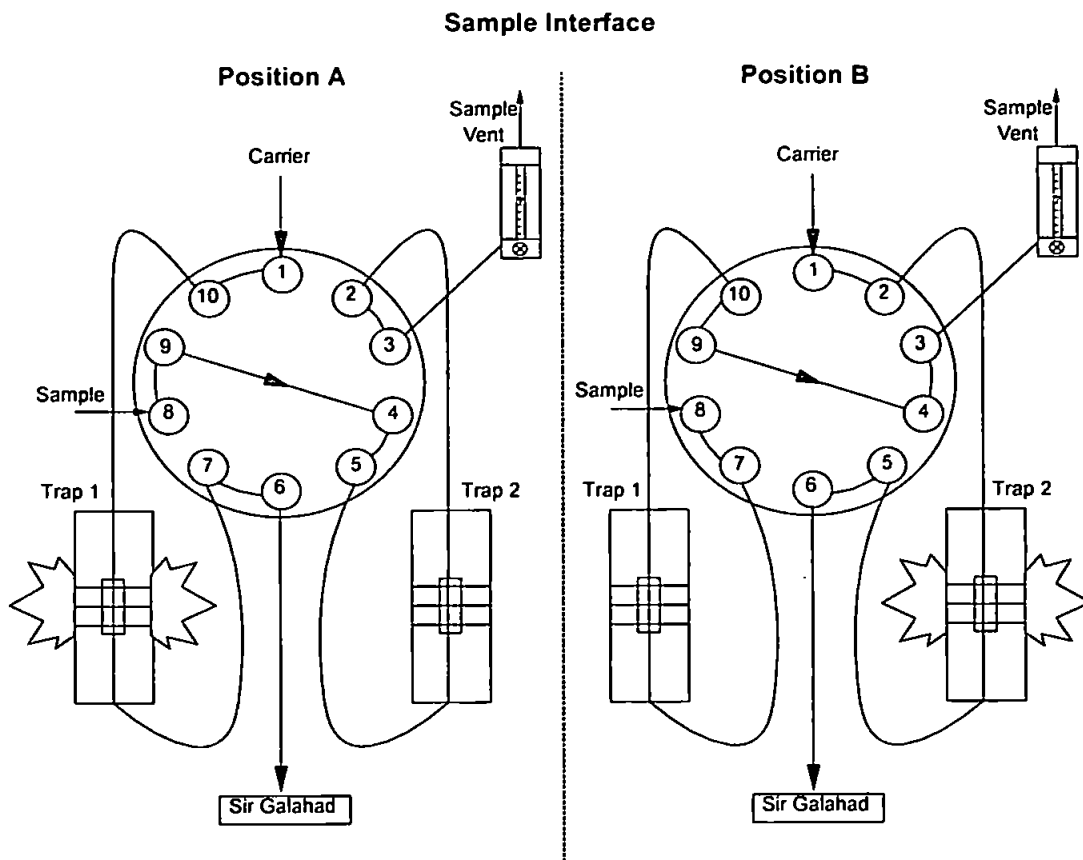


Figure 5.22. On-line sampling interface showing the pneumatically controlled 10-port rotary valve and sampling tubes in load and desorbition modes.

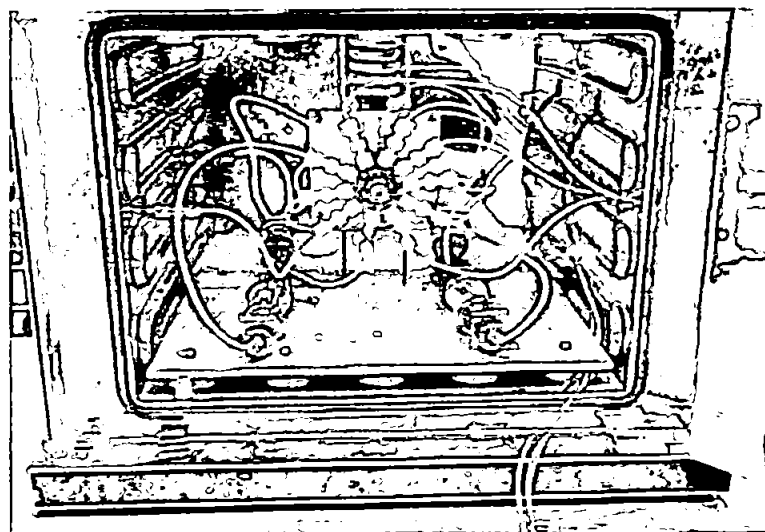


Figure 5.23. 10-port rotary valve connected to sampling tubes and located within a heated oven enclosure.

While one trap is collecting/preconcentrating the sample gas the other is desorbing the collected mercury into a stream of carrier gas which delivers the captured mercury to a fixed thermal desorbition system for secondary

desorption into the AFS detector. A control module located externally to the oven enclosure controls the rotation of the pneumatic rotary valve. Accurate measurement and control of the flow of sample through both sides of the rotary valve enables delivery of a precise volume of gas to each sampling tube.

Initially, the manual vapour injection technique is used to calibrate the system, however, a permeation source is then used as a means of secondary calibration based upon a re-slope principle. The permeation source can either be connected in front of the 10-port rotary valve or directly to the fixed instrument trap (calibration trap). Figure 5.24 shows some typical data obtained from the permeation source passing through the heated 10-port valve and through each of the sampling traps before being delivered to the instrument for measurement. By controlling the temperature and flow rate of the permeation gas an accurate standard to check for instrument drift is obtained. Incorporation of all of these units within a purged instrument enclosure produces an on-line monitoring system as shown in Figure 5.25.

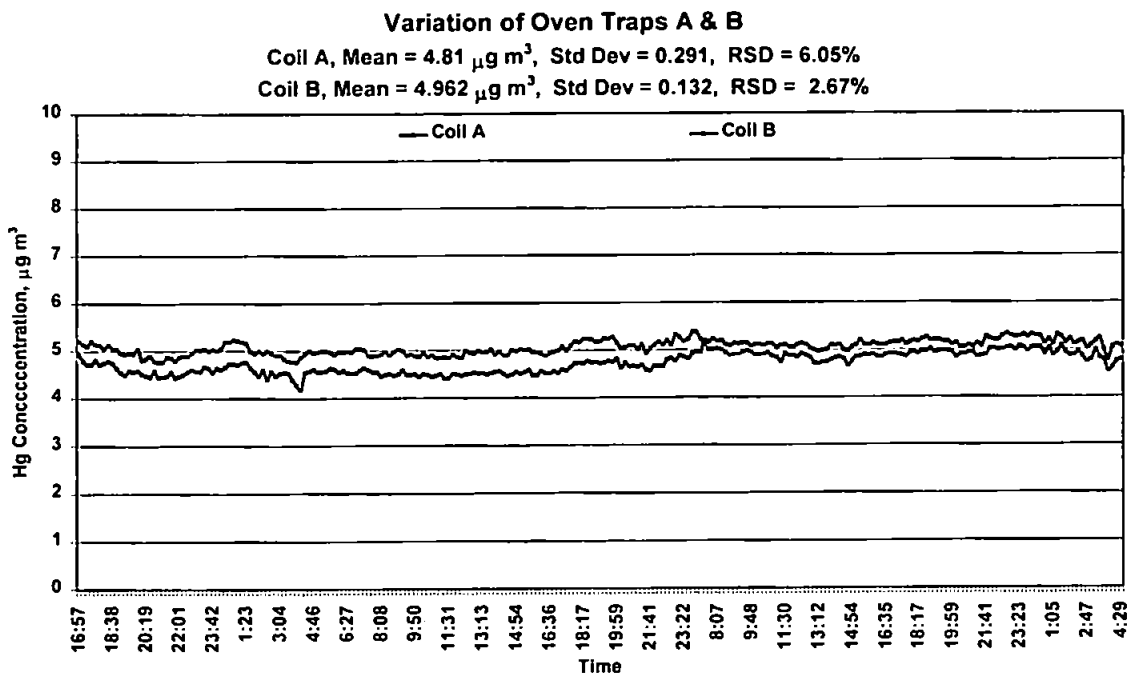


Figure 5.24 Typical permeation source data obtained through the on-line sampling interface

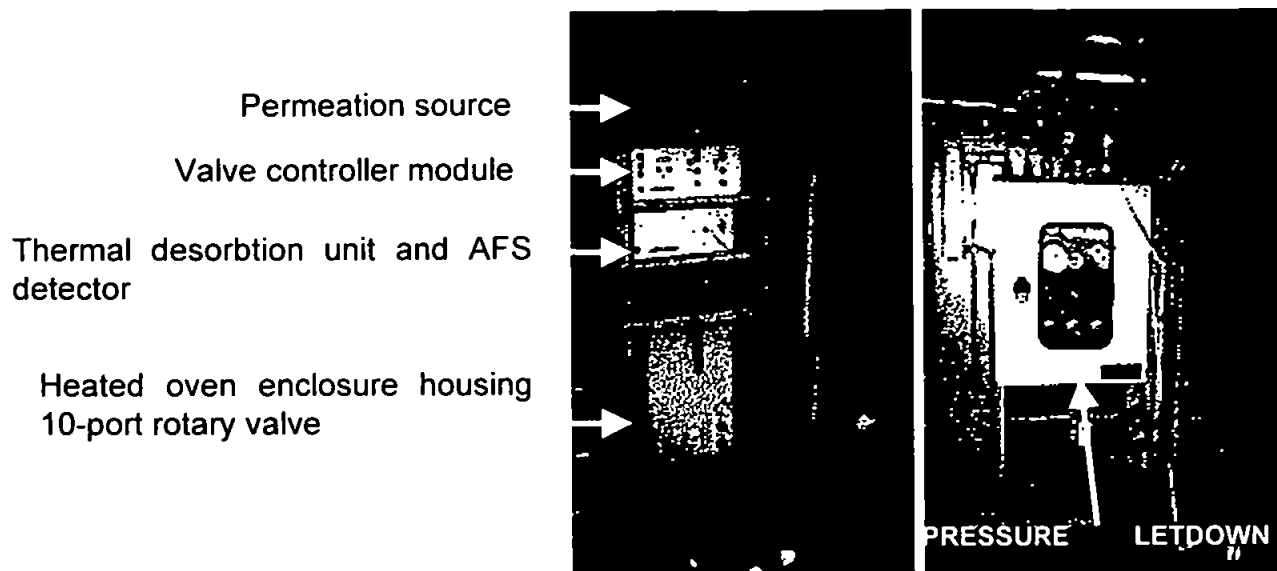


Figure 5.25. Fully automated natural gas mercury monitoring system

5.6 CONCLUSION

The development of a thermal desorption system coupled with an AFS spectrometer and calibrated by a vapour technique were the fundamental starting point for the development of a fully automated on-line mercury monitoring system. These modular devices were coupled together with a heated pressure regulator to produce an off-line sampling and analysis system. Further combination of these modular units and incorporation of switching valves allowed the automatic collection and delivery of a gas sample to a detector for measurement. The ultimate combination of all of these units with an in-built calibration device and powerful software should now enable the accurate automated monitoring of mercury in process streams.

Two methods of monitoring natural gas have been developed (Figure 5.26), the first allowing collection of a remote sample and subsequent analysis in the laboratory, and the second allows a fully automated monitoring system working directly on the process stream. Both of these developments are now becoming recognised within the field and implemented by petrochemical

companies who need to accurately monitor gas quality in order to protect downstream processing equipment. Thus, once again plant operators have the ability to confidently control and comply with gas quality standards.

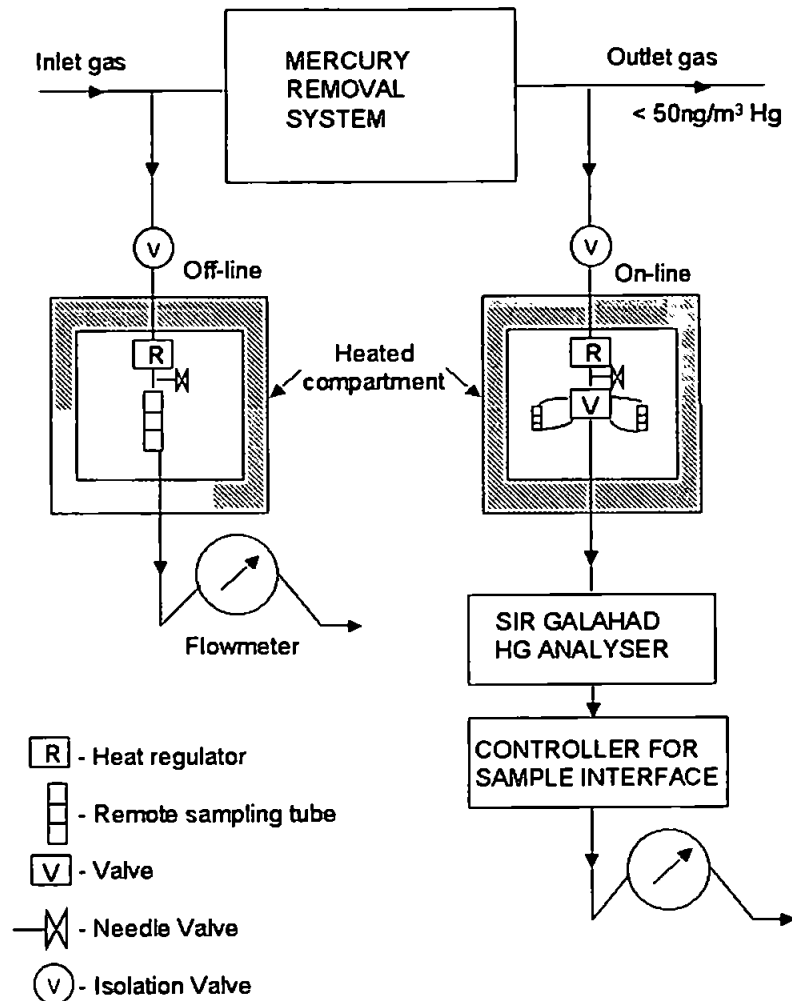


Figure 5.26. On and off line sampling systems for mercury monitoring

CHAPTER 6

CONCLUSIONS AND FURTHER WORK

6 CONCLUSIONS AND FURTHER WORK

6.1 CONCLUSIONS

An on-line mercury detection system has been successfully configured for the determination of mercury in incineration wastewater. The system allows continuous monitoring, 24 hours a day, every day with minimal operator supervision. Off-line chemistries were successfully applied on-line, resulting in a robust oxidation method catering for all forms of mercury present in the sample. Good agreement was obtained using two different oxidation techniques. The standards and reagents were proven to be effective and stable for more than 10 days. Reagent flow rates were adjusted for minimal consumption and operator attention. The on-line system is capable of sample collection, preparation, calibration, determination and report generation.

A similar manifold was successfully configured for the determination of mercury in concentrated sulphuric acid. Off-line chemistries were again successfully applied on-line. The systems components proved resistant to attack from concentrated acids and the standards and reagents were proven to be effective for more than 10 days. The system has proved effective for the on-line determination of mercury in concentrated sulphuric acid process streams, giving the process operators a greater degree of control of their production process.

The development of a thermal desorption system coupled with an AFS spectrometer and calibrated by a vapour injection technique was the fundamental starting point for the development of a fully automated on-line mercury monitoring system for natural gas. These modular devices were coupled together with a heated pressure regulator to produce an off-line sampling and analysis system. Further combination of these modular units and incorporation of switching valves

allowed the automatic collection and delivery of a gas sample to a detector for measurement. The ultimate combination of all of these units with an in-built calibration device and powerful software now allows plant operators to have an accurate mercury monitoring device.

Two methods of monitoring natural gas were developed, the first allowing collection of a remote sample and subsequent analysis in the laboratory, and the second allows a fully automated monitoring system working directly on the process stream.

All of these developments are now becoming recognised within the field and implemented by environmental protection authorities and chemical manufacturing facilities, giving plant operators the ability to confidently control and comply with environmental and quality standards.

6.2 FURTHER WORK

6.2.1 Chloralkali industry

Chapter 1 highlighted the chloralkali industry as being the largest industrial user of mercury. Here, mercury cells consume mercury by releasing the metal via different routes; in the caustic soda, chlorine gas, hydrogen gas, vented to air, in liquid effluents, in solid sludge and "unaccountable losses" usually attributed to accumulation within the process units. The most common method for removing Hg from caustic is to pass the liquor over a bed of activated carbon. Eventually the carbon becomes saturated and the beds breakthrough leading to high levels in the final product. Thus, the efficiency of the activated beds requires constant monitoring.

6.2.1.1 Caustic soda monitoring

The on-line liquid system developed in chapters 3 and 4 was modified to cater for 50 % m/v solutions of caustic soda. A schematic diagram of the on-line manifold configured for caustic analysis is essentially the same as that shown in Figure 3.6 except for the permanganate oxidant and hydroxylamine hydrochloride reductant. Presently, the system is undergoing commissioning at a European chloralkali facility. Initially the system has been evaluated by the manufacturer on a caustic pilot plant with encouraging results. The system is currently being commissioned to monitor 47% and 50% m/v NaOH process streams. Data obtained over a one-month period from a full scale production facility is shown in Figure 6.1.

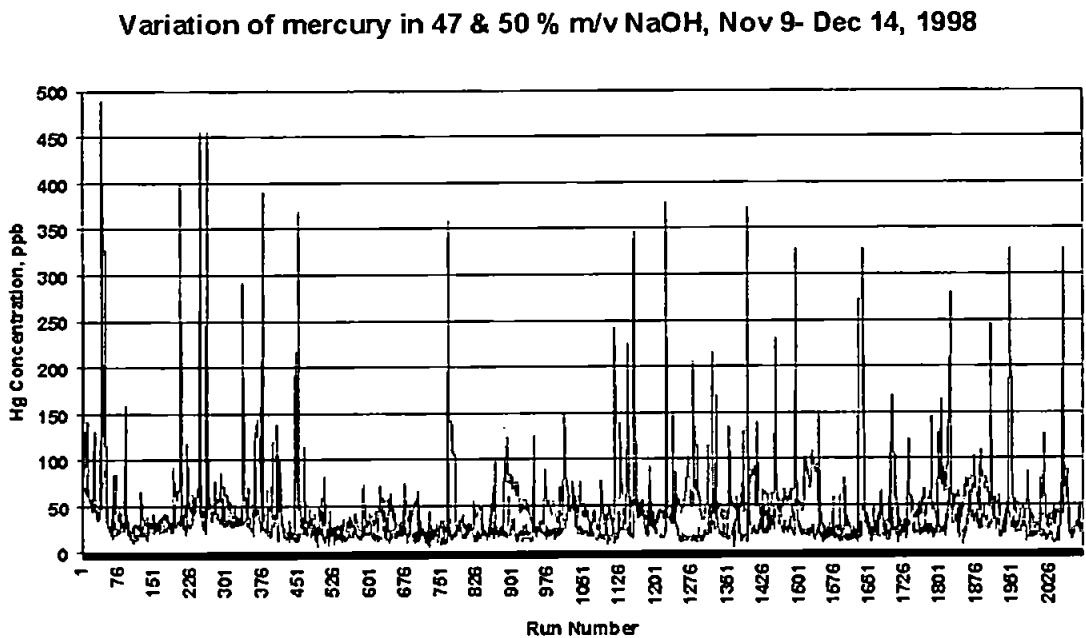


Figure 6.1. Variation of mercury in caustic soda process stream over a one-month period

6.2.1.2 Chloralkali wastewater monitoring

The major source of mercury-contaminated water in the chlor-alkali industry is the waste brine from the cell; levels typically range from 2-15 g Hg t⁻¹ of Cl₂.

Waste brine is usually combined with other aqueous mercury streams such as wash-down water, wastewater from filtering operations, washings from surface spillage, drainage from mercury cell rooms and condensates from hydrogen and chlorine gas cooling. The combined effluent is then treated by conventional sulphide precipitation and activated carbon techniques for mercury removal. Treated effluents are then normally discharged to the local river. Once again the manifold developed in chapters 3 and 4 has been adopted and configured for the continuous determination of mercury in chloralkali effluents. The system is based on a bromination oxidation pre-treatment stage followed by acidic tin (II) chloride reduction.

6.2.1.3 Mercury in cell room air

Mercury in cell room atmosphere will vary dramatically due to the amount of mercury used in the cathode and on the design of the cell room ventilation. A typical mercury cell room is shown in Figure 6.2. Here over 1500 tonnes of mercury are located within the electrolysis cell. Typical concentrations in the air above a bank of cells are in the range 10-50 $\mu\text{g m}^{-3}$, higher levels ($>200 \mu\text{g m}^{-3}$) can be encountered when cells are working inefficiently or during maintenance.

The UK health and safety guidelines recommend an occupational exposure value of 25 $\mu\text{g m}^{-3}$ over an 8 hour working day. Thus, mercury monitoring is an important consideration for adhering to emissions consents, providing data for both health and safety assessment and employee exposure within the cell room.

Some cell rooms use a high velocity ventilation system to withdraw air from the vicinity of the mercury cell and expel the contaminated air to atmosphere. At present, monitoring of the ventilation system is performed manually using hand-held mercury "sniffer" – a system based on pumping a sample of air through a UV

cell for determination. Although simple, this device is prone to contamination and is frequently inaccurate, giving only "ballpark figures" for the actual mercury concentration.

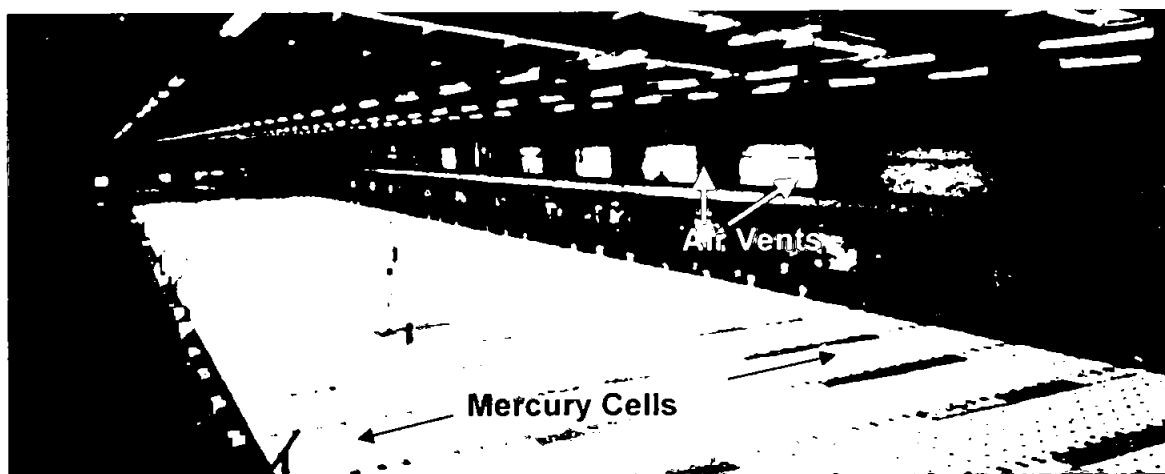


Figure 6.2. Mercury cell room with air vents indicated

A similar system based on the principles developed in chapters 3 and 4 has been adapted for mercury monitoring in cell room air. The instrument has been designed to determine gaseous mercury in air samples with full process and data control being achieved by use of a computer. Flexible software allows the operator to fully customise the instrument to suit the particular needs of individual facilities. The control and data management software allows for automatic calibration and analysis sequences with check standards at the required intervals. The main components of the instrument consist of a stream selection manifold, a pump, a rotary sampling valve, an atomic absorption spectrometer, an electronics module and a computer with the appropriate software as shown in Figures 6.3 and 6.4.

In the standard instrumentation set-up, the stream selection manifold is fitted with 12 solenoid valves. Typically, nine of these valves are connected to the sampling manifold leaving two valves for calibrants and one valve spare.

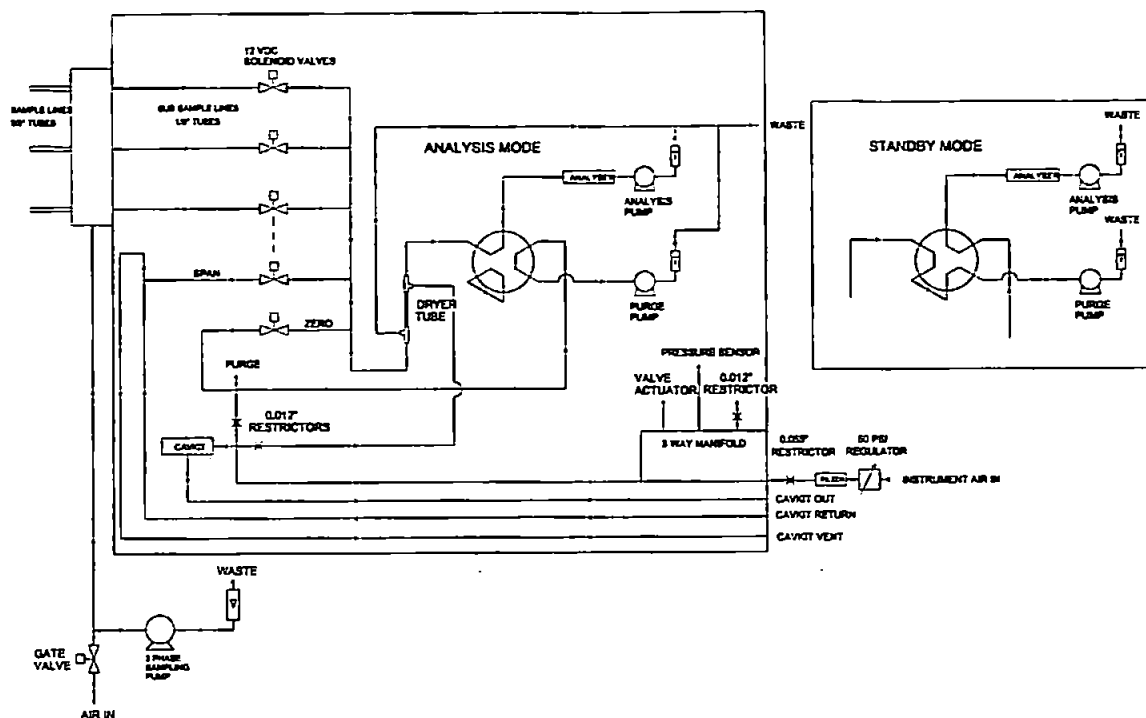


Figure 6.3. Schematic diagram of a continuous air monitoring system for use in mercury cell rooms

Selecting one of these valves will deliver the sample or calibration gas to the rotary sampling valve. A rotary sampling valve has been configured in a continuous flow mode, i.e. either the sample/calibration gas or blank carrier gas is continuously delivered to the detector at any one time. The observed signal is directly proportional to the amount of mercury present in the sample. The generated signal is then transferred to the p.c. for integration; the calculated signal is then measured relative to a stored calibration graph produced from a permeation device. The analysis cycle is repeated for each line in the sequence.

The software has been developed with its own embedded data trending and statistical package, allowing the operator to fully view the variation of individual sampling vents or groups of vents. Results can be calculated to produce mass balances. Automatic reports can be generated daily, weekly or monthly by the operator. The entire system is controlled fibre optically via a

master computer that is located within the control room over 100 metres from the instrument.

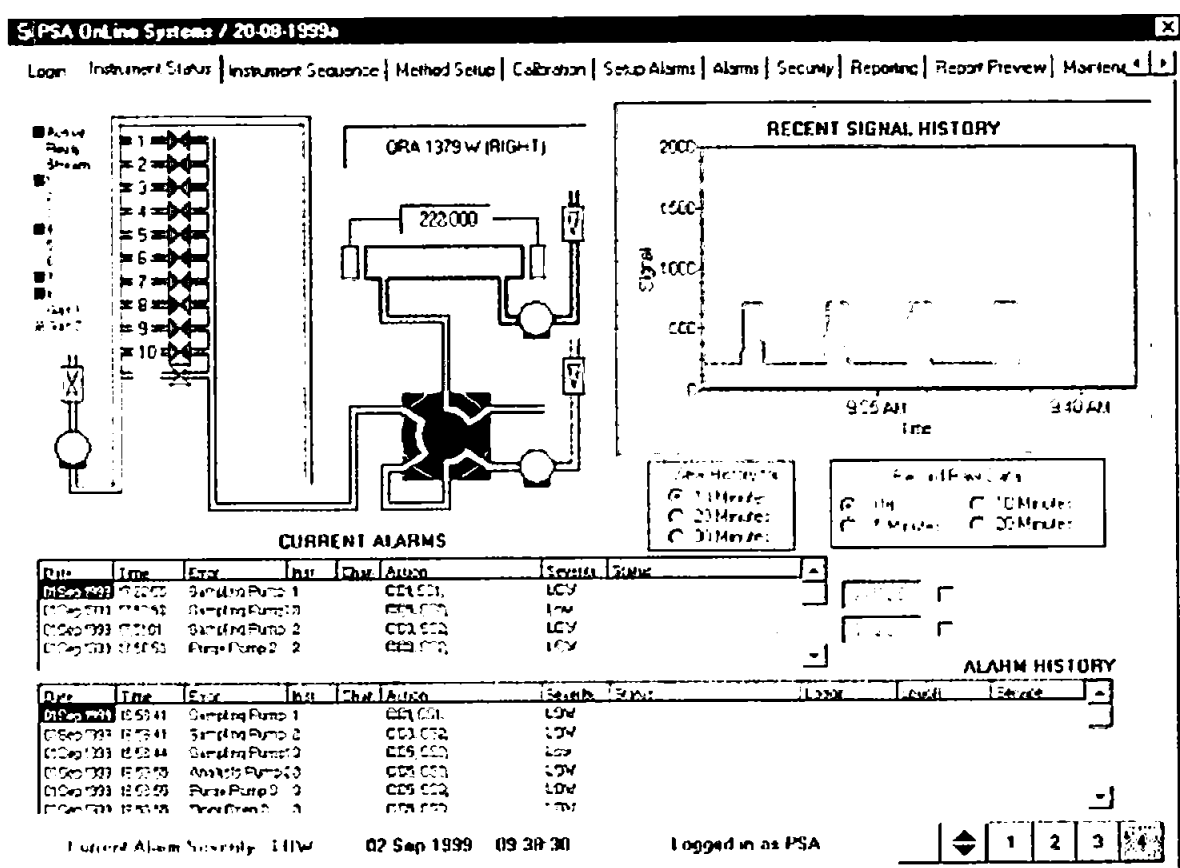


Figure 6.4. Graphical user interface designed for continuous air monitoring

6.3 CONCLUSION

In general it is anticipated that the system will ultimately become more robust to suit the industrial environment. Essentially, the system will be configured into separate modular 19" rack components allowing insertion into industrial instrument housing. The electrical and wet sections will be segregated and purged, thereby minimising corrosion of the instrument components from the surrounding environment. A more industrially robust computer system will be employed, with a graphical user-interface allowing both on-line analysis with manual intervention.

Remote operation has also been investigated through network, internet and wireless links. More rapid computer processing power is allowing the real time storage and statistical analysis of long periods of data. Soft computing techniques on peak shape analysis using neural networks and fuzzy logic algorithms are already methods being adopted in other analytical applications and could prove well suited to AFS detection systems

Further work on the systems sensitivity is being performed by integration of higher quality components. In particular, the signal processing could be improved by integration of a higher specification digital pre-amplifier system; this should reduce signal noise significantly and ultimately improve resolution. Additionally, better quality optical devices are also now readily available.

Additional investigations are being conducted into the reduction of reagent consumption. Reagent consumption could be reduced by miniaturisation of flow-through components and utilising micro-flow tubing, pumps, reactors and valves. Already, slower more stable peristaltic and piston pumps can offer increased control of low flow rates allowing more precise delivery of reagents and samples.

It is expected that through the advancement of computer processing, miniaturisation of components, more resistant and machinable materials the system will incorporate a greater degree of functionality allowing the integration of various modules to build a variety of process monitoring instruments for both aqueous and gaseous processes. The combination of these various improvements/developments provides an interesting opportunity to greatly enhance the application of the system to a variety of new low-level mercury monitoring applications. However, as always it will be legislation, performance and cost that will influence further development of the various systems.

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8 APPENDIX - PUBLICATIONS

At-line Determination of Mercury in Process Streams Using Atomic Fluorescence Spectrometry†

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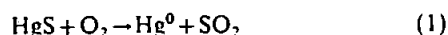
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Atomic fluorescence spectrometry (AFS) has been coupled with vapour generation sample introduction for the at-line determination of mercury in concentrated sulfuric acid production streams. Matrix and heat effects were overcome by the use of discrete sample injection techniques. A sample collection and pre-treatment manifold is described in combination with permanganate oxidation and SnCl₂ reduction chemistries for coupling with a fully automated instrument. Continuous monitoring of single grab samples of concentrated sulfuric acid over periods of 24 and 15 h resulted in precisions of 5.8 and 8.9% RSD and mean mercury concentrations of 1.11 and 1.08 µg g⁻¹, respectively, compared with 1.2 and 0.95 µg g⁻¹ obtained by a laboratory based method. The application of the instrument in on-site trials at a sulfuric acid plant is described. The mercury concentration in sulfuric acid was monitored continuously over a period of 10 d without intervention and showed excellent agreement with results of laboratory analyses performed over the same period.

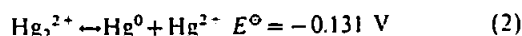
Keywords: *Mercury cold vapour; sulfuric acid; atomic fluorescence spectrometry; at-line determination; sample pre-treatment*

Sulfuric acid has many industrial applications ranging from fertiliser production to food processing. Consequently, users of acid have set stringent quality criteria specifically for mercury which need to be met by their acid suppliers. At present acid process streams at smelting plants are monitored manually several times a day for mercury, requiring that a sample be collected and analysed in the laboratory. This is laborious, prone to contamination and time consuming. It can often take up to a day before the mercury concentration in the acid is known. During this delay period several hundred tonnes of acid may have been produced which do not meet the requisite criteria.

The presence of mercury in sulfuric acid is due to the association of mercury(II) sulfide (cinnabar) with the sulfide bearing ores. When the sulfide ore is roasted in air at 600 °C the cinnabar decomposes to produce mercury vapour and sulfur dioxide:



The subsequent roast gas can then be passed over activated carbon filter beds to remove the mercury vapour. In some production plants the roasted gas is purged through a solution of mercury(II) chloride to form mercury(I) chloride, which precipitates, thus removing the majority of the mercury from the gas. For the disproportionation equilibrium:



It can be seen from eqn. 2 that Hg⁰ is capable of reducing Hg²⁺ to Hg₂²⁺, as the electrode potential favours the reverse reaction. This principle is sometimes used to remove mercury from the roast gas in the contact process. However, it should also be noted that any removal of Hg²⁺ by precipitation of insoluble compounds, or Hg⁰ by outgassing, will cause the reaction to proceed in the forward direction.

Although mercury removal rates of greater than 95% are obtained with such processes, some of the mercury is still transferred with the roast gas to the adsorber towers and is present in the final product acid. During this process it is unavoidable that some mercury compounds (Hg⁰; Hg₂Cl₂, HgCl₂) are also transferred with the wet roast gas to the reaction chamber.

The proportions of mercury species in the roast gas after scrubbing are unknown. One would assume that mercury(0) and mercury(I) would be oxidised to mercury(II) during the production of sulfuric acid. If the mercury is present as Hg⁰, Hg^I and Hg^{II} species it will be necessary to oxidise all the Hg^I and Hg⁰ to Hg^{II} in order to achieve a total mercury result. When the oxidant is in excess, complete oxidation to mercury(II) species is possible. Off-line, this oxidation would normally be performed using an oxidant such as potassium permanganate, potassium persulfate or bromine. After oxidation, the resulting Hg^{II} species can readily be reduced using an acidic solution of tin(II) chloride to give a total mercury result.

The toxic effects of mercury compounds on environmental systems have been well established over the last few decades, resulting in many techniques for their detection. Originally, colorimetric and spectrophotometric methods, which were based on mercury ions forming chelates with dithione and diphosphylthiocarbazon, were used.¹ These methods are troublesome and suffer from contamination and poor sensitivity. Today, the most commonly used method for determining mercury is cold vapour atomic absorption spectrometry (CVAAS), a method originally developed in 1963 by Poluetov and Vitkun.² It was not until 1968 that Haich and Ott³ refined and popularised this method; since then many modifications have been made to this principle.

The atomic fluorescence technique is particularly good for the determination of mercury as it is an atomic vapour at room temperature and undergoes resonance fluorescence. West,⁴ in 1974, showed theoretically that cold vapour atomic fluorescence spectrometry (CVAFS) should be more sensitive and produce considerably less spectral interference from non-specific absorption compared with the corresponding AAS technique.

Thompson and Reynolds⁵ were the first to use the cold vapour technique for the determination of mercury in 1975. They modified a conventional atomic absorption spectrometer. More recently Godden and Stockwell⁶ developed a non-dispersive fluorescence spectrometer specifically for mercury

† Presented at the Eighth Biennial National Atomic Spectroscopy Symposium (BNASS), Norwich, UK, July 17-19, 1996.

determination. Their system was based on a conventional molecular fluorescence spectrometer coupled to a vapour generation process. The detector arrangement of Godden and Stockwell⁶ was simple in design and rugged in construction and therefore an ideal starting point for the translation of a laboratory instrument into a process analyser.

There are several potential problems which are likely to be encountered during the determination of mercury in concentrated sulfuric acid. The first is the difficulty of obtaining a continuous sample for analysis which is representative of the main stream. This has to be delivered to the instrument with the minimum of delay, without significant change in composition or physical state, and at a level of cleanliness with which the analyser can cope.

The viscosity, corrosiveness and temperature of the acid must also be taken into account when designing such a system because hot sulfuric acid is extremely oxidising. The instrument must be capable of at-line digestion, automatic calibration and sensitive detection, as well as full data management. Ideally the system should also have some sort of error monitoring system. The long term dependability and stability required for process analysers is not usually encountered in laboratory techniques, so an accurate and reliable analytical instrument monitoring a high-throughput process can be a valuable asset. An inaccurate, unreliable instrument can be a menace which can lead to losses through lower efficiency or, worse still, through plant shutdown.

A bulk chemical manufacturer was approached to investigate the possibility of configuring an at-line system for the determination of mercury in sulfuric acid. The manufacturer currently analyses its acid stream three times a day manually, using CVAAS.

The sulfuric acid sample is 96% m/m H₂SO₄, has a density of 1.821 g cm⁻³, has an SO₂ dissolved gas content of approximately 0.1% m/v and is free from particulate matter. The temperature of the acid at the point of sampling is around 55°C. The acid contains approximately 10 mg l⁻¹ of Fe (from the stainless steel tubing used in the piping) and less than 1 mg l⁻¹ of As, Cd, Cr, Cu, Mg, Mn, Ni, Pb and Zn.

EXPERIMENTAL

Instrumentation

Basic features of at-line system

An at-line system was specifically designed to determine mercury in liquid samples with full process and data control via an IBM compatible computer. The software allows the operator to fully customise the instrument to suit the application; automatic calibration and analysis protocols can be fully programmed within the software. The unit also employs an error monitoring system which checks for the flow of sample, reagents and gases, as well as for leaks within the system. Should any of the reagents or gases fail to be present an alarm will sound and the instrument will shut down. The main components of the system are a stream selection valve, a peristaltic pump, a six-port switching valve, a gas-liquid separator, an atomic fluorescence spectrometer and a computer fitted with a 4–20 mA DAC output. The instrumental conditions typically used during at-line process analysis are shown in Table 1.

Sample collection

The sample was collected either via a fast loop principle from the flowing process stream or by sub-sampling a constantly replenished over-flow vessel. Hence, a fresh representative sample of the process stream was delivered to the instrument with minimum delay and no change in composition.

Table 1 Instrumental conditions for PSA 10.223 at-line mercury analyser

Carrier gas	300 ml min ⁻¹ argon
Sheath gas	300 ml min ⁻¹ argon
Dryer gas	2500 ml min ⁻¹ air
Autozero	On
Timer	On
Timer interval	15.00 min
Filter factor (smoothing)	4
Runs	1
Fit type	Least squares straight line
Gain	1000 × 4.0
Delay	120 s
Measure	150 s
Memory	120 s
Loop size	300 µl
Sample flow rate	0.7 ml min ⁻¹
Reductant flow rate	0.7 ml min ⁻¹

Sequence of events

With the standard instrument set up shown in Fig. 1 the stream selection device was fitted with four valves, any one of which could be selected at a given time. The sample/standard was pumped to a six-port discrete injection valve where a fixed volume of the sample was introduced to the mixing manifold. At the mixing manifold chemical pre-treatment was performed whereby the sample was mixed first with an oxidant to convert all the available mercury into the divalent state, Hg²⁺, then the mercury was reduced to the gaseous phase, Hg⁰, by reduction with tin(II) chloride. The mixing coils were 0.8 mm id and 200 and 150 cm long for the oxidation and reduction, respectively, resulting in respective residence times of 86 and 65 s. The gaseous mercury was stripped from solution using the gas-liquid separator in the presence of a carrier gas, and then passed through a hygroscopic membrane dryer (Nafion, Perma-Pure Products, Farmingdale, NJ, USA). The dried sample gas was then introduced to a fluorescence detector for determination. The detector returned a transient signal which was forwarded to the computer in BCD code, and then transmitted via a DAC output to the process control room through the system's Touchstone software.

Modes of operation

With an analysis program such as that shown in Table 2, the instrument can be configured into almost any analysis sequence. The at-line instrument has two modes of operation. The first is when the instrument performs one calibration daily and then analyses the sample repeatedly over the day against that single calibration, which is a feasible mode of operation given the excellent stability of the system, as demonstrated later. The second mode of operation is when the instrument continually re-calibrates itself between samples.

Reagents

Standards were prepared using a mercury(II) stock solution (Spectrosol, Merck, Poole, UK) in both 10% (v/v) and concentrated sulfuric acid (AnalaR, Merck). The reductant was prepared from tin(II) chloride dihydrate (AR, Aldrich, Gillingham, UK), a 4% m/v solution was prepared in 30% v/v HCl (AR, Fisons, Loughborough, UK). The reductant was purged with argon (Pureshield, BOC, Guildford, UK) for approximately 20 min in order to remove any residual mercury vapour. The oxidant was either a 0.1 M potassium bromate-potassium bromide solution (ConvoL, Merck) or a 5.0% m/v solution of potassium permanganate (Spectrosol low in Hg, Merck) in de-ionised water (Option 3, Elga, High Wycombe, UK).

turer's value (Table 4). This was probably due to the oxidation of Hg^{I} to Hg^{II} , or to the removal of other interfering species by oxidation. The potassium permanganate pre-oxidation resulted in higher recoveries than those obtained without oxidation, with a mercury concentration of $18.1 \mu\text{g ml}^{-1}$ (Table 4) being obtained, which was similar to that obtained by the bromination technique.

The results of the off-line investigations indicated that it was necessary to pre-oxidise the sulfuric acid sample in order to obtain close to 100% recovery for Hg. It is probable that pre-oxidation converted the Hg^{I} species to the Hg^{2+} ion, which is readily reducible with an acidic solution of tin(II) chloride. It would appear that around 50% of the mercury present in the sulfuric acid sample was present as a Hg^{I} salt, most probably Hg_2SO_4 .

The next stage was to transfer the chemistries and the sample to the PSA 10.223 at-line mercury analyser for further development.

Laboratory Trial

The at-line monitoring system was initially tested in the laboratory using a grab sample of concentrated sulfuric acid from a zinc smelting plant which was diluted to 10% v/v. During this trial the tests were performed using an acidified solution of potassium bromate-bromide as the oxidant. Fig. 2 shows the results of continual re-calibration and analysis. This resulted in a relative standard deviation (RSD) of 1.36% for the sample and less than 8.0% for the standards over the test period of 36 h. In three instances the sample peak height was greater than that of the top standard. The greatest variation appeared to be in the blank solution which was 10% v/v sulfuric acid, which may have been due to carry-over from the top standard.

It had previously been necessary to add hydroxylamine hydrochloride after the pre-oxidation stage in order to reduce excess oxidant; however, this was also eliminated by increasing the concentration of the tin(II) chloride solution from 2 to 4% so that it was in excess. Sample dilution was further reduced by using the oxidant stream as the sample carrier stream. These changes also improved the S/N. The bromination oxidation gave rise to a noisier signal than the permanganate oxidation, so it was decided to use the latter method for the site trials.

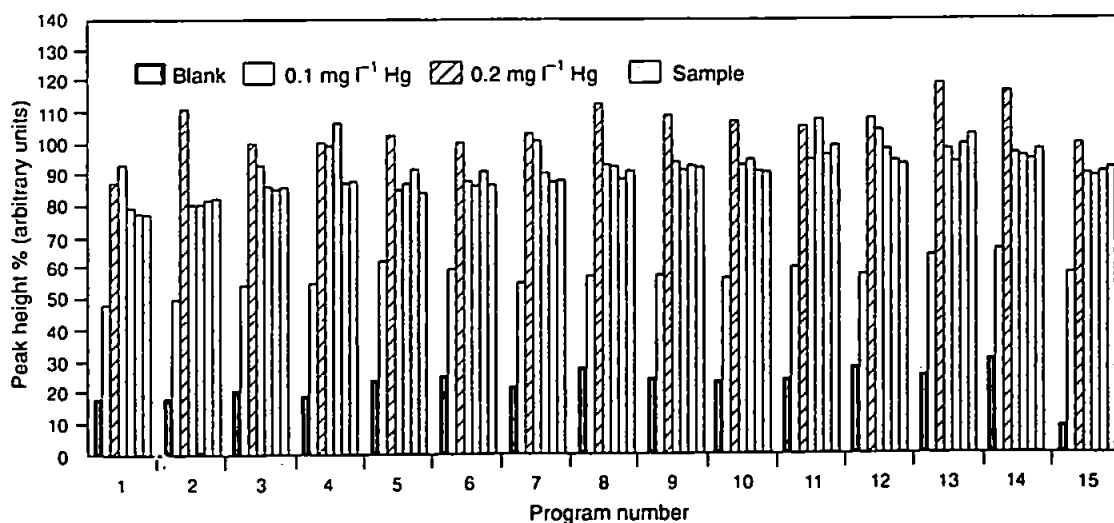


Fig. 2 Graph showing the variation in peak height % in the continuous re-calibration mode.

Off-line Site Trial

Having configured the system as described above, and using permanganate as the pre-oxidant, it was installed at a zinc smelting plant. Two separate production streams of sulfuric acid required monitoring for mercury, namely the final product 'white' acid and the un-bleached 'black' acid, the black colour being caused by carbon in the sulfur dioxide gas used to produce the acid.

Continuous recalibration mode

A single sample of concentrated 'white' sulfuric acid was obtained from the production line and analysed continuously for 15 h (36 analyses) using the at-line system operated in continuous recalibration mode, as shown in Fig. 3. This sample was also analysed using laboratory-based CVAAS for comparison. Mean results are shown in Table 5 and excellent agreement was obtained with the laboratory result. The standardisation procedure was also very stable, with the 0.543 and 1.358 μg

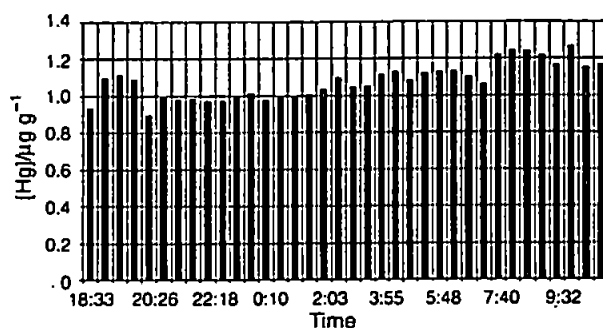


Fig. 3 Results of off-line site trial for the determination of Hg in 'white' sulfuric acid, showing the stability of the instrument when using the continuous re-calibration mode.

Table 5 Comparison of continuous mercury analysis with batch mode analysis for off-line site trial

	Hg concentration/ $\mu\text{g g}^{-1}$	
	Continuous AFS	Laboratory CVAAS
Continuous recalibration	1.08 ± 0.1 ($n=36$)	0.95
Daily calibration	1.11 ± 0.06 ($n=77$)	1.2

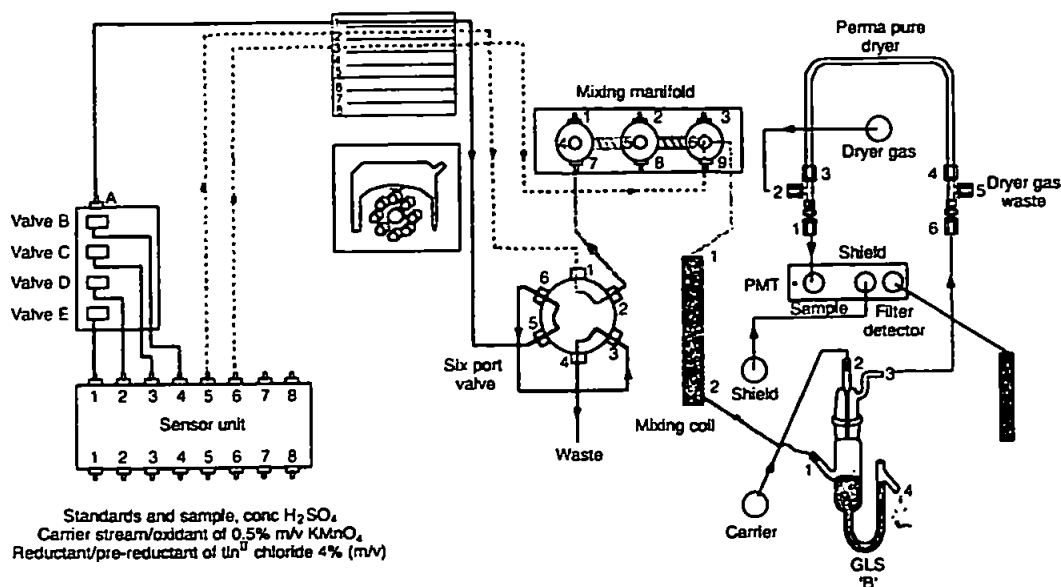


Fig. 1 Schematic layout of the at-line atomic fluorescence instrument for the analysis of sulfuric acid.

Table 2 Analysis program used for laboratory trials using the bromination chemistry

Line	Valve	Tag
1	B	Std 1, Blank 10% (v/v) H ₂ SO ₄
2	C	Std 2, 10 mg ml ⁻¹ Hg
3	D	Std 3, 50 mg ml ⁻¹ Hg
4	E	Sample ??? mg ml ⁻¹ (Sample, 10% v/v)
5	E	Sample ??? mg ml ⁻¹ (Sample, 10% v/v)
6	E	Sample ??? mg ml ⁻¹ (Sample, 10% v/v)
7	E	Sample ??? mg ml ⁻¹ (Sample, 10% v/v)
8	A (off)	Time-loop back to line 1

Table 3 Instrument settings for PSA 10.023 Merlin detector and PSA 10.004 vapour generator used for laboratory analysis

Carrier gas	300 ml min ⁻¹ argon
Sheath gas	300 ml min ⁻¹ argon
Sample/blank flow rate	8.0 ml min ⁻¹
Reductant flow rate	4.0 ml min ⁻¹
Amplification	1 × 7.5 = 7.5 (1–10000)
Dryer gas	2500 ml min ⁻¹ air
Filter factor (smoothing)	32
Delay	10 s
Rise	30 s
Measure	30 s
Memory	60 s

Method Development

To determine the efficacy of various oxidation methods the following sample pre-treatments were performed. (a) To analyse the sample at different dilutions, without any oxidation stage, using the standard additions approach. Omitting the oxidation stage produces a Hg⁰ and Hg^{II} result only because Hg^I will not be readily reduced to Hg⁰. (b) To analyse the sample using the proposed two oxidation methods, again with the standard additions approach (at 1 and 10% dilutions). Oxidising the sample will produce a total mercury result.

The acid sample was first analysed without any oxidation at a dilution of 1 and 10% v/v. Mercury standards were prepared in the same matrix at 20, 40 and 60 ng ml⁻¹ Hg. Next the sample was analysed using potassium bromate-bromide as the oxidant. To each acid-cleaned 100 ml calibrated flask, 2 ml of 0.1 M potassium bromate-bromide solution was added. Standard additions was again employed at the same level as before (20, 40 and 60 ng ml⁻¹ Hg). Each flask was then diluted to the mark with either a 1 or 10% solution of the acid sample. The flasks were then left to stand for approximately 20 min. Prior to analysis each flask was pre-reduced with a few drops of hydroxylamine hydrochloride to convert the excess bromine to bromide. The samples were then analysed in the same manner as the un-oxidised sample. Instrumental conditions are shown in Tables 2 and 3.

Lastly, the samples and standards were prepared by the same method as for bromination, except that the bromate-bromide was replaced with 5.0 ml of 5.0% m/v KMnO₄ solution as the oxidant.

RESULTS AND DISCUSSION

Method Development

The results for the oxidised and un-oxidised sample are shown in Table 4. These results suggest that around 50% of the mercury in the sample is likely to be present as mercury(I). The 1% v/v dilution gave exactly the same value as that of the 10% v/v solution (10.5 µg ml⁻¹ Hg), suggesting that the sulfuric acid did not cause a matrix interference in the mercury determination.

The bromination pre-oxidation resulted in a mercury concentration of 17.6 µg ml⁻¹ Hg, which was 92% of the manufact-

Table 4 Results for the comparison of oxidation sample pre-treatment methods

Oxidation pre-treatment method	Hg concentration in concentrated H ₂ SO ₄ / µg ml ⁻¹		
	This work	Manufacturer's value	Recovery (%)
10% sample, no oxidation	10.4 ± 0.04	19.0 ± 1.0	54
1% sample, no oxidation	10.5 ± 0.05	19.0 ± 1.0	55
10% sample, KBr-KBrO ₃ oxidation	17.6 ± 0.06	19.0 ± 1.0	92
10% sample, KMnO ₄ oxidant	18.1 ± 0.03	19.0 ± 1.0	95

g^{-1} Hg standards giving RSDs of 3.2 and 7.3%, respectively. The instrument was calibrated ten times over the analysis period.

Daily calibration mode

The stability of the system was also tested by calibrating the unit once at the start of the day; then analysing a single sample of concentrated 'black' sulfuric acid repeatedly for 24 h. Results of the continuous analysis are shown in Fig. 4 and illustrate the excellent stability of the unit in this mode of operation. Mean results are shown in Table 5, and show that the sample concentration varied less than 6% over 24 h and 77 repeat analyses. Also, excellent agreement between the continuous and laboratory systems was obtained.

At-line Site Trial

The system was now set up at-line, *i.e.*, connected to the production stream for continuous monitoring of the concentration of Hg in both 'white' and 'black' acid production streams. The instrument was calibrated over a 50 min period, then five determinations of Hg concentration were made at 9 min intervals, after which the cycle was repeated. Results for Hg concentration over a 10 d period are shown in Fig. 5. It is evident from the results that the concentration of Hg in both 'white' and 'black' acid streams followed a similar trend, with several peaks in concentration occurring. The regions of blank data between runs 67–70 and 60–62, for the 'white' and 'black' acids, respectively, represent periods of plant shut-down.

During the 10 d period only eight laboratory analyses were performed for each of the production streams. These results are shown in Table 6 alongside the results obtained with the at-line monitoring system, and excellent agreement was obtained. During the monitoring period the Hg concentration in the product acid rose above the $1 \mu\text{g ml}^{-1}$ action limit during the peaks shown in Fig. 5. These peaks could be identified much earlier using the at-line monitoring system, allowing the acid to be diverted to a low grade holding tank until the Hg concentration dropped back below the action level. This illustrates two of the major advantages of continuous at-line monitoring. Firstly, it is possible to identify the trend in Hg concentration, thereby allowing action to be taken much earlier than if only single grab samples were analysed once every day; and secondly, results were obtained in real time rather than after the 5 h delay typical of laboratory analyses.

CONCLUSIONS

The at-line mercury detection system was successfully configured for the determination of mercury in concentrated

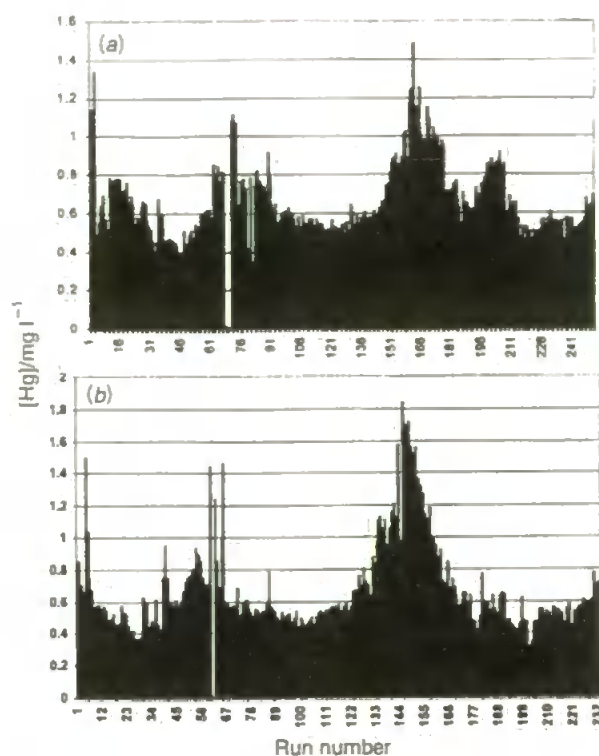


Fig. 5 Results of at-line site trial with continuous monitoring of the sulfuric acid production stream showing the variation in the concentration of Hg in: (a) 'white' acid; (b) 'black' acid over a 10 d period.

Table 6 Comparison of data for Hg concentration in 'white' sulfuric acid, obtained with the at-line continuous monitoring system and by off-line laboratory batch analyses

Sampling time†	Hg concentration/ $\mu\text{g g}^{-1}$	
	At-line analysis	Off-line laboratory analysis
21/09/96	1.25	1.3
22/09/96	0.64	0.6
23/09/96	0.61	0.6
24/09/96	0.58	0.6
25/09/96	0.75	0.8
26/09/96	0.70	0.8
27/09/96	0.56	0.5
28/09/96	0.64	0.6

† Off-line laboratory samples were taken at 6.30 am and at-line samples at either 6.20 am or 6.40 am.

sulfuric acid. The off-line chemistries were successfully applied at-line. A robust oxidation method was developed to cater for all forms of mercury which may be present in the acid. Good agreement was obtained using two different oxidation techniques. The permanganate technique was chosen over the bromination oxidation as it requires fewer reagents and minimises instrument signal noise.

The system components proved resistant to attack from concentrated acids. The standards and reagents were proven to be effective and stable for more than 10 d. The reagent flow rates were adjusted for minimal consumption so that the operator would only need to prepare the reagents once a week, thus minimising operator attention.

The sample collection manifold also proved effective for the delivery of a fresh representative sample of hot sulfuric acid to the instrument. The extreme weather conditions experienced (-12°C) did not appear to affect the instrument's performance

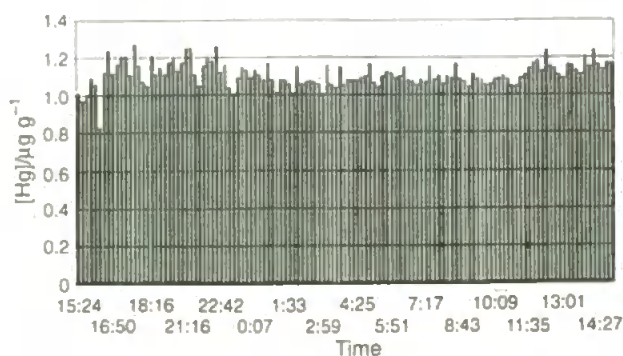


Fig. 4 Results of off-line site trial for the determination of Hg in 'black' sulfuric acid using the daily calibration mode.

in any way. Very good agreement with laboratory results utilising CVAAS was obtained from the at-line AFS system. The system was proved effective for the at-line determination of mercury in concentrated sulfuric acid process streams, giving the process operators a greater degree of control of their production process.

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The role of discrete sample injection in trace mercury analysis by atomic fluorescence spectrometry

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Coupling specific atomic fluorescence spectrometers to vapour generation techniques is a highly sensitive approach to the determination of trace levels of mercury. In many sample types the levels of the mercury content are extremely high and the matrix may have a deleterious effect on the measurement. This paper discusses the application of discrete sample injection techniques to broaden the range of analytes tested and the levels analysed. The limitation of linear dynamic range for fluorescence is the self-absorption effect. Reducing the effective sample size to below 100 μ litres allows a linear calibration up to 10 parts per million (ppm). This sample limitation, coupled to the software's ability to reset the sampling valve should the signal level exceed the maximum setting, ensures that levels of up to 100 ppm can be presented to the analyser. An additional advantage of the discrete sample injection applies to complex analytical samples, for example concentrated sulphuric acid. The effective dilution provided by this means overcomes any matrix interferences and quickly provides correct data. With proper care, the analytical range of the system described can extend over seven orders of magnitude from less than 1 part per trillion (ppt) through to 10 ppm.

Introduction

Over the past decade there has been considerable concern about the levels of heavy metals in the environment, especially mercury, arsenic, selenium and antimony. Since the authors became interested in this field, levels of mercury have received by far the most attention. Currently the legislation sets out the limits for mercury as the total content, whatever the form in which the mercury may be present. However, there is a pressing case for analysing the various species of mercury present; methylmercury, for example, is more than 1000 times more toxic than mercury in its inorganic forms. Recently Jones *et al.* [1] have suggested a simple gas chromatographical separation system, linked to a specific atomic fluorescence detector, to determine such species in a range of materials including soils, sludges and effluent.

In 1988, the reorganization of the UK water industry into privatized companies and a policing facility provided by the National Rivers Authority laboratories drew attention to the monitoring of mercury in drinking water. The levels required, and the sampling frequency which were dictated by the legislation, meant that a radically new direction for instrumentation was needed. The batch methods using atomic absorption detection available at this time provided neither the detection limits nor the throughput necessary.

Thompson and Godden [2] described an atomic fluorescence method for the measurement of mercury; Godden and Stockwell [3], using an available molecular fluorescence detector with subtle modifications, designed a simple but effective commercial variation of this with the additional potential for complete automation. In 1989, P S Analytical introduced the world's first fully automated mercury analyser based on these developments. Since then more than 20 commercial competitors have been introduced around the world. With each of these making various claims as to detection capabilities, it would seem to the analytical community that the determination of mercury at low levels is just a trivial matter. This is very far from the truth because at the levels required, often between 10^{-10} and 10^{-12} g litre, it is very difficult to get representative samples and reproducible results. With care to the sampling and methodology, levels below 1 ppt can be measured.

In the UK's water industry the atomic fluorescence measurement coupled to vapour generation techniques has become well established. The use of a hygroscopic membrane drier tube to continuously remove moisture developed by the vapour generator has been particularly useful in laboratory applications [4]. In addition, the range of analytes and concentration levels analysed has been increased using discrete sample injection techniques [5].

Figure 1 shows the layout of the fully automated instrument which can be used to analyse liquid samples. It comprises a random access autosampler, a vapour generator and the Merlin Atomic Fluorescence Detector. These instruments are controlled using an IBM compatible PC.

Figures 2 and 3 show the schematic arrangement of the vapour generator and the transfer of the mercury entrained in an argon carrier gas into the Merlin detector. The switching valve ensures a steady transfer from reagent blank to sample and this minimizes the inherent noise on the signal. A typical signal response for the continuous flow approach is shown in figure 4. The steady state signal is produced by a 10 ppt standard and from this it is easy to show a detection level below 1 ppt without preconcentration. The peak shape is specific to the sample type and the presence of interferences can be recognized should this peak shape deviate from the norm. Table 1 shows a comparison between continuous flow and batch analysis systems. Typically, the measurements can be made over seven orders of magnitude. The discrete sample injection approach allows the system to cope both with high concentrations of mercury; matrix interference effects can also be masked.

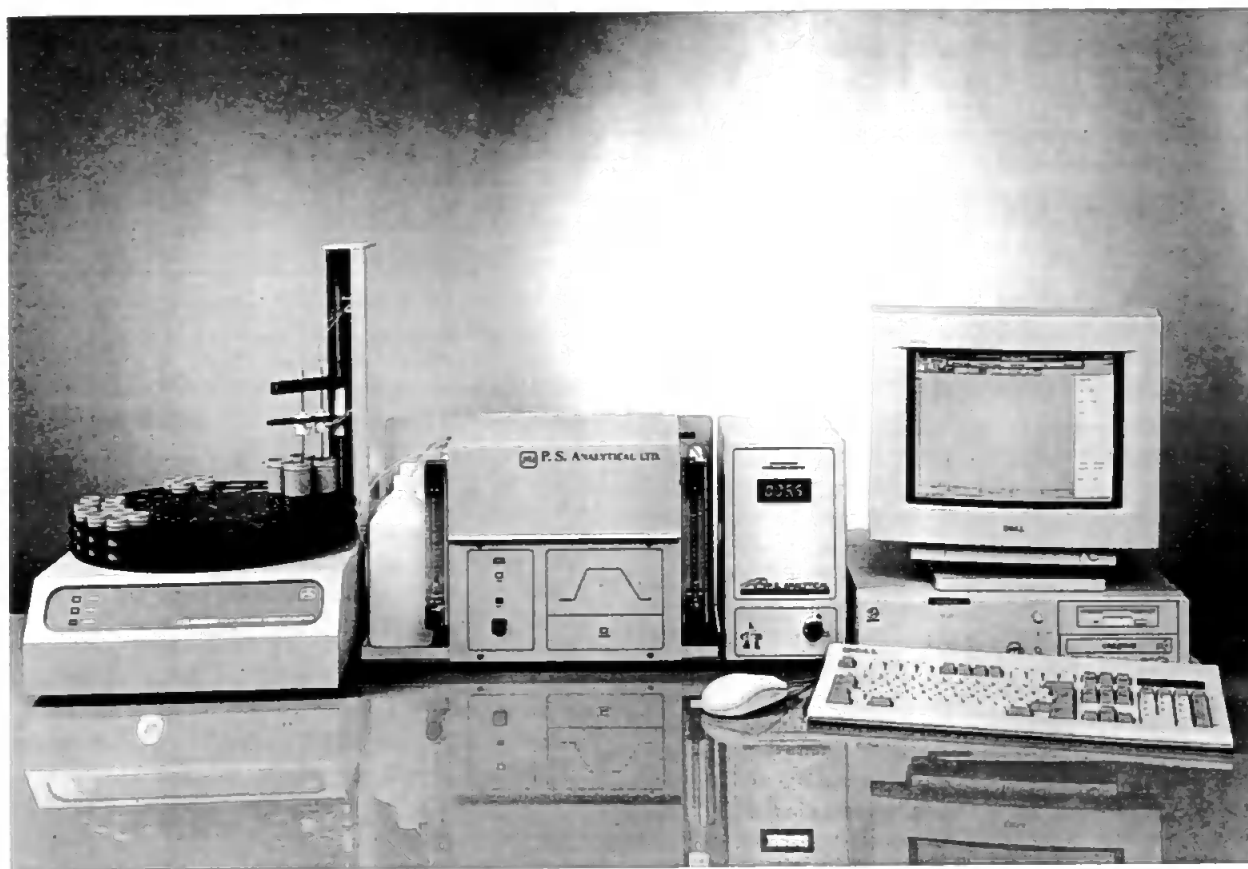


Figure 1. Merlin Plus system.

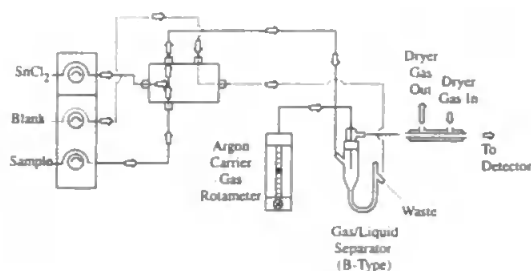


Figure 2. Hydride valve configuration for sampling.

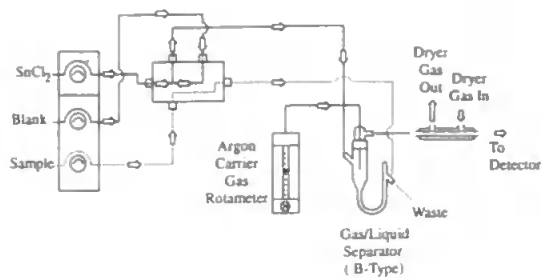


Figure 3. Hydride valve configuration for blank.

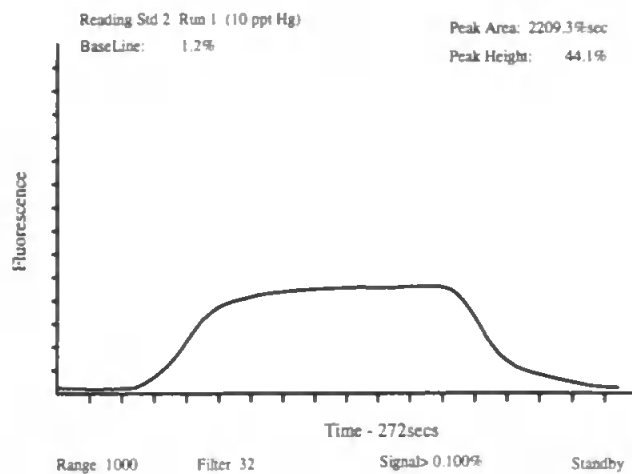


Figure 4. Typical signal response for the continuous flow approach.

Sensitivity

* Mercury continuous flow. Typical Instrument L.O.D. < 1.00 ppt.

* Further enhancement can be obtained by using the gold trapping technique, with typical improvements of greater than $\times 10$. This is achieved by using the PSA Galahad Pre-concentration Unit.

Table 1. The advantages and disadvantages of continuous and batch systems.

	Continuous flow	Batch analysis
<i>Advantages</i>	Precise control over reaction conditions Constant generation of hydrogen Experienced operators not required Precisions of approx. 1% easily obtainable in linear range	Small sample requirement Economical reagent usage Inexpensive equipment
<i>Disadvantages</i>	Large sample volume required Long analysis time (60 s)	Operator intensive Precision is function of injection technique Intermittent production of hydrogen Time consuming

Further reduction of the detect levels has recently been repeated by Cossa *et al.* [6] using an additional concentration step onto a gold/platinum trap. Figure 5 shows the instrumental configuration required for this.

Table 2 sets out the advantages of atomic fluorescence. These basically relate to selectivity and sensitivity, especially the wider linear dynamic range which can extend across many orders of magnitude.

Table 3 sets out the few limitations of the technique. When specifically looking at the situation with mercury these are significantly overcome using the PS Analytical design concepts. The presence of self-absorption at high concentrations and the possibility of matrix effects in, for example, contaminated land samples can be seen as a problem area. This paper shows how the introduction of small discrete samples into the flowing stream can, if properly controlled:

- (1) Extend the dynamic range of the analyses.
- (2) Effectively eliminate matrix effects by dilution.
- (3) Provide the basis of a flexible approach to on-line analyses.

Fluorescence techniques have typical limits of detection below 10 ng l^{-1} with linearity to 100 ng ml^{-1} . The linear calibration range stretches over four orders of magnitude which is obviously beneficial in view of the wide range of mercury concentrations found in the environment.

Table 2. Advantages of atomic fluorescence spectrometry.

Sensitivity attainable is controlled by the intensity of the light source.
Equipment can be less complex than that needed for AAS or AES.
High sensitivity attainable into the far UV (AAS and AES are insensitive).
Good linearity.
Low spectral interference.
High selectivity.
Analytical line summation.

Table 3. Disadvantages of atomic fluorescence spectrometry.

Quenching from gaseous species in atom cell.
Scattering from light source.
Self absorption at high concentrations.
Poor sensitivity for elements which absorb and emit in the visible region compared to AES.

Samples with concentrations exceeding the linearity are susceptible to self-absorption. This process is best explained using a standardized fluorescence cell like that shown in figure 6.

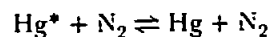
This theoretical model assumes that the light beams are parallel and that there is uniform atomic concentration and temperature. At high concentrations, incident radiation passing through Δl may be lost by absorption before excitation can occur. Useful fluorescence may also be lost by reabsorption in the region ΔL . In an ideal situation these regions would be infinitely small, thereby minimizing self-absorption. Figure 7 shows a typical profile obtained using the continuous flow approach for a $2000 \mu\text{g l}^{-1}$ mercury solution and the self-absorption process is clearly evident. As the concentration increases, there is a rapid rise in signal until the concentration has reached a level where self-absorption occurs. At this point the signal begins to fall, in severe cases to zero. When the sample is removed the concentration begins to decline and the signal begins to rise once more. Carry-over times between samples can be up to 5 minutes depending on the concentration of mercury present.

The atomic fluorescence signal magnitude can be reduced with the use of alternative carrier gases, such as nitrogen or air. These gases have been found to reduce the fluorescence signal by eight and 30 times, respectively, due to quenching. This is basically radiation-less deactivation of excited atoms due to collisions with foreign species present in the cell. The effectiveness of this process is dependent on the rate at which collisions occur, the type of non-radiative process involved and the effective cross-section of the quenching species. The fraction of absorbed photons actually re-emitted as fluorescence radiation is known as the fluorescence yield, ϕ .

This is defined as:

$$\phi = \frac{B_{ij}}{\text{Total probability per second of de-excitation}}$$

where B_{ij} is the Einstein coefficient for fluorescence emission. The total probability of de-excitation is the summation of B_{ij} with the rate of all non-radiative processes contributing to quenching. The quenching process occurring with mercury in the presence of nitrogen or air is due to inelastic collisions involving transfer of energy. The process for nitrogen is thus:



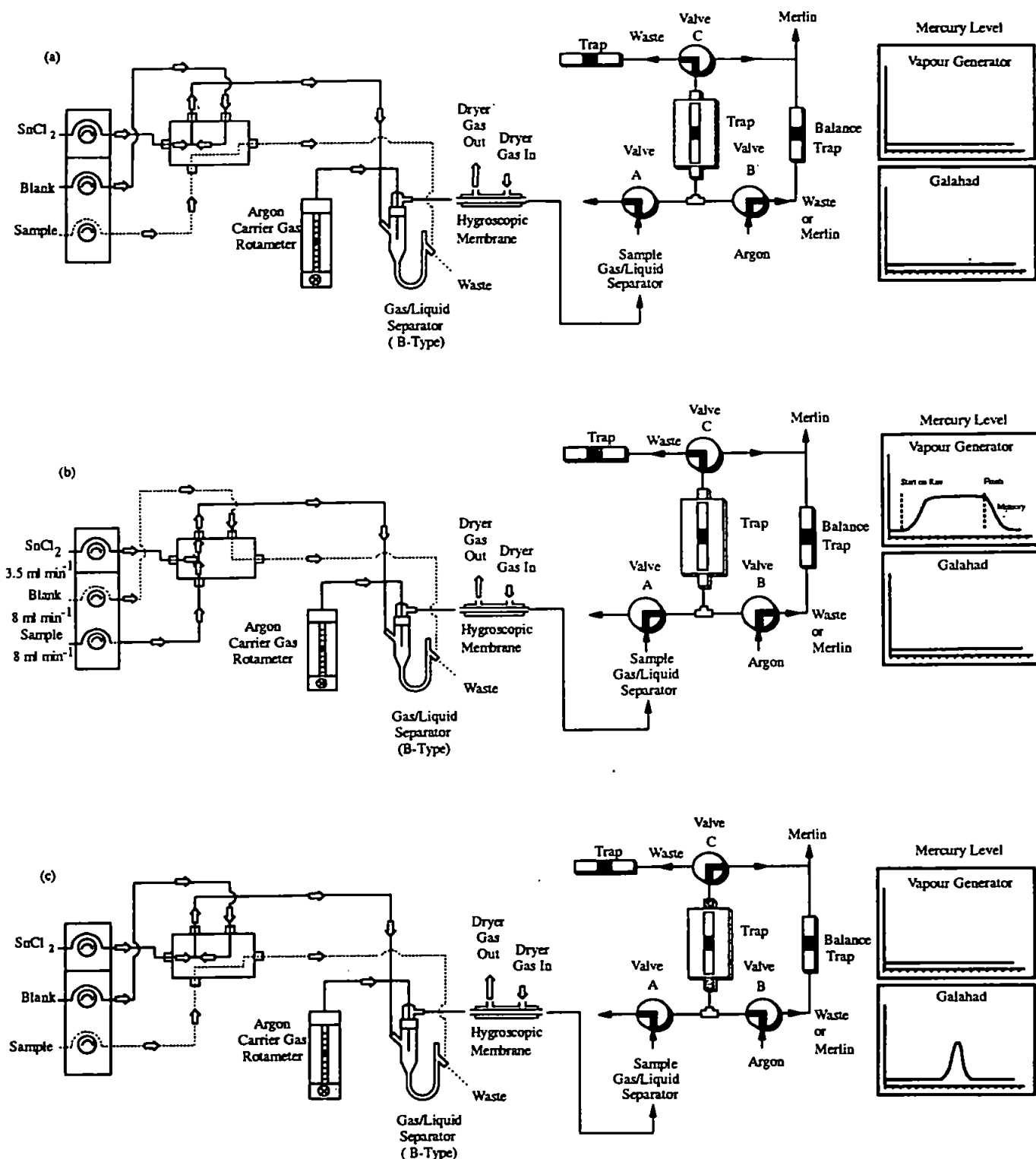


Figure 5. Instrumental configuration.

where the superscript * is used to indicate the excited state. The rate, r , of each collision is defined as the number of excited mercury atoms quenched per second per unit volume and can be expressed in the form:

$$r = k[\text{Hg}^*][\text{N}_2]$$

where k is the rate constant for the process. The probability of an excited mercury atom being quenched is therefore $r/[\text{Hg}^*]$. Hence the fluorescence yield factor for mercury

with quenching caused by nitrogen will be:

$$\phi_{253.7} = \frac{B_{10}}{k[\text{N}_2] + B_{10}}$$

where B_{10} is the Einstein coefficient for the excited state to the ground state transition. It therefore follows that the maximum value of ϕ is unity where no quenching occurs. This, however, is unlikely to occur.

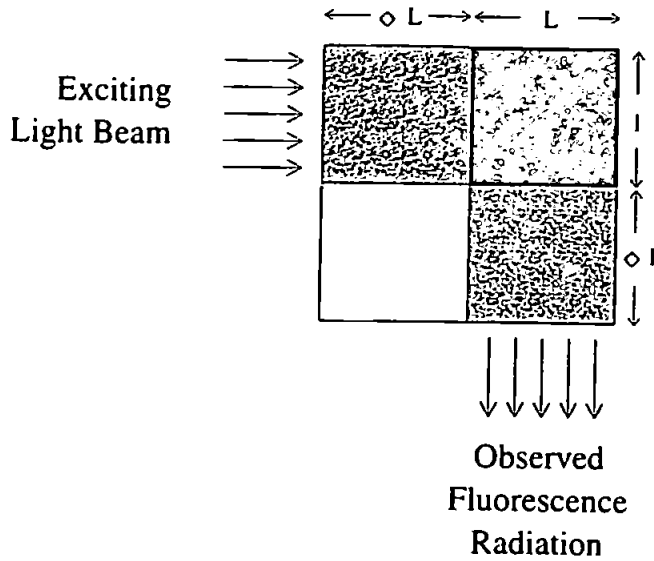


Figure 6. Standardized fluorescence cell.

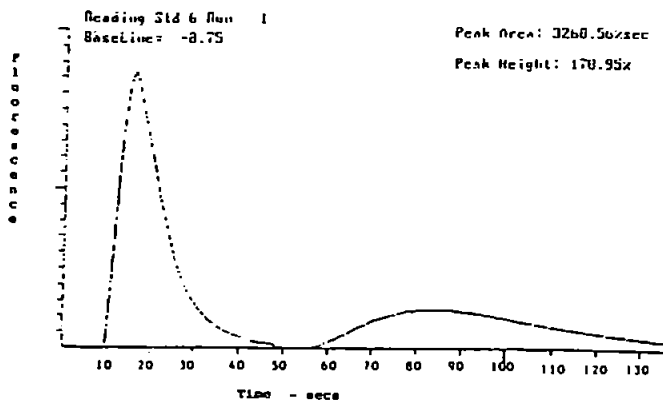


Figure 7. Typical peak shape, illustrating the process of self-absorption, using the continuous-flow approach for a $2000 \mu\text{g l}^{-1}$ solution of mercury.

Although a reduction in signal is clearly observed, the quenching process has no relation to linearity because the self-absorption process is dependent on the atomic concentration and the atom cell dimensions. The reduction in signal from quenching therefore has no practical use in this application. The analytical response curve for argon and nitrogen is shown in figure 8 for continuous flow vapour generation.

Discrete sample analysis typically uses volumes between 50 and 200 μl . Although not as sensitive as the continuous flow approach, it is less susceptible to self-absorption and matrix interference. A schematic arrangement for a discrete sample analyses is shown in figure 9. This approach has been subsequently superseded by using the standard P S Analytical vapour system configuration for the 10.004 model. With this instrument all the time cycles of the vapour generator are programmed by the computer software. The discrete volume is therefore determined as a fraction of flow rate and the time of valve opening. The limitation on this effect is the dead volume within the switching valve itself. This allows the upper limit of the calibration range to be increased. Figure 10 shows three analytical response curves corresponding to 75, 100 and 200 μl loop sizes. The smaller volumes gave higher upper limit calibration ranges, with slightly less sensitivity. An estimation of the sensitivity is again obtained from the slope of the curve at the point where deviation from linearity occurs. Table 4 summarizes the effect of sample volume on linearity.

Samples containing levels of mercury exceeding the linear range are still susceptible to self-absorption; a typical profile is shown in figure 11. The profile corresponds to a $100\,000 \mu\text{g l}^{-1}$ solution of mercury, and the self-absorption is clearly observed. However, this is not as severe as that for continuous flow and the carry-over times between samples with high levels is negligible. This allows the analysis of total samples to proceed with minimal delay.

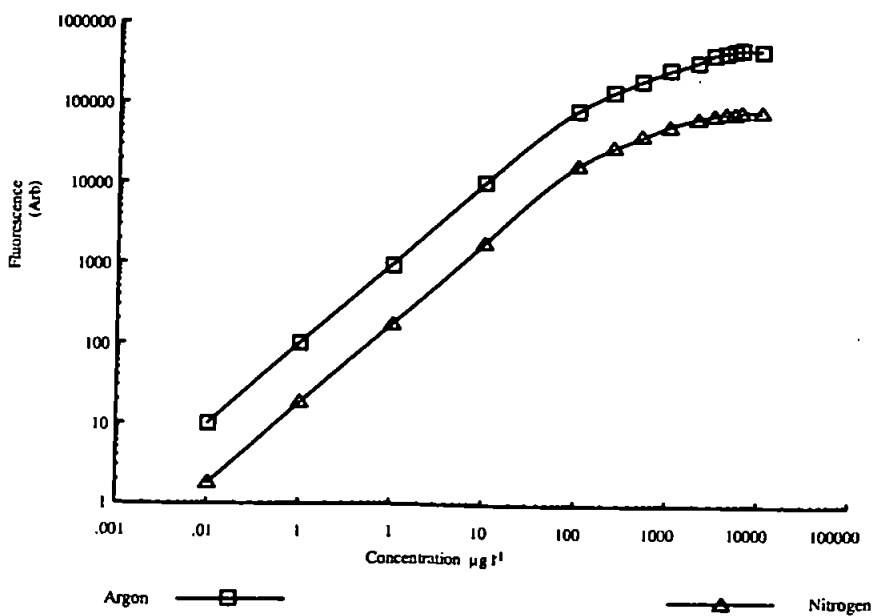


Figure 8. Analytical response curves for continuous-flow atomic fluorescence spectrometry using both argon and nitrogen carrier gases.

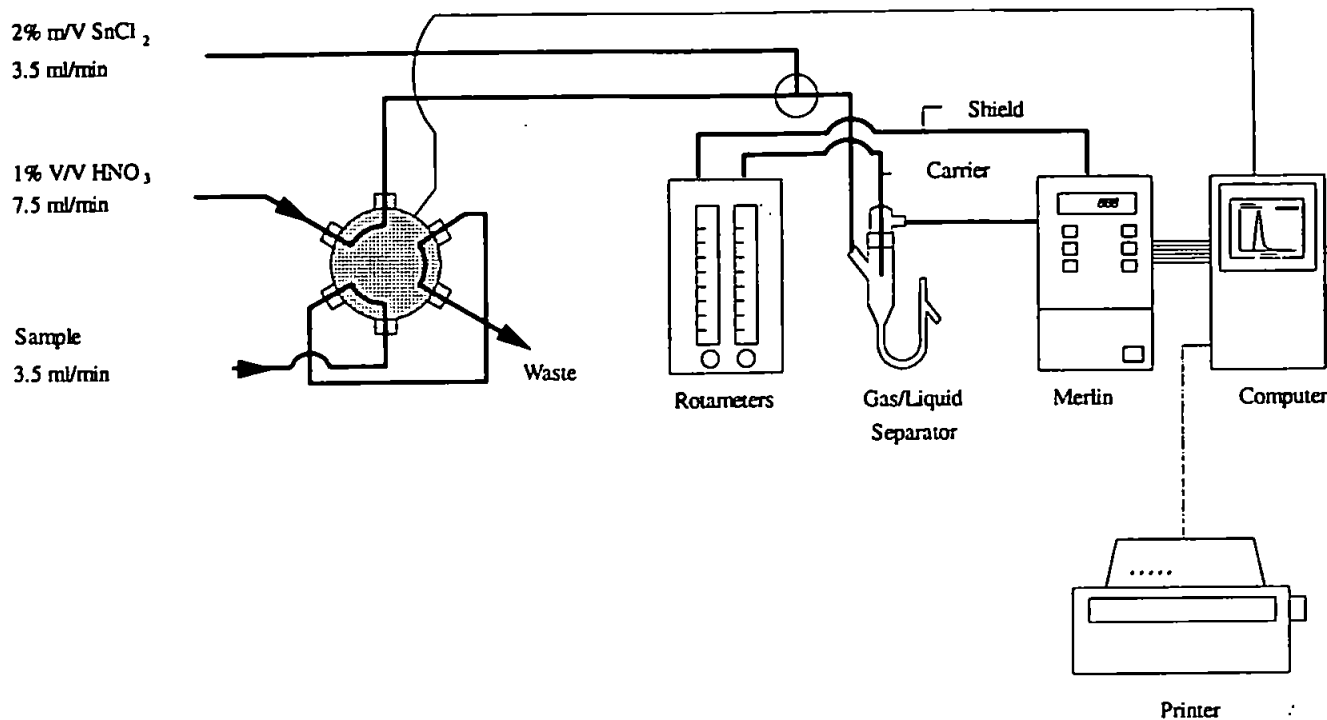


Figure 9. Schematic arrangement for a discrete sample analysis.

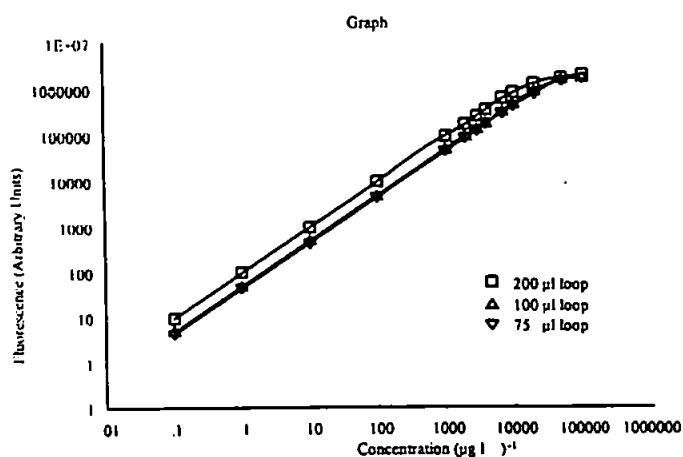


Figure 10. Three analytical response curves corresponding to 75, 100 and 200 µl loop sizes.

Table 4. The effect of sample volume on linearity.

Sample volume (µl)	Upper limit calibration range (mg l ⁻¹)	Slope
75	10.5	3.7
100	10	4.4
200	7	8.4

To assess the validity of the flow-injection cold vapour-atomic fluorescence spectrometry (CV-AFS) technique, a range of certified reference materials and zinc battery anodes has been analysed for mercury. These results are shown in table 5. Table 5 shows that accurate, precise quantitative measurements can be made using the

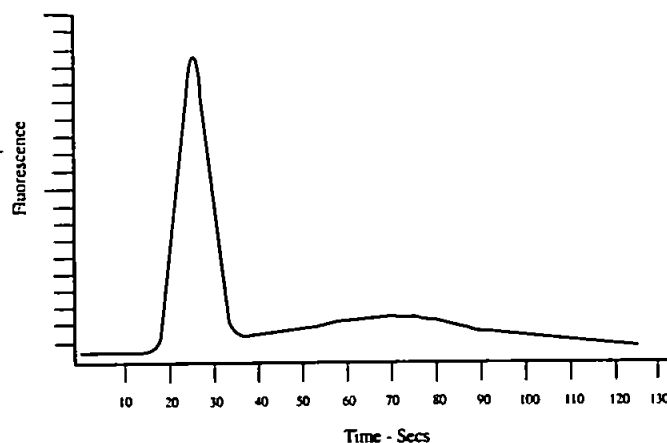


Figure 11. Typical peak shape, illustrating the process of self-absorption, for the flow-injection approach for a 100 000 µg l⁻¹ solution of mercury.

Table 5. Determination of mercury in certified reference materials and battery anodes.

Certified reference material	Expected/certified concentration	Concentration found	Weight dilution
NIST SRM 1641b (mercury in water)	1.52 ± 0.04 (µg ml ⁻¹)	1.41 ± 0.04 (µg ml ⁻¹)	0
NBS SRM 3133 (spectrometric solution)	10.00 ± 0.01 (µg ml ⁻¹)	9.89 ± 0.20 (µg ml ⁻¹)	2500
Zinc Anode A	1000 (µg ml ⁻¹)	1060 ± 30 (µg g ⁻¹)	200
Zinc Anode B	0	4.11 ± 0.29 (µg g ⁻¹)	200
Zinc Anode C	1200 (µg ml ⁻¹)	1150 ± 43 (µg g ⁻¹)	200

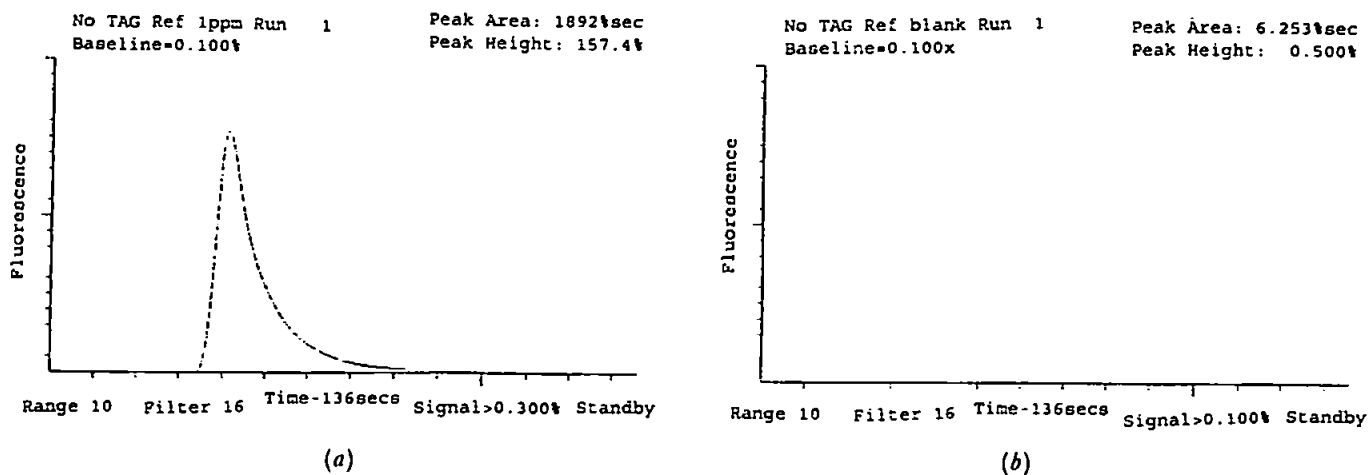


Figure 12. Analysis of 1 ppm followed immediately by blank—the signal trace for this is running along the baseline. Levels higher than 1 ppm will automatically be reset to blank when the software senses that the signal level will go off-scale.

flow-injection CV-AFS approach. The advantage of this system is that minimal sample dilution is required, which considerably reduces the sample preparation time and errors involved in large serial dilutions. One further advantage is that matrix interference is reduced because the analyte is separated from the matrix by generation of the gas and because small volumes are utilized.

Another major advantage of the discrete approach is that there is little interference or carry-over from one sample to another. This allows linear calibrations up to 10 ppm (as shown in table 4). However, it is possible to analyse samples up to 100 ppm with little or no carry-over between the high and low sample. The signal from 100 ppm will provide a detector overload, but the selection valve in the vapour generator will quickly switch to the blank/standby situation thereby returning the signal to the baseline. The next sample to be analysed can be accurately determined. Figure 12 illustrates this point with results for a sample greater than 100 ppm followed by a blank.

The application of the discrete sample injection and the capabilities of the continuous flow approach can be effectively married together using the method chaining approach developed by P S Analytical. The detector has a pre-amplifier allowing selection of gain ranges between 1 and 1000. In standard operation mode, the gain range is pre-selected for different concentration ranges. One gain range will allow a calibration span of two orders of magnitude. This provides the most accurate and precise methods of analysis. Samples which contain concentrations above the calibration range are normally diluted manually after the analytical run. The method chaining facility allows different methods with different gain ranges to be changed together, so that no manual dilutions for samples that are above the calibration range are required.

The discrete sample mode can be used to assign samples to the appropriate calibration ranges. With a sampling rate of 80 samples per hour, the samples can be quickly

screened to estimate levels. The reproducibility of the discrete injection mode is illustrated in figure 13, which shows replicate analyses in the ppb region for a mercury standard solution containing $1 \mu\text{g l}^{-1}$.

In method chaining, up to five different methods, each with a unique calibration, can be coupled together. This can be illustrated by reference to two calibration methods. In the first, the calibration range is set between $0-1 \mu\text{g l}^{-1}$; if samples above $1 \mu\text{g l}^{-1}$ are analysed offscale, recognition will switch the solution to the reagent blank, thus conserving the sample and minimizing carry-over. After the autosampler programme is complete the system is recalibrated at a higher range, such as $0-100 \mu\text{g l}^{-1}$ and these samples, which previously went offscale, are re-analysed. All conditions on the vapour generator are set automatically by the software programme. The operational sequence of the method chaining is activated from the autosampler programming mode.

On-line applications

Discrete sampling has a major advantage when dealing with complex matrices, especially with concentrated acids or alkalis. The effective dilution step has been extremely beneficial when combined with the extremely low detection capabilities of the detector to analyse such samples. For on-line process analyses this benefit has further advantages: sample volume is reduced; the risk of contamination between corrosive materials and the instrumentation is minimized; and the response time to changes in sample concentration is also reduced.

In comparison to laboratory analyses, the chemistry involved must be more complex in order to cope with the digestion of all forms of mercury to mercury(II), prior to the tin(II) chloride reaction. The authors have directed their research to a number of chemical regimes, but in this paper reference is only made to the application to concentrated sulphuric acid.

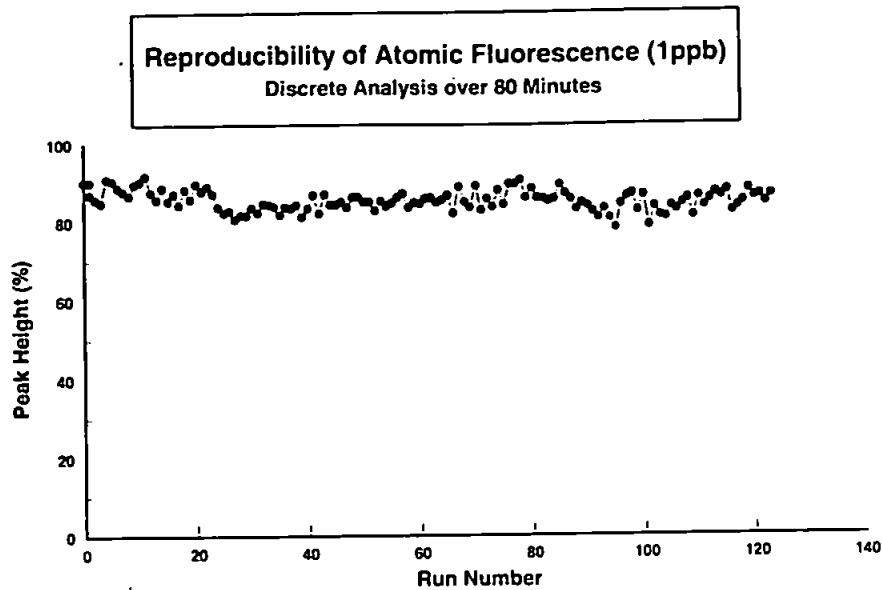


Figure 13. Response curve—the method chaining facility allows the user to run up to five different analytical methods in sequence.

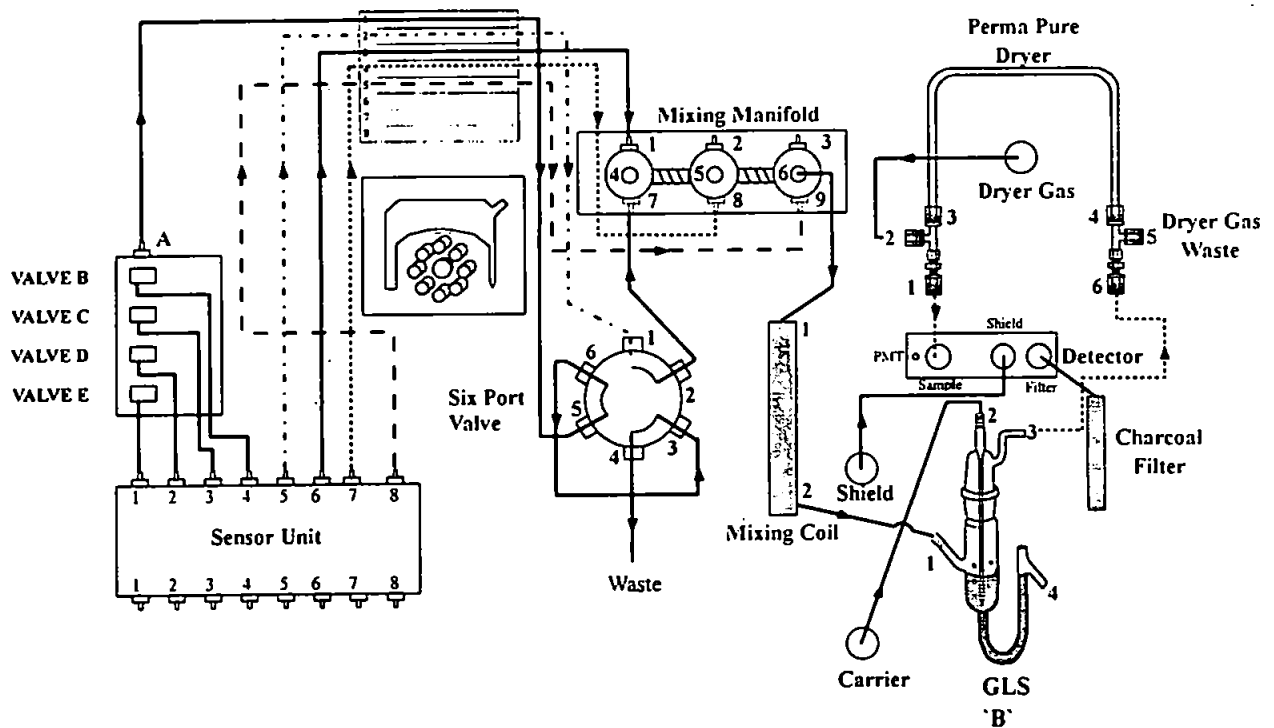


Figure 14. Schematic arrangement of the chemical manifold required for the determination of mercury at low levels in concentrated sulphuric acid.

Table 6 shows the specific considerations that require attention prior to translating a laboratory instrument to on-line applications. Reagent consumption is a prime consideration since it is desirable that little, if any, maintenance is required at rates greater than one week.

Figure 14 shows the schematic arrangement of the chemical manifold required for the determination of mercury at low levels in concentrated sulphuric acid developed by Brahma *et al.* [7]. The oxidation or digestion

Table 6. Specific considerations required to translate laboratory instrumentation to process applications.

- Conversion of all mercury species to divalent mercury.
- Low reagents consumption and reagent stability.
- Stable and rugged detection system.
- Reliable interface between sample stream and on-line system.
- Fault diagnostics with feedback system.
- Data processing via CPUs.

Changed Hg by Online A.F.S. Hg 3 Stds to 1.086ppm

Method	Signal	Sampler	Tag	Reference	Done	Runs	7 Jun 96
HGONLIN1	-0.50%	None	SAMPLE	nointerfer	244	1	11:35:22
Library	Method	Calibrate	Options	Analyse	Results	Setup	TouchStone

```

Method: Hg by Online A.F.S.
Curve Fit : Least Squares Straight Line
Measured by : Peak HL

Flow Injection Valve Setup
DELAY      MEASURE      RESET
130sec     200sec         100sec
Loop: 100ul      Fill Rate: 1 ml/min

PSA Merlin Calibration Setup:
RANGE 10      FINE 10.0      ZERO Auto
Range & Running 1/4s set automatically
SENSOR
1: Blank           2: Low Standard
3: High Std       4: Sample
5: 20% HCL        6: 0.1 Br/BrO3
7: 1%OHNH3Cl     8: 2% SnCl2
N.B.All Pump Lines RED-RED
    
```

F1-Help F2-Keep Displayed F3-Print F4-Edit Esc-Menu

Figure 15. Methods page from the computer software.

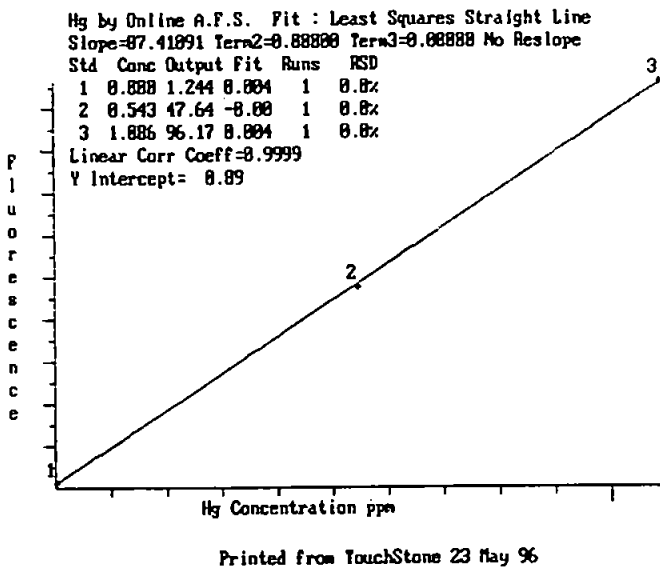


Figure 16(a). Simple response for a repeat sampling sequence.

step is provided by the reaction of potassium permanganate. This is then followed by a conventional tin II chloride reduction to form mercury vapour which is introduced into the detector. Figure 15 shows the methods page from the computer software. To minimize matrix interference effects and excessive heat generation, the system is used in a discrete sampling mode. Reagent flow rates are kept at a level of 0.5 ml min to conserve reagents and maximize the time between reagent changes in the instrument. The analytical cycle performed is to analyse a blank, a 100 ppb standard, a 200 ppb standard and then the sample stream four times prior to repeating the analytical sequence to fit the analytical needs at the time. The inherent sensitivity of the atomic fluorescence detector allows air (which

provides a 30-fold quenching of the signal) to be used as a transfer gas. For process applications, this provides the site managers with a considerable comfort factor because the dangers of asphyxiation due to other carrier gases are overcome.

The analysis is operated in a similar manner to the laboratory instrument, which is somewhat different to conventional laboratory analyses. Repeat cycle discrete analyses are performed using the software facilities to continuously update the calibration and blank values; this means that the results are continuously updated. Figure 16 shows a simple response for a repeat sampling sequence and a calibration graph over a 48-hour period.

Hg concentration (mg/l) in Sulphuric acid

Mean = 0.59ppm Std Dev = 0.06ppm RSD = 9.54%

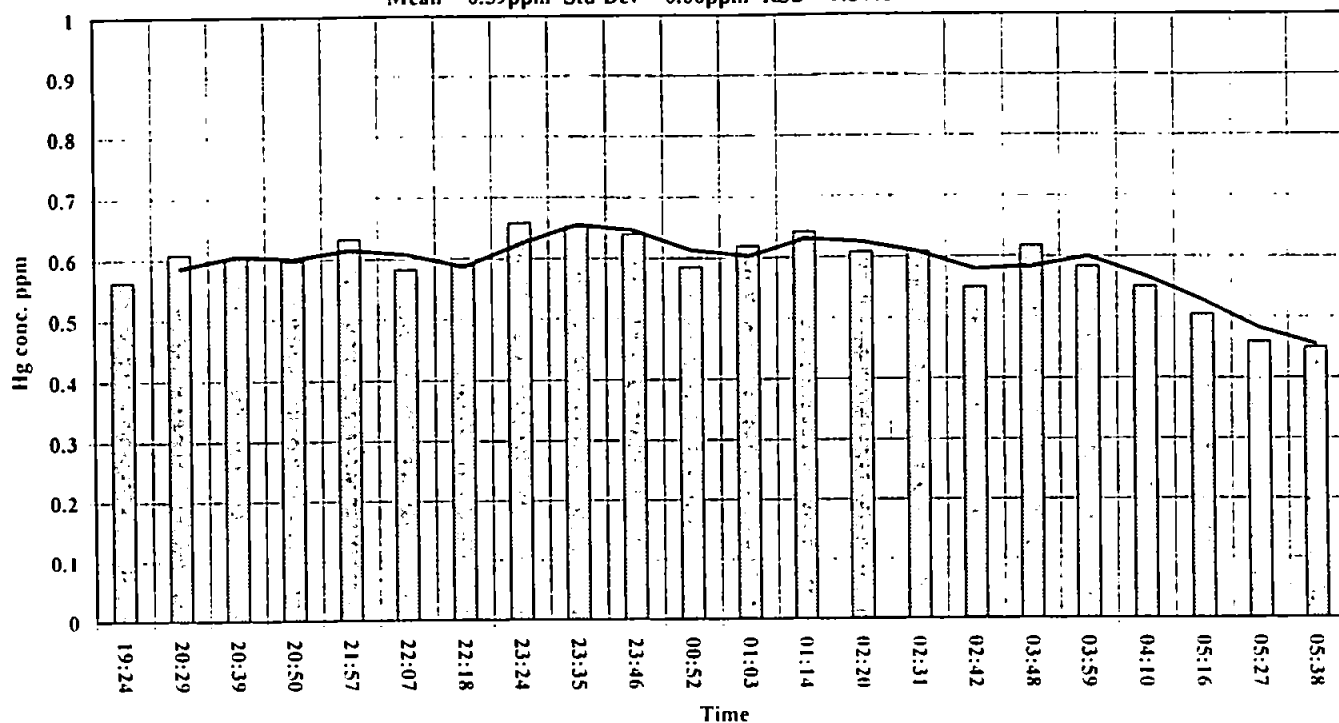


Figure 16(b). Calibration graph over a 48-hour period.

Conclusions

The sensitivity of the continuous flow vapour generation system coupled to atomic fluorescence provides extremely low detection levels. The combination with discrete sample introduction extends the linear dynamic range of the instrumentation to encompass seven orders of magnitude. In addition, this mode of operation extends the capabilities of the system to handle complex matrices and also to provide extremely versatile on-line process instrumentation.

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