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MERCURY SPECIES IN NATURAL GAS CONDENSATE

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ABSTRACT

MERCURY SPECIES IN NATURAL GAS CONDENSATE

AZMAN BIN SHAFAWI

The presence of ultra-trace levels of mercury in industrial gas and condensate streams is a cause of both environmental and production concern. The toxic nature of the element, in all forms, together with its ability to shut-down large processing plants dictates a need for its accurate and precise measurement.

The study which investigated the recovery of various mercury species, spiked into synthetic and real condensate samples using conventional and new digestion and/or extraction techniques showed recovery was dependent upon the speciation. Using the most efficient technique, L-cysteine with persulphate, recoveries of over 90 % were obtained for diphenyl mercury, ethyl and phenyl mercury chlorides and mercury chloride. The recovery of 15% for the important dimethyl mercury species limits the use of this technique.

A novel technique has been developed for the determination of total mercury in complex liquid hydrocarbons. Samples (up to 1.0 ml) were vaporised (400°C) and swept through a gold-coated silica trap maintained at 200°C, which retained all mercury species and discarded the matrix. The trap when heated to 900°C released the mercury for measurement by atomic fluorescence spectrometry (AFS). The recoveries for eight mercury species spiked (10 to 50 ng ml^{-1}) into toluene and condensate were generally over 90 %. The instrumental limit of detection (LOD) was 11 pg. The total mercury content of gas condensates, gasolines and heavy oils were determined.

Gas chromatography coupled, *via* a pyrolysis interface, with AF detection was able to determine mercury species in gas condensate, at picogram levels (LOD: 2.5 to 7 pg) using a direct sample injection procedure. For a given column system the positive identification and quantification of up to eight mercury species was obtained. A maximum injector temperature of 125 °C was recommended, to avoid the conversion of species. Mass balance calculations show a strong correlation between the total mercury content and the sum of the lower dialkyl mercury species, for all condensate samples studied.

Three commercially available mercury removal systems, A, B and C produced a reduction in the mercury content of hydrocarbon streams under pilot plant conditions. The two stage system, 'A', produced a minimum of 30 % conversion from organomercury to elemental mercury after the hydrogenation reaction in stage 1. While elemental mercury was adsorbed by the stage 2 reactor, the organomercury species were not removed. The single stage adsorber 'B' showed 100 % removal efficiency for three dialkyl mercury species in liquid hydrocarbon streams. The removal efficiency for adsorber 'C' was species dependent. Two common condensate species gave values of 50 to 80 % removal efficiency while the third species showed time-dependent bleed-off.

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AUTHOR DECLARATION

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Signed .....

Date 18-1-99

CHAPTER 1

INTRODUCTION

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1.1 PETROLEUM INDUSTRY

1.1.1 Natural Gas and Natural Gas Condensate

Natural gas and natural gas condensate are complex mixtures of hydrocarbons. The source of natural gas is mainly from gas fields and that associated with crude oil fields and gas processing (1). It is believed that natural gas is formed from the decomposition of crude oils or coal deposits. It contains mainly methane and ethane and if it is more than 95 % methane (excluding other inorganic gases i.e. carbon dioxide, nitrogen, helium, oxygen etc.), it is known as 'dry' natural gas. When it contains larger amounts of other gaseous alkanes such as ethane, propane and butane it is known as 'wet' natural gas. Natural gas may also contain small quantities of higher hydrocarbon isomers such as pentane, hexane and heptane. In general, natural gas composition depends upon its origin. Sometimes wet natural gas may even contain a hydrocarbon as high as octane. These higher hydrocarbon components are separated and recovered as a liquid and used as fuel, or as refinery and petrochemical feedstocks.

In the petroleum industry, the refining process can be defined as a combination of processes that converts crude oil and other natural gas into marketable products (1). However, for the gas industry, natural gas refining is usually referred to as a gas separation process which converts natural gas feed stock via a combination of separation and purification processes to produce marketable products either for direct utilisation as a fuel or as a feedstock material for other petrochemical processes.

Petrochemical processes can be defined as a combination of processes that utilise specific feedstock, with either liquid or gas products obtained from refining or gas separation, for bulk production of speciality chemicals (1). Catalysts are usually involved in the processes.

Natural gas condensate is a liquid hydrocarbon mixtures that is an associate product of natural gas. It is a highly volatile mixture that results from a separation or condensation of heavier hydrocarbon fractions of natural gas, or recondensation of hydrocarbons from crude oil off-gas. The composition of condensate depends very much on the origin of the source. It is typically a mixture of hydrocarbon isomers i.e. paraffins, naphthanes, aromatics, with the carbon number of C_5 to C_8 but sometimes up to C_{15}. A butane fraction may also be present as a minor constituent of these condensates. Natural gas and natural gas condensates also contain other impurities such as sulphur compounds and of most concern is the presence of toxic elements such as mercury and arsenic.

1.1.2 Characteristics of Natural Gas Condensate

The typical properties of natural gas condensate are shown in Tables 1.1 and 1.2. A condensate obtained from a natural gas field in Malaysia is taken as an example. The condensate samples contain a mixture of hydrocarbons such as paraffins, naphthanes and aromatics. The composition of these condensates include paraffins with carbon numbers as high as 15. Based on these properties, the condensate is as good as the naphtha fractions obtained from the processing of crude oil and can be considered as having a 'high value petroleum fraction' for applications other than as a fuel.

Tests	Unit	Results		Methods
		Condensate 1	Condensate 2	
		Recovery	Recovery	
Initial boiling point- IBP	°C	32.1	31.0	ASTM D 86
5 % vol. recovered	°C	44.3	44.0	
10 % vol. recovered	°C	48.4	48.7	
20 % vol. recovered	°C	54.8	56.4	
30 % vol. recovered	°C	61.7	64.6	
40 % vol. recovered	°C	70.1	74.4	
50 % vol. recovered	°C	80.6	86.5	
60 % vol. recovered	°C	93.1	100.4	
70 % vol. recovered	°C	107.6	116.1	
80 % vol. recovered	°C	128.4	140.5	
90 % vol. recovered	°C	167.5	192.7	
95 % vol. recovered	°C	219.3	246.5	
Final boiling point -FBP	°C	264.6	285.5	
Percent recovered	% vol.	98.0	97.6	
Percent loss	% vol.	0.4	0.7	
Residue	% vol.	1.6	1.7	
Recovery @ 200° C	% vol.	93.9	91.5	
Density @ 15° C	$kg\,l^{-1}$	0.7141	0.7245	ASTM D1298-85
API, Gravity @ 60 ° F	-	66.59	64.78	Calculated
Basic sediment & Water	% vol.	0.00	0.00	ASTM D4007-81

Table 1.1 : Physical properties of some Malaysian condensates

NO	Hydrocarbon Type	Carbon No	Content (wt %)	
			Condensate 1	Condensate 2
1	PARAFFINS	P3	0.85	0.74
		P4	6.78	6.24
		P5	9.52	8.55
		P6	9.46	8.5
		P7	10.74	9.30
		P8	7.86	7.08
		P9	3.86	3.89
		P10	1.63	2.17
		P11	1.1	1.77
		P12	0.85	2.2
		P13	0.54	1.69
		P14	0.22	1.94
		P15 plus	0.16	4.49
	TOTAL PARAFFINS		53.57	58.56
2	OLEFINS	O3- O12+	0.0	0.0
	TOTAL OLEFINS		0.0	0.0
3	NAPHTHANES	N3	-	-
		N4	-	-
		N5	0.94	0.87
		N6	5.03	3.75
		N7	17.13	13.69
		N8	2.53	1.83
		N9	2.82	2.47
	TOTAL NAPHTHANES		28.45	22.61
4	AROMATICS	A3	-	-
		A4	-	-
		A5	-	-
		A6	1.55	1.38
		A7	5.33	4.70
		A8	6.28	5.92
		A9	3.76	4.1
		A10	0.65	1.35
		A11	0.21	0.71
		A12	0.2	0.67
	TOTAL AROMATICS		17.98	18.83

Table 1.2 : Hydrocarbon type analysis (PONA analysis) of BSTB condensate

1.1.3 Natural Gas Condensate Usage

As a hydrocarbon mixture and having properties almost similar to petroleum naphtha fractions, the condensate is obviously a very valuable feedstock. It can be used in a variety of applications either as a blending stock to crude oil for refinery processing or it can also be used as a feedstock to various petroleum/petrochemical processes (1). One of the most important is as a feedstock for catalytic cracking or thermal cracking, for the production of intermediate products such as hydrogen, methane, ethane, ethene, ethylene, propane, propene, C_4 hydrocarbons, high grade petrol and residues (fuel oil), and for catalytic reforming processes for the production of aromatics and alicyclic compounds. The intermediate products from these two building block processes can be used in various secondary refinery and petrochemical processes or as a final product, depending on either economic or market demands.

1.2 MERCURY IN NATURAL GAS AND THE PETROCHEMICAL INDUSTRY

Mercury contamination is considered to be a 'critical severity' risk with a 'frequent to probable' probability of occurrence (2). On a risk factor scale 1 to 9 (9 = very low risk), the lack of a properly placed and operating mercury trapping unit in natural gas plants, petrochemical and refinery complexes is considered to be a risk factor of 2 or 3(3). Thus within the design and operation of gas, liquefied natural gas (LNG), refinery and petrochemical facilities, which operate with mercury-tainted feeds, a safety management scheme strongly recommends the implementation of known protective measures to lower the risk factor.

Knowledge of the total mercury content and of the different species present in natural gas condensate is extremely important. Mercury in most forms is highly toxic, particularly when

present as the organo-mercury species and this causes great environmental concern. In addition, the damage caused to industrial plants by the presence of mercury species can be financially crippling especially when unscheduled shut-downs are forced. An example of distribution of mercury in gas condensate from South East Asia is shown in Table 1.3:

Fractions		% total mercury by weight
1	(Boiling points (B.P.) < 36 ° C)	8.9
2	(B.P. 36 - 100 ° C) - Light naphtha	27.6
3	(B. P. 100 - 170 ° C) - Heavy Naphtha	33.8
4	(B. P. 170 - 260 ° C) - Kerosene	16
5	(B. P. 260 - 330 ° C) - Diesel	7.4
6	(330 + ° C) - Residue	6.3

Table 1.3 : Distribution of mercury in gas condensate from south East Asia **(7).**

1.2.1 Mercury in Natural Gas Industry

Mercury occurs naturally, in trace quantities, in natural gas. Although difficult to generalise, the typical mercury concentration in natural gas/natural gas condensate is between 1 and 200 $\mu g\ m^{-3}$ **(4,5,6)**. Although the concentration of mercury in natural gas and natural gas condensate may be considered to be very low, the effect is cumulative because it almalgamates. Mercury in natural gas condensate may be present in various chemical states: metallic, organic or inorganic forms, that all show unique species-dependent physical, physiological and chemical properties **(7,8,9)**. Table 1.4 shows the examples of mercury species that may be present and in general they correspond to the boiling point of condensate **(7)** .

Compounds	Formula	Boiling Point (°C)
Dimethyl mercury	$Hg(CH_3)_2$	96
Diethyl mercury	$Hg(C_2H_5)_2$	159
Di-isopropyl mercury	$Hg(iC_3H_7)_2$	170
Dipropyl mercury	$Hg(C_3H_7)_2$	190
Dibutyl mercury	$Hg(C_4H_9)_2$	206
Metallic mercury	Hg°	357

Table1.4: Boiling point of mercury species that may be present in a condensate **(7)**.

The implications from the presence of mercury in natural gas was not reported until 1973, when a catastrophic failure of an aluminium heat exchanger occurred at the Skikda liquefied natural gas plant in Algeria **(6, 10,11,12)**. Investigations determined that mercury corrosion caused the failure and that the mercury may have come from an accidental source, such as test instruments used in plant and field start-up **(6)**.

After the Skikda failure, a study of the Gronigen field in Holland revealed similar corrosion in the gas-gathering system. Carbon dioxide was initially thought to be the cause, but later investigations pointed to naturally occurring mercury, with concentrations ranging from 0.001 to as high as 180 $\mu g\ m^{-3}$ **(11)**. In the Far East i.e. the PT Arun LNG plant in Indonesia, the catastrophic-leak in an aluminium heat exchanger was reported to be caused by breakthrough of mercury from the mercury removal bed **(13)**. The most recent mercury contamination incident was again through the failure of the aluminium-made cold box in the Petroleum Authority of the PTT plant in Thailand **(12, 14, 15)**. Other petroleum companies

such as PETRONAS in Malaysia are also experiencing the presence of mercury in their natural gas and gas condensate. A mercury analysis and distribution study carried out in 1984 in the offshore fields indicated that the natural gas contained between 1 to 57 $\mu g\ m^{-3}$ of mercury.

In a maintenance shutdown of one of their gas plants in February 1991, approximately 1.2kg of elemental mercury (accumulated through a three year period since the last turn-around) was collected in the liquefied petroleum gas (LPG) molecular sieve regeneration system **(16, 17)**. The mercury was suspected to be carried over in LPG products and was trapped in the molecular sieve during LPG treatment. However, to date no catastrophic failure has been reported by this company.

The presence of mercury in oil and gas is recognised world-wide and has been reported for fields in Australia **(18)**, the Commonwealth of Independent States **(12, 19)**, Western and Southern Africa, Chile and Venezuela **(20)**, Canada, in several states in the US (Kansas, Texas, Utah, Colorado, Oklahoma, and Wyoming) **(21, 22)**, as well as The Irish Sea, Japan and China **(22)**.

1.2.2 Mercury in The Petrochemical Industry

As with the gas industry, several petrochemical companies, using natural gas liquids containing mercury, have also had some unfortunate experiences of damaging cryogenic heat exchangers at their petrochemical complex arising through mercury induced corrosion in the low temperature separation trains **(12, 23, 24)**. In addition, the upgrading of mercury-contaminated natural gas condensates by steam cracking has led to severe mercury poisoning of down-stream selective hydrogenation catalysts in many countries throughout the world **(23)**. For example, palladium-based catalysts are used for selective hydrogenation

of acetylenic species in steam cracking of C_2, C_3, C_4 and other cuts. The few $\mu g\ l^{-1}$ mercury species which can be present in the very wide boiling range in a condensate steam cracker feed, are concentrated into the light fractions of the cracker effluent. It was reported that condensate feed containing 60 $ng\ ml^{-1}$ of mercury shortened the selective hydrogenation catalyst cycle period from 1000 days to less than 30 days **(12)**. The catalyst deactivation was accompanied by this greatly reduced catalyst life-time because of active metal (palladium) sintering which occurs when eliminating the mercury during catalyst regeneration. It was also noted that the regeneration gas used, was also contaminated with mercury. Other petrochemical processes directly or indirectly utilise a catalyst with precious metals such as platinum, palladium, nickel etc. as an active surface. The presence of mercury in any stream of a petrochemical process may easily poison the process. At least one study has addressed the subject of adsorption and desorption of mercury on platinum and palladium surfaces **(25)**.

1.2.3 'Acceptable limits' for Mercury Content in Process Streams

The presence of mercury in the feed to gas and petrochemical plants will increase the risk of corrosion of plant equipment and contamination of the environment. In general, the lower the mercury content of the feed stream, the better. However, lower limits which are industrially accepted standard are as follows:

Natural gas	:	0.01 $\mu g\ m^{-3}$
Natural gas liquids	:	less than 5 $ng\ g^{-1}$

These values are below the level considered to be dangerous to humans. The OSHA regulations stipulate that the time weighted average (TWA) mercury content in air should not exceed 50 $\mu g\ m^{-3}$ in an 8 hour working shift for a 40 hour week **(26)**. For the purpose of comparison, the mercury level in the respiration air from an individual having an

amalgam filling is as high as 10 $\mu g\ m^{-3}$ **(27)**. Thus, although the concern for mercury from hydrocarbon streams is an environmental issue, the driving forces are plant safety and operations issues **(12)**.

As stated, the presence of mercury in natural gas can cause severe corrosion of plant heat exchangers and poisoning of expensive catalysts used in downstream processing units. Both lead to severe operational problems. In order to protect the equipment used in the liquefaction process, it is necessary to reduce the mercury content to between 10 and 20 ng m^{-3}, i.e. by a factor of 10^4.

1.2.4 Corrosion effect from mercury upon process plant

Trace amounts of mercury in LNG should concentrate in the heavier liquid phases, such as the butanes and above. However, the more damaging mercury concentrations will most likely occur in the cycled gas stream where losses are made up from the plant products, methane through to pentanes **(10)**.

Since mercury-induced corrosion occurs only in the presence of liquid water, the temperature at which corrosion occurs must be between approximately 0°C and the highest temperature at which a water dew-point can occur. There is only one condition of operation in which this temperature can occur, i.e. when the plant is allowed to warm above 0 °C, for example for shut-downs.

The characteristics of mercury corrosion **(10, 13)** are as follows:

- Attack on exchanger tubes is often on the refrigerant side.
- Elemental mercury is found and not compounds of mercury.
- The corrosion product is usually oxide or hydroxide.
- Liquid water must be present.
- Corrosion is more likely with the electropositive metals.

Mercury induced corrosion of aluminium cold-box equipment can proceed via two mechanisms; mercury-induced stress cracking and mercury-catalysed oxidation by water **(6, 10, 11, 12, 13)**. The mechanism of all corrosion caused by the presence of metallic mercury takes place in the following sequence:

- Elemental mercury amalgamates with the surface layer of the metal being corroded.
- The minute amount of base metal alloyed with the elemental mercury is exposed intimately, a short-circuited corrosion cell is formed between the mercury and the base metal with liquid water as an electrolyte.
- In the presence of pure water and inert gases, the base metal in the amalgam is corroded gradually by reaction with water.

If an acid anhydride, such as CO_2 or H_2S is present, the corrosion product is the metal carbonate or sulphide.

1.2.4.1 Mercury-induced stress cracking.

Mercury forms amalgams (alloys) with almost all metals and leads to embrittlement of the metals. Some brazed aluminium heat exchangers are known to have a magnesium-rich phase at the aluminium metal grain boundaries (due to precipitation during welding). When liquid mercury is brought into contact with this anodic phase, dissolution occurs by the following reaction:

$$4\,Hg + Al_3Mg_2 \rightarrow 2\,MgHg_2 + 3\,Al \quad \text{.....(1.1)}$$

Dissolution of the grain boundary is accelerated rapidly when 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. The embrittlement may occur with the metals that have a high diffusion rate into mercury.

1.2.4.2 Mercury-catalysed oxidation by water

The enthalpies of reaction and Gibbs free energies of formation of various oxides from reaction between metals and water at 25 °C are given in Table 1.5. The net enthalpy and net free energy change for aluminium are highly negative. The reaction with water is exothermic and goes to completion at, essentially, room temperature. The reason that aluminium is not normally attacked by water is its tightly adhering oxide film (alumina), a protective layer, which is not present when aluminium is amalgamated with mercury in an anaerobic atmosphere **(15)**. Small fissures in this layer render the clean metal surface susceptible to local oxidation by water. These chemical reactions, for aluminium, can be described by the following equations:

$$Al_x(s) + Hg_y(l) \rightarrow Al_{(x-2)}(s) + Hg_yAl_2(l) \quad \text{.....} \quad (1.2)$$

$$Hg_yAl_2(l) + 3\,H_2O(l, v) \rightarrow Hg_y(l) + Al_2O_3(s) + 3\,H_2(g) \quad \text{.....} \quad (1.3)$$

Other metals, such as copper, require heat for the reaction to be sustained and will not proceed to completion. Therefore, copper would not be expected to be attacked by liquid water even in an amalgam, except at elevated temperatures. However, over a long period of time, copper will be weakened by amalgamation, through alteration of its crystal structure **(10)**.

The corrosion resistance of stainless steel is dependent on the hard, tough, chromium oxide film that is formed. Here, it can be can postulated that metallic mercury forms an amalgam

with chromium, iron or nickel, with subsequent corrosion by liquid water or an aqueous acidic phase **(10)**.

Corrosion Reactions	Diffusion rate ($cm^2 s^{-1} \times 10^5$)	$\Delta H_{298 K}$ (kcal mol^{-1})
$2 Al + 3 H_2O = Al_2O_3 + 3H_2$		- 207.0
$2 Ag + H_2O = Ag_2O_3 + H_2$	1.1	54.3
$Cd + H_2O = CdO + H_2$	2.1	1.7
$2Cu + H_2O = Cu_2O + H_2$	1.1	21.8
$Zn + H_2O = ZnO + H_2$	1.6	- 19.3
$Ti + 2 H_2O = TiO_2 + 2H_2$		- 98.9
$2Cr + 3 H_2O = Cr_2O_3 + 3H_2$		- 82.8
$3Mn + 4H_2O = Mn_3O_4 + 4H_2$		-78.8
$2Fe + 3H_2O = Fe_2O_3 + 3H_2$		- 7.1
$3Co + 4H_2O = Co_3O_4 + 4H_2$		45.2
$Ni + H_2O = NiO + H_2$		6.2
$Sn + 2 H_2O = SnO_2 + 2H_2$	1.68	-10.9
$Pb + H_2O = PbO + H_2$	1.16	11.4

Table 1.5 : Enthalpies of reaction between metals and water at 25 ° C and diffusion rate of metals into elemental mercury at ambient temperature **(28, 29)**.

The nickel reaction needs some input of heat to proceed. In contrast, the chromium reaction will proceed readily at room temperature if the chromium oxide film is broken **(10)**. From the above, the following generalisation can be made for corrosion that is induced through mercury amalgamation:

- Liquid water must be present
- The metal involved must be above nickel in the electrochemical series for the reaction to proceed spontaneously at room temperature.

1.2.5 The Petroleum Industry and Environmental Impacts from Mercury

The oil industry and its products impinge on all aspects of the environment. The seas, from its extraction and transportation; the land, from the impacts of extraction, pipelines, processing plants and use; and the atmosphere, from its gaseous products and by-products. It is implicated in 'high profile' pollution, from accidents and ecosabotage at wells and refineries, the decommissioning of marine installations, major spills at sea, through to the contribution from its gaseous products to the greenhouse effect and respiratory diseases **(30)**.

Mercury is a naturally occurring contaminant in geological hydrocarbons and is distributed freely throughout production, processing, transportation and consumption systems. As shown in Table 1.6, hydrocarbons from different geological locations contain mercury in microgram levels. The values shown are an estimation **(31)** and may change from time to time, depending on geological factors and production practices.

Production and processing of gas and gas condensates containing mercury, invariably leads to contamination of equipment and can generate waste in the form of sludge and spent adsorbent material **(31)**. The toxic contaminants from these activities can enter into the *environmental cycle and food chains* easily, through emission during processing stages or unregulated disposal of wastes or accidents.

The incident, in 1965 in Minamata Bay in Japan led to almost 50 deaths with hundreds being seriously ill caused by mercury poisoning **(32)**. The problem was traced to a discharge by a chemical company. Other incidents involving mercury in the petroleum and petrochemical industry have been discussed earlier in this chapter.

Location	Mercury Concentration	
	Gas ($\mu g\ m^{-3}$)	Liquids ($\mu g\ kg^{-1}$)
Europe	100 - 150	-
South America	50 - 120	50 - 100
Gulf of Thailand	100 - 400	400 - 1200
Africa	80 - 100	500 - 1000
Gulf of Mexico (USA)	0.02 - 0.4	-
Overthrust Belt (USA)	5 - 15	1 - 5
North Africa	50 - 80	20 - 50
Malaysia **(16, 17)**	1- 200	10- 100
Indonesia **(13)**	200 - 300	10 - 500

Table 1.6 : Estimated world levels for mercury in natural gas and condensate **(31)**

The primary avenues of environmental contamination and worker exposure to mercury involve the following:

- Emission

  The majority of the emissions involve exploration and production, marketing and refining, from the use of fuel or from controlled flaring and venting, which are necessary for safe operation **(33)**.

- Spillage of mercury from instruments thus contaminating soil.

  Soil contamination from spillage of mercury has been reported and has occurred at compressor stations, metering stations and processing facilities **(34, 35)**.

- Accumulation of spent mercury-adsorption material and spent catalysts **(31)**.

  Adsorbents are used to remove mercury from gas and/or liquid streams. The sorbent materials are packed in beds designed to optimise contact. Over time, they become expended and require replacement. The spent adsorbent therefore, constitutes a secondary waste for a processor that employs this technology.

- Equipment contamination by deposition of mercury from feedstocks.

  Aluminium cryogenic equipment used in LNG and olefin processes can accumulate mercury by deposition from gases and liquids as they are cooled. The accumulation can cause equipment degradation in the form of cracking that causes leaks **(36)**.

- Accumulation of sludge in condensate transportation vessels and storage tanks and pipeline pigging debris **(31)**.

  Mercury can deposit in pipelines, transportation vessels and storage tanks.

- Waste waters and formation waters, from processing well systems may contain mercury compounds.

  Treatment for mercury and other toxic species is essential, to ensure these waters are free from contaminants, when discharged to the environment or for recycling into the process stream.

1.2.6 Regulation and guideline levels for mercury in the environment

Mercury and mercury compounds are neurotoxins and are heavily regulated (Table 1.7) **(31, 37, 38)** with a trend that has been towards increased stringency. There are many pages of federal regulations that may apply to mercury waste originating from produced gas or gas processing. It is important to consider how a hazardous waste is produced when establishing legislation.

Sampling and analysis of elemental mercury spills are complicated by the non-uniform dispersal of mercury in soil. The analysis of contaminated materials for determination of waste classification or treatment efficacy, has historically used an EPA approach that was not equally sensitive to all mercury species. The current situation is in transition, but analysis for 'total mercury' is becoming the only allowable method to classify mercury containing-material **(31).**

Agency	Description	Value
WHO	• Guideline for drinking water mercury (all forms)	0.001 mg l^{-1}
	• Provisional tolerable weekly intake	0.3 mg total mercury 0.2 mg methyl mercury
Regulations		
OSHA	• Permissible exposure limit (PEL) Time-weighted average (TWA)	
	Organomercury compounds	0.01 mg m^{-3}
	Mercury vapour	0.05 mg m^{-3}
	• Ceiling limit	
	Mercury (aryl and inorganic)	0.01 mg m^{-3}
	• Short term exposure limit	
	Organo (alkyl mercury compound)	0.03 mg m^{-3}
Guidelines		
NIOSH	• Recommended exposure limit (REL) for occupational exposure to mercury (TWA)	0.05 mg m^{-3}
	• Immediate dangerous to life or health (IDHL) level	
	Mercury	28 mg m^{-3}
	Organo (alkyl) mercury compounds	10 mg m^{-3}
	• Short-term exposure limit (STEL) mercury as Hg (skin)	
	Alkyl compounds	0.03 mg m^{-3}
EPA	• Ambient water quality criteria to protect human health:	144 ng l^{-1}
	Ingestion of water and aquatic organisms	146 ng l^{-1}
	Ingestion of aquatic organism only	146 ng l^{-1}
	• Carcinogenic classification Oral reference dose (RfD)	Group D
	Mercury, inorganic only	0.3 μg kg^{-1} day^{-1}
	Mercury, alkyl and inorganic	0.3 μg kg^{-1} day^{-1}
	Methyl mercury	0.3 μg kg^{-1} day^{-1}
	Phenyl mercury acetate	0.08 μg kg^{-1} day^{-1}

Table 1.7 : Summary of regulations and guidelines regarding mercury and mercury compounds **(31, 37, 38)**.

1.3 TRACE MERCURY DETERMINATION

In general the expression 'trace' can be considered as a concentration below 100 $\mu g\ g^{-1}$. Element-specific detection techniques such as atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), and atomic fluorescence spectrometry (AFS) are widely used for the determination of mercury.

Atomic absorption spectrometry is the term used when radiation usually in the range 180 to 800 nm, is absorbed by the atom under measurement. The term emission spectrometry is applied to the measurement of light emitted from a flame or a plasma by chemical species after the absorption of energy as heat or as chemical energy (i.e. chemiluminescence). If only the emission from atoms is observed, the term atomic emission spectrometry is preferred. The re-emission of radiation from an atom having previously absorbed light is termed atomic fluorescence. Atomic fluorescence spectrometry is discussed in more detail in section 1.5.

The determination of mercury by cold vapour atomic absorption detection was first published in 1968 **(39)**. Since then, the determination of mercury at $\mu g\ ml^{-1}$ levels or less has received considerable interest. The importance of sampling and sample storage as well as methods of analysis have also been acknowledged. The use of AAS has emphasised the sensitivity and ease of application **(40)**. Atomic absorption was used as a replacement technique to an earlier calorimetry technique **(41)**. Non-flame atomic absorption and fluorescence spectrometry, with sample introduction which includes pyrolysis, furnace techniques, combustion, and reduction-aeration (cold vapour, (CV)), were simple and sensitive, but experienced difficulties in giving accurate determinations in natural samples **(42)**. The determinations were mainly in environmental materials, but some coverage of the analysis of food and biological materials was also undertaken **(43)**.

1.3.1 Mercury Vapour Generation Technique

Vapour generation is a technique that provides an ideal sample introduction procedure for atomic spectrometry. It has been applied to the determination of trace elements in a wide range of matrices. The advantages of the technique include the following; separation of the analyte from the matrix (to minimise later matrix interference), high efficiency of sample introduction, a large sample volume can be used and this yields excellent relative detection limits, the method is easily automated and chemical speciation determination is possible **(44)**. Several vapour generation methods have been used to bring mercury into the vapour phase **(45)**. These are described in the sections below:

1.3.1.1 Reduction-aeration (cold vapour generation) (45)

This is the most convenient and widely used method for sample introduction of mercury. Mercury has a vapour pressure of 0.16 Pa at 20 °C, corresponding to a concentration of ~14 mg m^{-3} in air and mercury has a tendency to form a stable molecule in the flame **(46)**. Mercury in aqueous solution (in an inorganic form, either originally or from conversion of organo mercury by oxidation or acid digestion) is treated with a reducing agent and is then swept out of the solution in its elemental vapour form by bubbling a suitable gas through it. The most typical reducing agent used is tin (II) chloride, although tin (II) sulphate has also been used. Sodium borohydride also has been used by a few workers but raises certain safety implications. In addition, the evolution of large amounts of hydrogen increases quenching if AFS detection is employed.

Examples of total mercury determined by the CV-AAS technique following acid digestion of the sample material include the analysis of; sewage sludge, sediment and soil; **(47)** moss and humus **(48)**, marine biological materials **(49)**; environmental and marine biological samples **(50)**, blood **(51)**, urine **(52)**, urine with correlation with dental amalgam restoration

(53), human bone (54), dogfish muscle and marine harbour sediment (56); crude oils and natural gas condensate (57) and dry fish (58, 59). Tin (II) was used as reductant in the majority of these procedures but a significant minority used borohydride.

For CVAFS, the examples include the analysis of; water and soil samples (56); environmental samples after microwave digestion (61); river water samples (62); urine samples (63) and sea water samples using an on-line oxidation, flow injection method (64).

1.3.1.2 Direct heating

In this method, the sample is first 'ashed' and then 'pyrolysed' under controlled temperature conditions. The technique always suffers from matrix interferences due to the high volatility of mercury that restricts the ashing temperature.

1.3.1.3 Electrolytic amalgamation

This involves mercury being plated on to a copper cathode during electrolysis. The cathode is then heated in a similar manner to that described in section 1.3.1.2, to release the mercury (45).

1.3.1.4 Direct amalgamation

In this method mercury vapour is collected on a silver or gold collector from which it is released by heating. The method may be employed after those methods described in sections1.3.1.1 or 1.3.1.2 as a pre-concentration technique.

A gold-coated sand trap was reported to be the only collector to efficiently retain the mercury content of air samples in a comparison with activated charcoal and silver-coated sand (65, 66). The trap was not affected by sulphur compounds or other airborne

interfering substances, the nature of the mercury compound or the flow rate of the air samples.

1.3.2 Preconcentration techniques prior to vapour generation.

1.3.2.1 Amalgamation

Preconcentration of mercury can be performed easily using traps or collectors. Mercury vapour is collected in these traps and later released for detection using a heating step. This allows not only preconcentration, but also the possibility of separating interfering substances from the sample before measurement.

Pre-concentration techniques have been used in the determination of mercury, by CVAAS, in water, air, sediments and other environmental samples. Examples include gold amalgamation **(67-75)**; a gold-platinum collector (90 % Au, 10 % Pt) **(76)** and a gold -platinum coil in wet natural gas **(8,77,78)**. Preconcentration *via* amalgamation with atomic fluorescence detection has also been achieved. Examples include, amalgamation on silver wire **(79)**, gold wires or wool **(80 - 82)** and gold-platinum wire **(83)**.

1.3.2.2 Complexing agents

Example of pre-concentration techniques using chemicals/reagents prior to vapour generation include the chelating ion exchanger Spheron Thiol **(84)**, mercury chelate-forming reagents such as diethyl dithiocarbamate and pyrollidin-1-dithioformate, dithizone **(85)** and other sulphur containing compounds such as l-cysteine **(86)**.

1.3.3 Mercury Speciation

The determination of different mercury compounds (Hg^{o}, Hg^{+}, Hg^{2+}, organomercury halides, etc.) can be carried out either on-line with species detection or off-line with total

mercury determination. The speciation of mercury compounds is important because of the varying level of toxicity associated with the different forms in which mercury can occure **(46)**.

Chromatographic techniques coupled with various element specific detection system are the most commonly used methods for speciation. These techniques include gas chromatography (GC), high performance liquid chromatography (HPLC), and ion chromatography

1.3.3.1 Speciation by chromatography coupled with AAS

A GC separation method for organomercury compounds with quartz furnace AAS detection was reported **(87)**. The species CH_3Hg^+ was ethylated in an aqueous ethanolic solution with $NaB(C_2H_5)_4$ to prevent the species co-eluting with dimethyl mercury (DMM) or Hg^o. The same derivatization has also been reported **(88)** to determine CH_3Hg^+ (as $C_2H_5HgCH_3$) in fish after dissolution in alkaline methanolic solution.

A preconcentration step with a dithiocarbamate resin before GC separation has been described by Emteborg *et al.* **(89)**. The separation of CH_3Hg^+ from Hg^{2+} in rain samples has been achieved by using an anion-exchange column **(90)**. Sarzanini *et al.* reported the used of cation exchange ion-chromatography to separate mercury compounds after *in-situ* cysteine complexation **(86)**. Liquid chromatography (LC) was coupled with CV-AAS with continuous flow reduction by tin (II) chloride for the mercury alkane-thiolates and $NaBH_4$ for reduction of inorganic, methyl- and ethyl mercuric compounds was reported by Fujita *et al.* **(91)**. The use of vesicles of didodecyldimethylammonium bromide as a mobile phase for separation of CH_3Hg^+ and Hg^{2+} by HPLC-CV-AAS has improved the CV generation of mercury **(92)**. Separation of several mercury compounds by reversed phase HPLC has also

been reported. Prior to detection, the ligand and matrix were destroyed by potassium persulphate ($K_2S_2O_8$). Real condensate samples have been analysed but suffered from severe sample matrix interference (9). The use of a silver trap and gold trap, in an attempt to differentiate between inorganic and organic forms of mercury in natural gas has been conducted (77). Some improvements in the speciation of mercury in natural gas condensate have also been achieved using on-line gold-platinum wire amalgamation trap or solid-phase micro-extraction with capillary gas chromatography-microwave-induced plasma-atomic emission spectrometry (78). However, the efficiency of the gold-platinum wire trap has been reported earlier, only able to give 50 % recovery of dimethyl mercury (77).

1.3.3.2 Speciation by chromatography coupled with AFS

Gas chromatography (GC) was coupled with CVAFS by Bloom and Fitzgerald (93) for the determination of mercury species after preconcentration from air on a Carbotrap column. Gas chromatography was also employed by Jones *et al.* (94) for total and organic mercury determination in water, soil and tissue samples. Water samples were brominated and preconcentrated onto sulphydryl cotton fibres and organic mercury was extracted into methylene chloride before being separated. Jian and McLeod (95) performed speciation on a column of sulphydryl cotton for rapid sequential determination of CH_3Hg^+ and Hg^{2+} in natural water by FI-CV-AFS.

1.3.4 The Determination of Mercury in Natural Gas Condensate

Knowing the exact concentration of mercury in the plant feeds and its destinations in the plant is one key to preventing contamination. Further assurance can be obtained by analysis for mercury in all industrial plant products and effluents on a routine basis. This is important since the gas and liquid feeds to gas processing plants (GPP) originate from different oil and gas fields. The mercury concentration can vary from time to time

depending on the distribution ratio of the gas and oil coming on stream. Hence, any prediction for mercury concentration in the feed gas for the GPP is more difficult to make. Figure 1.1 **(16)** shows that the concentration of the mercury in the feed stream to a GPP varied throughout the duration of the 300 day monitoring exercise.

The determination of mercury in natural gas and natural gas condensate was not properly and systematically carried out before the 1980's. This led to an underestimation of the actual mercury content of the gas processing stream, hence resulting in the problems encountered.

The determination of mercury in natural gas and gas condensates is made difficult by the very low concentrations involved and the complexity of the sample matrix. This dictates that either a highly sensitive detector or a large sample volume or both is needed. A variety of techniques with different sensitivities are presently available for the determination of mercury in general samples and some are listed in Table 1.8.

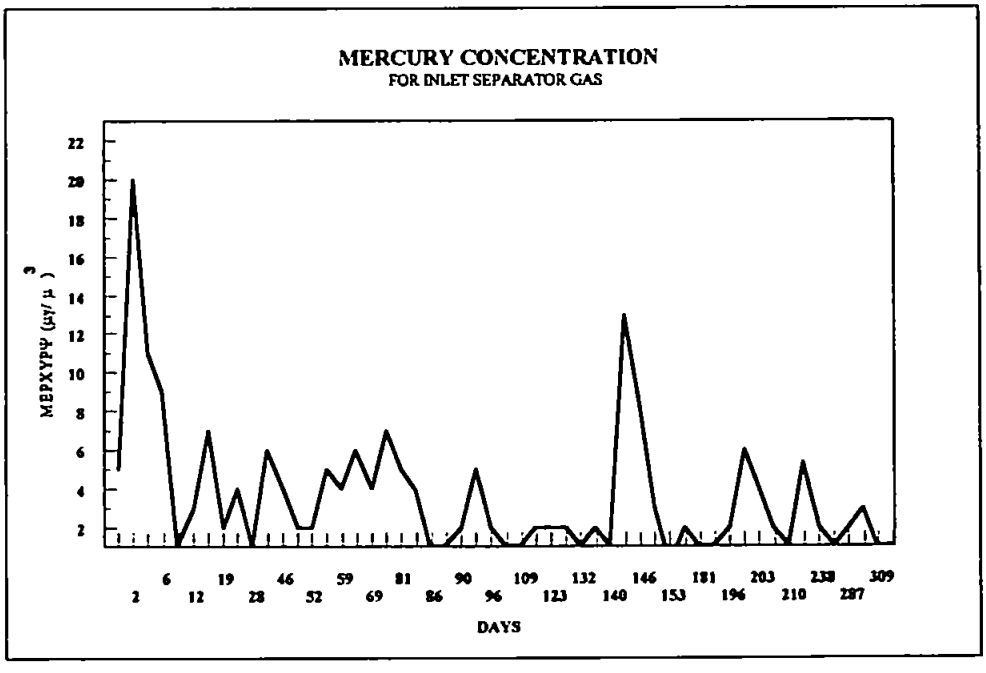

Figure 1.1 : Mercury content in feed natural gas (monitored for a duration of about 300 days)

Methods	Detection limit (ng)
Calorimetric	2000
X - ray Fluorescence	10
Neutron Activation	2
Gold Film	0.5
Differential Pulse Voltammetry	0.04
Cold Vapour Atomic Absorption (CVAAS)	0.01
Cold Vapour Atomic Fluorescence (CVAFS)	0.0001
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) **(119)**	0.001 ng ml^{-1}
Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) **(119)**	50 ng ml^{-1}

Table 1.8: Examples of micro-trace techniques available for the determination of mercury content **(5, 6, 11, 31, 119)**

1.3.4.1 Total mercury in natural gas condensate

Current practices for the determination of total mercury in condensates are based on acid digestion with an oxidising solution **(8, 9, 12, 77, 78, 96 -100)** such as acid persulphate, bromide/bromate solution, potassium permanganate, etc., or high temperature reactions with air or oxygen **(98)**, to produce inorganic mercury. This is followed by a cold vapour technique **(77, 96)** i.e. the addition of a reducing agent such as tin (II) chloride, to release mercury in its elemental form, which is then swept to a suitable spectrometric detector for measurement.

Detectors based on differential conductivity using a Wheatstone bridge are compact, relatively inexpensive and easy to operate. Historically, this technique was used for mercury

measurement by a majority of gas plant operators in the 1980's. The major disadvantage is that the detector is very sensitive to impurities which may not have been filtered out of the sample such as carbonyl sulphide, water, carbon dioxide and other absorbed gases. Thus, this technique is susceptible to massive overestimates of the mercury content in samples and analytically, of dubious quality.

Detectors based on conventional AAS or a dedicated instrument designed for the purpose offer far superior performance. Since this method is based on the absorption of a specific wavelength of light by atomic mercury, spectral interference is very unlikely. This instrument is very reliable, gives reproducible results and has a good detection limit. One disadvantage is that it is a very expensive outlay for use as a dedicated detector compared with other techniques.

The technique of AFS is more sensitive than AAS. These instrument offer high precision and accuracy, are easy to operate and are less expensive than AAS, but they do required argon gas for operation. The technique of AFS is discussed in detail in section 1.5.

The determination of total mercury in petroleum and petroleum products was first achieved in early 1975 **(97)**. The method involved an acid decomposition in a closed system, and the use of Wickbold oxy-hydrogen combustion. The decomposed or digested samples by the above method were then analysed by a cold vapour atomic absorption technique. The long winded method was said to be capable of detecting mercury to a concentration level of 5 - 10 ng g^{-1}. Other digestion methods include; the use of concentrated nitric acid and potassium persulphate **(98)**, high pressure-ashing using a quartz tube wet oxidation procedure with concentrated nitric and hydrochloric acid added, for the digestion step **(99)**. Most recently, the recoveries of dimethylmercury and diphenyl

mercury added into heptane/condensate samples were 98 % and 95 % respectively **(57)** when a digestion with acidic bromine water to convert organomercury species to ionic was used.

All of the above used acidic tin (II) chloride, added into the aqueous layer of digested samples to reduce mercury from the ionic form to elemental mercury. The mercury released (cold vapour technique) was detected by atomic absorption spectrometry. However, these methods required large amounts of reagents and are often complicated and time consuming, thereby increasing the risk of analytical errors and raising detection limits through high and variable blank levels **(8, 77)**.

Recently, a dedicated analyser for the determination of mercury in naphtha has been developed **(96)** (the NIC mercury analyser-SP-3D). The method is applied over a detection range of 0.1 to 10,000 ng ml^{-1}. The analyser consists of a controller, a mercury atomiser (asher) and a mercury detector. The sample is decomposed by heating in the instrument in the presence of a special additive. The mercury vapour in the gaseous product is retained in the mercury collector as a gold amalgam. The mercury is liberated by heating the collector to 700 °C. The vaporised mercury is carried to an absorption cell with pure carrier gas and detected by the cold vapour atomic absorption technique. One disadvantage of the instrument is that only about 100 mg of sample can be processed at a time resulting in problems for samples with low mercury concentration and in representative sampling. Sample throughput is also limited.

1.3.4.2 Mercury speciation in natural gas condensate

The determination of different mercury compounds, or 'speciation', in gas condensate is of interest not only because of the ecotoxicological aspect but also because of the interest in

those problems associated with the processing, utilisation and movement of gas condensate which contains mercury **(9)**. Effects such as pollution, the failure of process equipment, the poisoning of catalysts, worker exposures etc., make speciation work necessary. At present it is not well known which chemical forms of mercury are present in natural gases and gas condensates and, in addition, methods for the determination of total mercury concentrations must be regarded to be of unproven reliability because of a lack of adequate standard reference materials and poor accuracy **(6)**.

In recent years, many methods have been developed for the speciation of mercury in various types of samples. However, there has been limited success with complex organic liquid matrices due to the analytical chalangges those samples offer. Among these methods two basic categories can be distinguished **(9)**; first, a distinction is seen between inorganic mercury and organic mercury on the basis of special separation techniques **(9,77,78, 86 - 95)** and second, the identification of inorganic mercury can be distinguished from organic mercury by chemical treatments such as reducing reagents ($SnCl_2$) **(101, 102)**.

The present techniques available for the determination of specific-species of mercury are based on the combination of a separation technique such as GC or HPLC with different detectors **(9, 77, 78, 86 - 95)**. The main detectors used are electron capture detector (ECD), optical emission spectrometry (OES), AAS and AFS.

The first attempt at speciation of mercury in gas condensate was performed using HPLC coupled with CVAAS **(9)**. Various mercury species in an aqueous system were separated by reversed phase HPLC using gradient elution to investigate the preliminary condition required. Prior to measurement, the organic ligand and the matrix were destroyed using potassium persulphate and the mercury reduced to its elemental form by $NaBH_4$. However,

when applied to real gas condensate, serious instabilities and interferences occurred. The technique was only suitable for semiquantitative determination and was unable to determine all the possible species present in the real condensate sample.

An extraction scheme, used to isolate various organic and inorganic mercury species prior to Grignard derivatization of the ionic forms (to produce non-polar, butylated derivatives) and species-specific detection by GC-MIP-AES, was also suggested **(77)**. However, the efficiency of the extraction procedures for organomercury were often very poor and so, quantification was not reliable.

The determination of mercury species in gas condensate by on-line amalgamation traps (gold/platinum wires) for the collection of mercury species separated by capillary GC for detection by MIP-AES was able to remove the carbon background emission and allowed the determination of dimethyl mercury in condenste down to a detection limit of 0.24 $\mu g\ l^{-1}$. Untreated condensate, or condensate reacted with butylmagnesium chloride, can be injected into a gas chromatograph without the need for dilution or sample clean-up **(78)**. Problems associated with species separation were noted while artifacts due to derivatization must also be considered.

Most recently the speciation of mercury in condensate was achieved by using GC-ICP-MS. Five species of mercury i.e. elemental mercury, mercury (II) chloride, DMM, methyl ethyl mercury (MEM) and DEM were identified. However no organomercury halide species were detected in the majority of samples analysed **(187)**.

1.4 MERCURY REMOVAL METHODS IN THE PETROLEUM AND PETROCHEMICAL INDUSTRY.

Mercury removal systems for both gas and liquid streams are available commercially. However, a plant with removal facilities is still experiencing mercury contamination in their process steams. This is because of the limited information concerning the mercury species present in the streams. This lack of information leads to technical difficulties in deciding the most suitable mercury removal system.

1.4.1 Mercury Removal From Natural Gas

Eliminating mercury from natural gas requires the use of a mercury trapping material. These products vary in utilisation as a function of the gas compositions, i.e. hydrocarbon dry or wet, the level of water saturation, process conditions and the process scheme. In general, it is recommended to remove mercury as far upstream as possible. A summary of mercury removal systems for natural gas are presented in Table1.9 **(3,6,7, 10-14, 31, 103).**

1.4.2 Mercury Removal from Natural Gas Condensate.

Mercury removal from natural gas condensate is very different to that of natural gas because of the liquid phase operation and because of the types of mercury present in the condensate. At this time three technologies are claimed to be effective for the removal of total mercury from feeds which are destined to be upgraded by steam cracking or aromatization (reforming). There are several manufacturers, but most of the products are still under development i.e. at the pilot plant stage.

1.4.2.1 The 'DSM' process

DSM has stated that sulphide-containing resin materials are effective for the direct removal of mercury from condensate **(23)**. The resin is claimed to be effective for both elemental

and organomercury species. This technology is proposed for feeds containing mercury contents as high as 1 $\mu g\ ml^{-1}$ **(104)**. The sensitivity of the resin to other contaminants such as arsenic and nitrogen compounds is not known. The other examples of this system are, TP214 (Bayer), S-929 (Purolite International) and GT73 (Rohm and Haas)

	Method	**Comments**
1	Chemisorption on sulphur-impregnated activated carbon	Method typically used in the industry Example: HGR (Calgon Carbon), Mersob (Nucon Division), CMG 275 (Procatalyse/Acreon), MR3 (JGC).
2	Adsorption on activated carbon	Low saturation loading but cheap.
3	Adsorption on molecular sieve	Common sieves have low capacity; big beds.
4	Adsorption on metal sulphide impregnated on mesoporous alumina	Low resistance to both capillary condensation and liquid carry-over Example: CMG 273 (Procatalyse/Acreon)
5	Adsorption by amalgamation with a metal such as aluminium, silver zeolites, copper, gold, metal sulphides, and metal oxides	High investment cost, lower capacities Example: HgSiv (UOP), Tosoh (Mobil)
6	Oxidising solutions- potassium permanganate, sodium hypochlorite, and sodium vanadate	Regeneration problems; system contamination
7	Acid absorption of mercury-acidic permanganate and chromic acid	Increased corrosion; low saturations; system contamination
8	Chemical reaction with H_2S	Increased corrosion; limited H_2S access; impact on marketing.
9	Condensation and separation	Poor removal efficiency: liquid contamination
10	Stripping through liquid hydrocarbon medium	Poor removal efficiency: liquid contamination

Table 1.9: Summary of mercury removal systems **(6)**

1.4.2.2 The Institut Francais du-Petrole (IFP)-RAM processes.

The RAM processes are designed to convert all non-metallic forms of mercury into the elemental form before feedstock enters the process side of the plant for upgrading to fuel and petrochemical intermediates **(7, 105)**. The process operates in two stages. The first stage of the process comprises a reactor loaded with a hydrogenolysis catalyst, MEP841 (Procatalyse). Both ionic and organomercury species are stated to be converted to metallic mercury, in the presence of hydrogen which is subsequently trapped in the second stage. The second stage operates at a temperature below 100 °C in the presence of CMG 273 (Procatalyse) which is the elemental mercury trapping material. However the efficiency of the first reactor in converting trace concentration of ionic and organomercury compounds in complex mixtures of hydrocarbons (condensate) into elemental mercury is not well known.

1.4.2.3 Japanese Gasoline Corporation (JGC) process

The JGC technology system **(106)** is also a two step process which involves the catalytic decomposition of ionic and organomercury compounds to metallic mercury in the strict absence of hydrogen but it employs relatively higher temperatures (more than 200 °C). The catalyst used in this decomposition stage is 'MR13 catalyst'. The mercury trapping step (second stage) is carried out at lower temperatures using sulphided CoMo hydrotreating catalyst (MR3).

1.4.2.4 Other processes.

There are several other manufactures who also claim to be producing a mercury removal system for gas condensate. However most of them are still at the pilot plant stage or under development stage. Examples include Katalco (5156, 5157), Calgon (HGR), UOP and UCC .

1.5 ATOMIC FLUORESCENCE SPECTROMETRY

1.5.1 Background

Atomic fluorescence spectrometry is an analytical technique used to determine the concentration of elements in samples **(107)**. This technique was studied as early as 1902 by Wood, **(108)** and by Nichols and Howes **(109)** who looked at fluorescence in flames. Neither of these studies dealt with the possible analytical applications of atomic fluorescence. Winefordner and Vickers, in 1964 **(110)**, investigated the possibility of using atomic fluorescence as a practical analytical technique. They used metal vapour discharge tubes as sources and were able to obtain sensitivities of better than 1 $\mu g\ ml^{-1}$ for mercury, zinc, cadmium and thallium in an acetylene-oxygen flame. The development of a continuous source added another dozen elements to the list of possibilities **(111)**. Since then, several studies have been carried out on the development of AFS both in the area of analytical capability/analytical application for real samples and in the refining of instrumentation including conventional source excited AFS **(112- 115)**.

The determination of mercury using AFS was pioneered by Thompson *et al.* in the 1970s **(116)**. The instrument described was a dispersive system based on a modified FAAS and offered a detection limit of 0.02 $\mu g\ l^{-1}$. Non-dispersive AFS has also been investigated **(117)**. However the increased light gathering power of non-dispersive system is often offset by background scatter from the flame atom cell. This was overcome by Godden and Stockwell **(118)** who developed a filter fluorimeter that took advantage of the fact that mercury in atomic form is a vapour at room temperature and therefore does not require a flame to generate atomic species. As mercury vapour is monoatomic, a flame for mercury atomisation is unnecessary if the mercury in the sample can be converted to the elemental form. The low affinity of mercury for oxygen, nitrogen and argon allows maintenance of mercury vapour at relatively high concentration in these gases **(43)**. Four main methods

have been used to bring mercury into the vapour phase; reduction-aeration, direct heating, electrolytic amalgamation and direct amalgamation **(119)**. Reduction-aeration, by means of a reducing agent and sweep gas is by far the most popular. Use of this method improves detection limits by two or three orders of magnitude, compared with those based on simple flame atomisation methods. At present, CVAFS and CVAAS are the most widely used techniques for the determination of mercury. The advantages of AFS are that it is relatively cheap and simple to operate. In the absence of particulate/aerosol carry over from the CV technique and flames, there is no interference from source scattering, which contributes to its low LOD and high sensitivity. However, the ability to perform multi-element determinations is not yet available. Automated mercury analysers, based on AFS, are however, commercially available and several systems can be obtained allowing solid, liquid and gas samples to be analysed.

The determination of mercury by flow injection analysis (FIA) has also been introduced **(95, 120-122)**, utilising the mercury pre-concentration and release techniques previously outlined.

1.5.2 Atomic Fluorescence -Principles and Instrumentation

1.5.2.1 Principle

AFS uses radiation from a line or continuum source to excite atoms to a higher electronic state. The fluorescence radiation that is emitted as the excited atom returns to the ground state is measured. There are several types of atomic fluorescence which are characterised by the excitation and de-excitation mechanism involved in the transition **(107, 113 -115, 123)**.

The basic types of fluorescence are given in Figure 1.2:

Resonance fluorescence

The fluorescence radiation is of the same wavelength as the absorbed radiation. This type of fluorescence is used most often for quantitative analysis.

Stokes- Direct line fluorescence

Occurs when an electron in an excited state emits radiation and returns to a higher energy level than the one from which the electron originally absorbed radiation. The wavelength of the emitted radiation is longer than the wavelength of the absorbed radiation.

Stoke- Stepwise line fluorescence

Different upper levels are involved in the excitation and de-excitation process and again the wavelength of emitted radiation is longer than the wavelength of the absorbed radiation.

Thermal assisted fluorescence

This occurs if the excitation process involves radiation excitation followed by further thermal excitation.

The intensity of the atomic fluorescence radiation is proportional to the intensity of the absorbed radiation and to the concentration of the analyte atom. The intensity of atomic fluorescence is diminished by collisions between excited atoms and other molecules in the atomisation source. This process is called quenching.

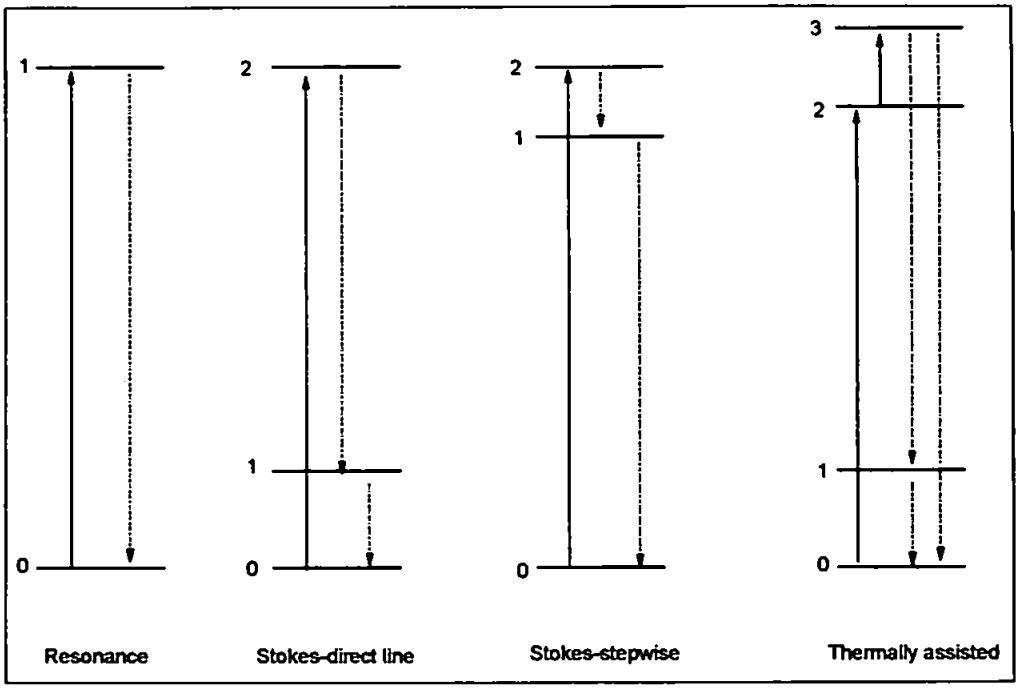

Figure 1.2: Energy transitions in atomic fluorescence **(124)**

1.5.2.1.1 Fluorescence of mercury atom

Many AFS measurements are based on resonance fluorescence. For the determination of mercury, the resonance fluorescence transition line of 253.7 nm (from the 6 $^3P_1$ excited state to the 6 $^1S_1$ ground state of mercury) is employed in most cases (Figure1.3). Excitation of mercury to the 6 $^1P_1$ excited state, followed by a Stokes stepwise fluorescence transition, is troublesome and is rarely used because the atmosphere and most flames absorb very strongly at this wavelength (185.0 nm). Despite this, a few studies using this line have been reported **(125, 126)**.

The fluorescence intensity (I_f) is directly proportional to the intensity of the irradiating source (I_o) as shown in equation 1.4. Therefore the sources intensity, over the frequency range of the absorption line, is very important in ensuring the sensitivity in AFS. The concentration of analyte in the atom reservoir or fluorescence cell is included in the term C and the fluorescence intensity I_f is linearly proportional to the concentration of analyte at

low concentration (45, 115, 123). Any quenching species in the atom reservoir or fluorescence cell affect the fluorescence intensity. The intensity of mercury fluorescence has been shown to be enhanced if a poor quencher such as Ar or He is used instead of N_2 or air as a carrier gas in the AFS method (125, 126).

$$I_f = k \phi I_o C \quad \text{..... (1.4)(45)}$$

where

k = Constant ($l/4\pi$)

l = path length in the direction of the detection system, m

4π = number of steradians in sphere (fluorescence is isotropic), sr

ϕ = fluorescence (quantum) efficiency

I_o = intensity of the source at the absorption line wavelength

C = concentration of atoms.

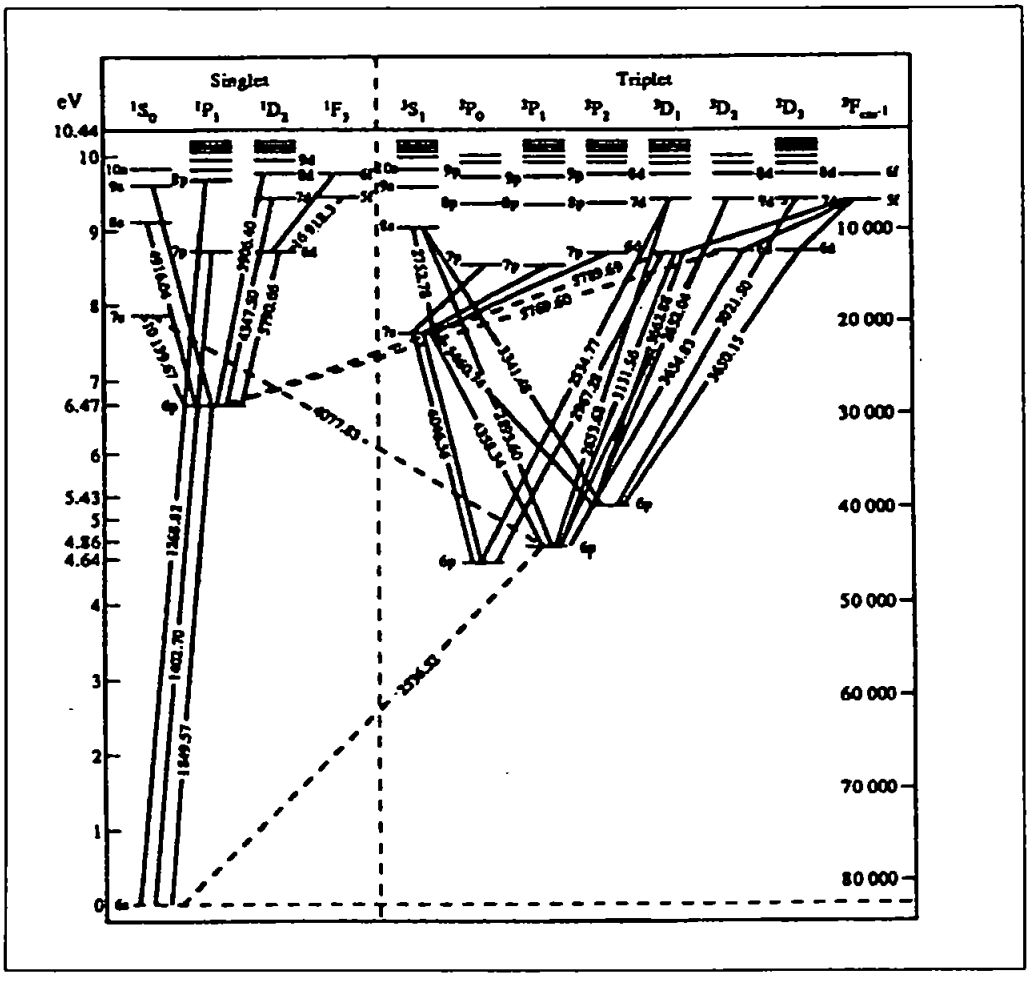

Figure 1.3: The atomic states and energy levels of mercury (43)

1.5.2.2 Instrumentation

A typical single-element atomic fluorescence spectrometer consists of an excitation source, an atomiser, a wavelength selector, a detector and a readout/computer. The components are identical to those used for AAS, but in a different arrangement, i.e. with the excitation source and emission detector at right angles around the analyte atom 'cell'.

For AFS, the ideal source would be stable and would provide intense radiation at the excitation wavelength for the element of interest. The most often used conventional light sources are the hollow-cathode lamp (HCL) **(127, 128)**, the electrodeless discharge lamp (EDL) **(129)**, vapour discharge lamp **(130)** and continuum-source lamp. Major advances in instrumentation have been achieved by the replacement of conventional excitation sources with lasers that provide sufficient intensity to saturate atomic transitions, and hence provide the maximum fluorescence signal **(127, 131)**.

The atom cell converts the sample into gaseous atoms. Commonly used atom cells for AFS include flames, plasmas and electrothermal atomisers. For mercury, the cold vapour technique is preferred and in this case, the atom cell is little more then a channelling reservoir for mercury atoms which allows the intense source to be directed at the analyte.

A wavelength-selection device serves to discriminate against light of all wavelengths except for the fluorescence wavelength of the analyte. Monochromators have been employed widely as wavelength selectors for AFS because of the ease of wavelength selection. However, in some dedicated systems, interference or similar filters have been used.

The photomultiplier tube (PMT) has remained a popular detector in AFS because of its sensitivity and long linear dynamic range. A schematic diagram of a commercially available AFS detection system is shown in Figure 1.4.

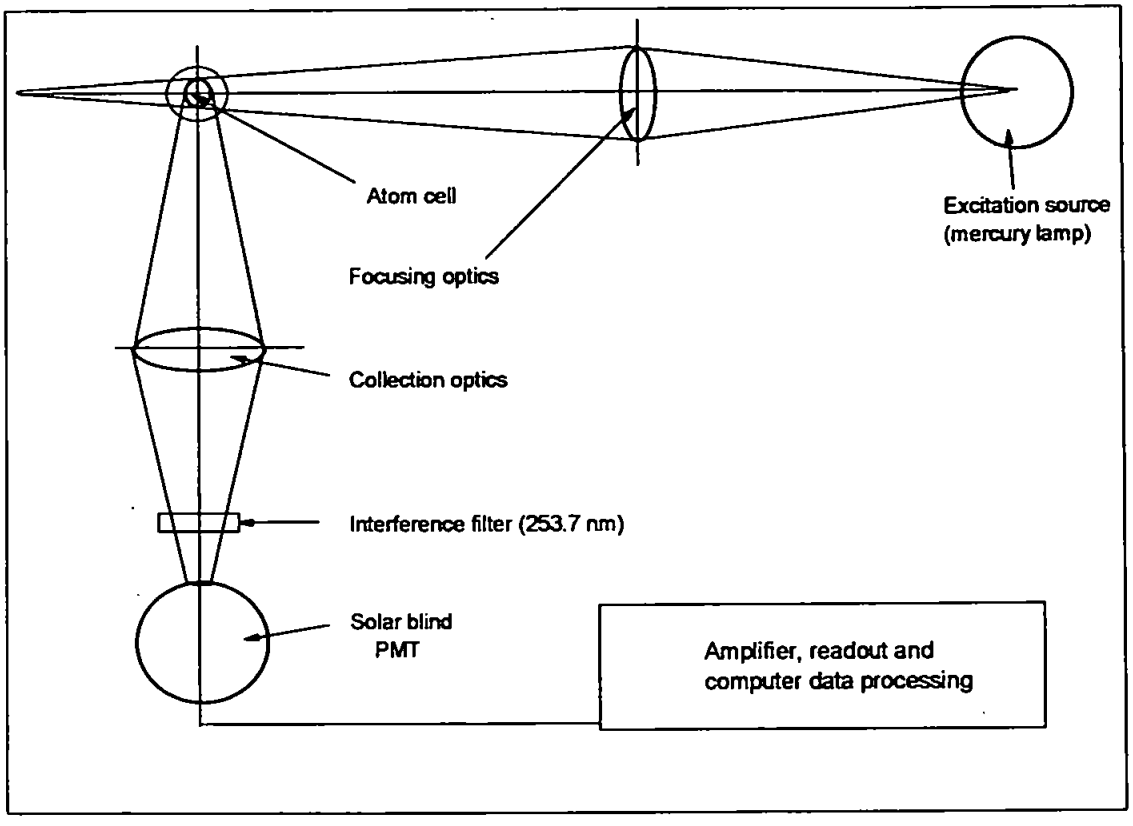

Figure 1.4 : Schematic diagram of a commercially available atomic fluorescence detector.

1.5.3 Interferences

AFS with line source excitation is free from spectral interferences. The use of a continuum source increases the risk of emission of fluorescence radiation from elements other than the analyte within the bandpass of the monochromator or filter. Background emission from the atomiser can be compensated for using a modulation technique **(107)**.

Since, in resonance AFS, the measured radiation has the same wavelength as that of the excitation source, it is difficult to distinguish scattering from fluorescence. Non-resonance

AFS does not suffer from this drawback, as the fluorescence signal is measured at a wavelength different from that of the excitation source. Matrix interferences in AFS are due mostly to light scattered from particles present in the atomiser and ion molecular fluorescence of matrix compounds **(107)**.

The possible interferences encountered in the determination of mercury by AFS are divided into those occurring in the gas phase ("gas phase interferences") and those occurring in the liquid phase or during the mercury vaporisation stage ("liquid phase interferences") **(43)**.

1.5.3.1 Gas phase interferences.

This type of interference consists of quenching of the mercury fluorescence and absorption of the mercury excitation line in the 253.7 nm region. Argon is the best carrier gas for fluorescence measurements because of its small cross-section for quenching **(125, 126, 137)**. Replacement of air by argon resulted in approximately a 100-fold increase in fluorescence signal **(95, 122, 126 132-134)**; replacement of nitrogen by argon resulted in an increase of the fluorescence signal by factors of 4 to 15 **(125)**. Other gases such as, H_2, CO, D_2, CH_4 and CO_2 also caused quenching **(131-132)**. Mercury atoms excited at the 253.7 nm line, should be de-excited much more rapidly by H_2 than by N_2. Thus tin (II), is a better reductant compared with $NaBH_4$ for AFS. Organic solvents with a high vapour pressure, such as acetone, benzene and ethanol caused a decrease in the mercury fluorescence signal **(125)**. The vapour of unsaturated and aromatic organic compounds that absorbed at the 253.7 nm region also interfered with the fluorescence signal **(138)**.

1.5.3.2 Liquid phase interferences.

Many inorganic species do not interfere with the determination of mercury by cold vapour methods, and the mercury vaporisation step undergoes a near-complete separation from

other constituent in the solution. Depressive interferences can be caused by noble metals such as Au, Pt, Pd and Ag **(139, 140)** and by certain transition metal ions. The effects are concentration dependent.

Some substances, producing very stable complexes with mercury ions, interfere with the reduction step to its elemental form unless the complexes are decomposed before reduction. Interferences effects can also be seen by the presence of bromide, iodide, cysteine, sulphide, thiosulphate and Se (IV) **(141-144)**.

1.5.4 Advantages and limitations of atomic fluorescence.

Some advantages **(112)** of the technique include the following:

- Increasing the radiation intensity should linearly increase the fluorescence intensity.
- Fluorescence intensity, as a function of concentration of fluorescing atoms, is linear at low concentration levels, making the procedure especially useful for trace element determination.
- Fluorescence spectra are simple, so high resolution spectrometers are unnecessary. In contrast to atomic absorption, a radiation source producing a narrow spectral line is usually required.
- linear range covers 3-4 order of magnitude

The limitations **(112)** of atomic fluorescence includes the following:

- Self-absorption effects occur at higher concentrations, producing a non-linear response with concentration.
- Reactions in a flame sample cell are similar to those observed in atomic absorption and these can cause problem in the preparation of a standard analytical curve.

- Quenching of fluorescence in certain sample systems can reduce the sensitivity of the method.
- The quantum efficiency varies with flame temperature and flame composition: thus, as with any analytical method based on comparison with standards, adequate control of these factors must be observed.

1.6 AIMS AND OBJECTIVES OF THIS STUDY

A knowledge of the total mercury content and the different species in natural gas and natural gas condensate is extremely important. Mercury in most forms is highly toxic, particularly when present as the organomercury species and is a cause of great environmental concern. In addition, the damage caused to industrial plants by the presence of mercury species can be financially crippling especially when unscheduled shut-downs are forced.

A recent paper (77) stated that 'At present it is not well known in which chemical forms mercury is present in natural gas and natural gas condensate, and, in addition, methods for the determination of total mercury concentrations must be regarded to be of unproven reliability due to lack of adequate standard reference materials and poor accuracy'. No reliable or precise quantitative analytical methodology has been published for even total mercury due to difficulties of low species concentration (total mercury can be < 1 $\mu g\ m^{-3}$ for natural gas and < 1 $ng\ ml^{-1}$ for gas condensate).

The aims of this project are:

1. To develop an accurate and precise, and if possible, a simple, rapid and robust procedure for the determination of 'total' mercury in gas condensate and other complex liquid hydrocarbons. This will involve studies of :

   - digestion and/or extraction techniques for mercury with cold vapour generation and atomic fluorescence detection. Various characterised digestion and/or extraction techniques will be tested together with some modified and new procedures. The use of an AF detection technique, due to the superiority of its sensitivity toward mercury.
   - The novel technique of vaporisation and trapping of mercury species at elevated temperatures with atomic fluorescence detection.
   - Spiking of real gas condensates and other complex hydrocarbons with known mercury species and measurement of recoveries.

2. To develop a technique to identify, the mercury species in gas condensate and liquid hydrocarbons. One area of interest is the use of coupled techniques e.g. gas chromatography with atomic fluorescence detection. For this coupling, a pyrolysis interface is required.

3. To use the developed techniques, for total mercury and species measurement, to evaluate fully the efficiencies of several, commercially available mercury removal systems (adsorbents) for gas and gas condensate plants. The use of a pilot plant facility which simulates real 'plant' conditions will be required to perform the study.

CHAPTER 2

THE DETERMINATION OF TOTAL MERCURY IN NATURAL GAS CONDENSATE BY DIGESTION AND EXTRACTION - COLD VAPOUR ATOMIC FLUORESCENCE SPECTROMETRY

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THE DETERMINATION OF TOTAL MERCURY IN NATURAL GAS CONDENSATE BY DIGESTION AND EXTRACTION - COLD VAPOUR ATOMIC FLUORESCENCE SPECTROMETRY

2.1 INTRODUCTION

The accurate determination of mercury at the ng ml^{-1} level in organic material samples has become increasingly important, as its potential as a hazard to both health and industrial safety has become more widely recognised.

Mercury occurs naturally in trace quantities in air **(6)**, natural gas, natural gas condensate and other petroleum samples **(4-25)**. Although difficult to generalise, the typical mercury concentration is in the 1 to 1000 $\mu g\ m^{-3}$ range. While the mercury content is seemingly low in gas and gas condensate, the large quantities processed in 24 hours result in very large absolute amounts of mercury entering the environment. The subsequent health implications are compounded by the fact that mercury is a cumulative poison.

Several method-based digestions have been reported **(47-64,147-152)** and various combustion techniques **(97, 99)** have been used to decompose organic material prior to obtaining the mercury in aqueous solution for the final measurement. However, these materials have generally been a relatively containing much higher concentration of mercury while the matrix of these samples are less complex than those found in petroleum samples. In order to determine the 'total' mercury concentration, it is necessary to oxidise any organomercury compounds (cleavage of the mercury-carbon bond) prior to the reduction step. One favoured method used with aqueous samples is the oxidation using an acid bromate with bromide mixture **(153, 154)**. A variety of combinations of acids (HCl,

H_2SO_4 , HNO_3, $HClO_4$) and oxidants; MnO_4^-, $S_2O_8^{2-}$, $Cr_2O_7^{2-}$ and H_2O_2 (permanganate, persulphate, dichromate and peroxide respectively) have been utilised **(155 -158).** It is of note however, that these procedures are not generally used with hydrocarbon samples. Prior to analysis, any excess oxidant is removed, for example using hydroxyl ammonium chloride. The presence of certain oxidants can produce an interference effect due to fluorescence quenching and/or suppression of the reduction reaction **(141-144)**.

Before the 1980's, the determination of total mercury in natural gas condensate was not performed routinely. No standard validated method was available for the petroleum industry and those methods that were used, would not be considered rigorous and systematically. The determination is difficult due to the low concentration of mercury, complexity of the matrix and the highly volatile nature of the samples. Currently, 'total' mercury levels are estimated routinely but no suitable mercury standard reference material, fully validated, is available. The methods used are based upon digestion **(8, 9, 12, 77, 78)** or ashing **(95, 97, 99)**. As noted previously the mercury species content of condensate is still under review but may be present in the forms of dialkyl, alkyl halide, inorganic salt and sulphur bonded mercury. The absent of in-depth study of this matrix in the literature has resulted in various methods being adopted, and therefore producing different mercury values from the same or similar samples.

Historically, the most extensively used method for measurement of mercury has been Cold Vapour Atomic Absorption Spectrometry (CVAAS)**(46 - 59)** and Cold Vapour Atomic Fluorescence Spectrometry (CVAFS)**(60 - 64)** both with preconcentration **(65 - 85)** and without preconcentration **(46 - 64).** In CV systems, the mercury in the samples is first oxidised to inorganic mercury (II) using a suitable oxidant and then reduced to elemental mercury by addition of excess reducing agent. Due to the appreciable vapour pressure of

elemental mercury, mercury vapour is rapidly volatilised when a carrier gas (usually argon) is bubbled through the solution containing inorganic mercury and tin (II) chloride (acid or alkali medium). The liberated mercury, purged from the solution, is subsequently delivered to a suitable detection system.

The reduction of mercury (II) with tin (II) is shown below.

$$Hg(II) + Sn(II) \rightarrow Hg^{\circ} + Sn(IV)$$

The reduction of mercury (II) results in some of the elemental mercury remaining in solution. It is therefore necessary to agitate the liquid to release mercury. This is performed within a gas liquid separator as illustrated in Figure 2.1.

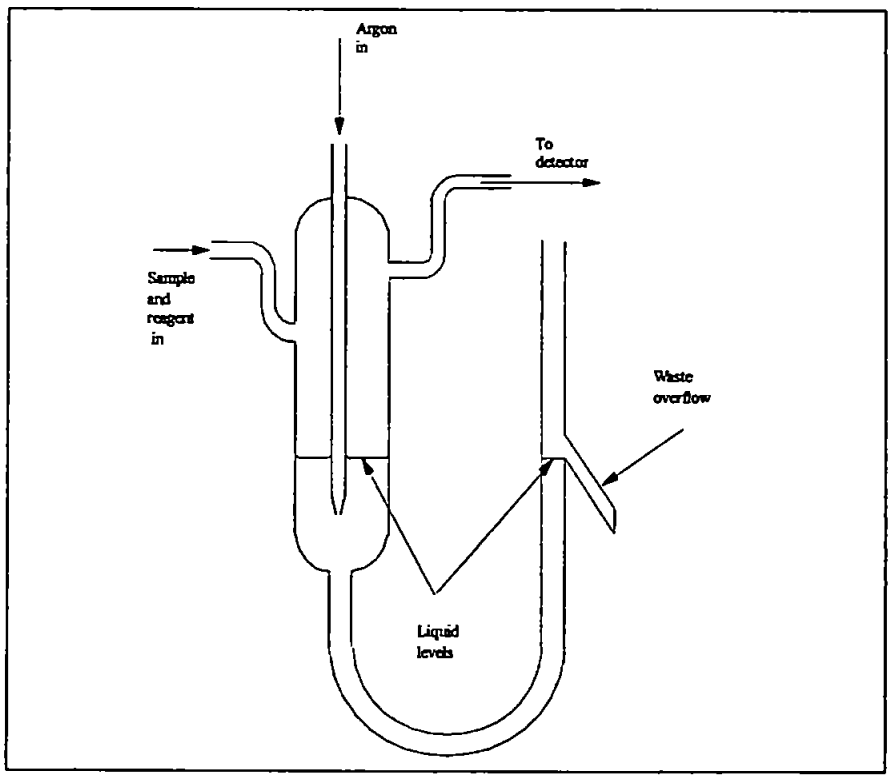


Figure 2.1 : Gas-liquid separator for mercury cold vapour generation (the tin (II) chloride scheme)

2.1.1 OBJECTIVE OF THE STUDY

The major area of importance is the digestion technique, used to release and extract mercury. Recoveries for ' total ' mercury will be studied using different digestion techniques with various known species, spiked into both synthetic and real base condensates. Efficient digestion techniques should then allow a suitable, detection system to be integrated.

A study of several wet digestion procedures will be carried out in order to evaluate the effectiveness of the procedure for treating gas condensate samples prior to total mercury measurement.

The determination of total mercury from digested and/or extracted samples (in aqueous form) can be carried out by continuous vapour generation atomic fluorescence spectrometry after reduction by acidic or alkaline tin (II) chloride.

2.2 EXPERIMENTAL

2.2.1 Mercury species

Six mercury species were used in the spiking experiments of control and ' real ' base condensate samples, dimethyl mercury (DMM), (Strem Chemical, Massachusetts, USA), methyl mercury chloride (MMC), ethyl mercury chloride (EMC), phenyl mercury chloride (PMC) (Johnson Matthey, Royston, Herts, UK), diPhenyl Mercury (DPM) (Aldrich, Dorset, UK) and Conostan metallo-organic mercury standard (MBH, Analytical Ltd., Barnet, England).

2.2.2 Reagents

All reagents were of analytical grade unless otherwise stated. $SnCl_2$, NaOH, n-hexane, toluene, HNO_3, HCl, H_2SO_4, hydroxyl ammonium chloride and ascorbic acid were obtained from Merck, Dorset, UK., and propanol was obtained from Aldrich England. High purity de-ionised water purified by a Milli-Q analytical reagent grade water purification system (Millipore, Chester, Cheshire, UK) was used throughout either for preparation of solutions or for cleaning of glassware.

Individual mercury and organomercury stock solutions ($HgCl_2$, $(CH_3)_2Hg$, C_2H_5HgCl, C_6H_5HgCl, $(C_6H_5)_2Hg$ and Conostan metallo-organic mercury standard (dialkyldithiocarbamate) were prepared by dissolving the compounds in AnalaR toluene. To prepare the stock solution (1000 μg ml^{-1} as Hg) for C_2H_5HgCl, C_6H_5HgCl, and $HgCl_2$, the species were initially dissolved in a small quantity of propanol prior to dilution in toluene. Standard $HgCl_2$ solutions were prepared by diluting the stock solution in 10 % v/v nitric acid. Tin (II)chloride (5% m/v) was used as reductant. All stock solutions were stored in a dark bottle and kept in the refrigerator at 4 °C. The stock solutions were prepared freshly every two weeks. Working analytical solutions were prepared everytime the procedures were carried out.

2.3 INSTRUMENTATION

A PS Analytical Ltd. (PS Analytical, Orpington, Kent, UK), automated continuous flow vapour generation system (PSA 10.004) was used to generate gaseous mercury from samples. A schematic diagram is shown in Figure 2.2. Detection and measurement of mercury was achieved using an atomic fluorescence spectrometer (PSA 10.023 Merlin). The basic instrumentation is described in Chapter1, section 1.5 (Figure 1.4). The switching valve that alternates between sample and reagent blank solutions was computer controlled

and typically 8 ml of sample was introduced, although the volume could be varied so that only a small quantity of sample may be used. The instrumental operating conditions are outlined in Table 2.1.

All of the instrumentation outlined was automated and controlled using Touchstone Software (M023T150, PS Analytical, Orpington, Kent, UK). The two different units are connected to a computer through a Digital I/O card.

Parameter	**Value**
Reductant flow rate (ml min $^{-1}$)	3.5
Reagent blank flow rate (ml min $^{-1}$)	8.0
Sample flow rate (ml min $^{-1}$)	8.0
Carrier gas flow rate (l min $^{-1}$ Ar)	0.3
Sheath gas flow rate (l min $^{-1}$ Ar)	0.3
Dryer gas flow rate (l min $^{-1}$ Ar)	2.6
Delay time (s)	25
Rise time (s)	30
Analysis time (s)	30
Memory wash time (s)	50

Table 2.1 : Operating condition for continuous flow mercury vapour generation

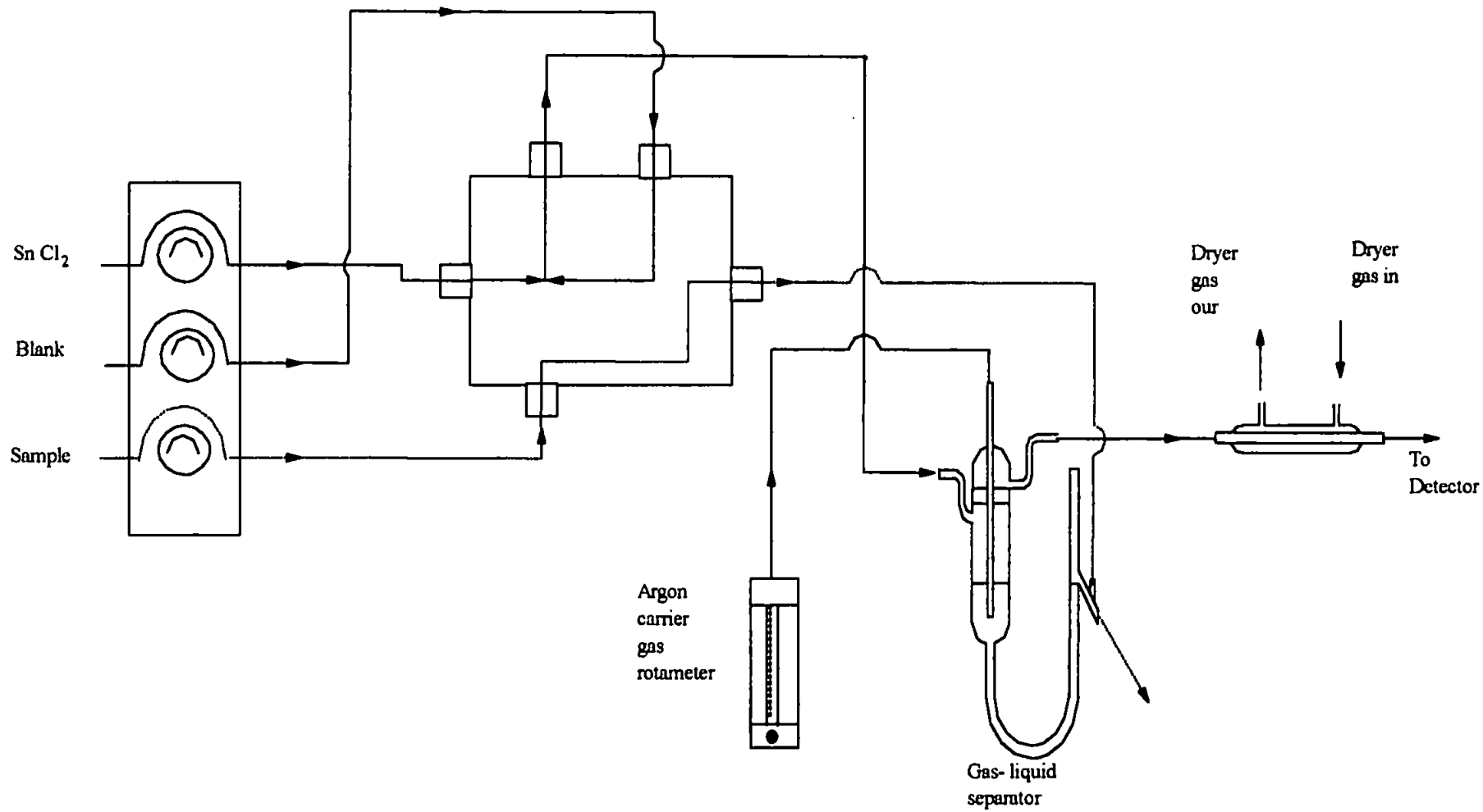


Figure 2.2 : Schematic diagram of continuous flow vapour generator
(shown in the blank position, dotted line represents the flow of the sample solution)

2.4 SAMPLE DIGESTION AND EXTRACTION PROCEDURE USED IN THE STUDY

A series of different digestion and extraction procedures were employed. In each case 5 ml of sample (hydrocarbon matrix and/or base condensate, designation used in the study; BC - Base Condensate, SBC-Spiked Base Condensate, HC-Hydrocarbon Mixture, SHC- Spiked Hydrocarbon Mixture, T-Toluene and ST-Spiked Toluene), was treated in such a way to produce intimate contact with each of five aqueous digestion and/or extraction routes. This would allow transfer of the mercury-containing species to the aqueous layer prior to its reduction for cold vapour generation.

2.4.1 Calibration

Calibration was performed by spiking Hg(II)Chloride into the matrix matched aqueous phase from each digestion/extraction procedures and continuing through the vapour generation step and AFS measurement.

2.4.2 Preliminary studies using acid-persulphate digestion

Samples of condensate (5 ml), spiked with Conostan organometallic mercury compound (10 and 20 ng ml^{-1} as Hg) were digested with 10 ml of nitric acid (conc.) and potassium persulphate (0.1g or 0.2 g) in a three necked round bottom flask fitted with a reflux condenser. The samples were stirred and heated to 40 °C for 2 hours. The flask was allowed to cool before the condenser was rinsed with Milli-Q de-ionised water. The lower aqueous layer was separated into a 50 ml volumetric flask and diluted to volume with Milli-Q water. A reagent blank was prepared by substituting toluene for the condensate sample. Tin(II)chloride (5% m/v) in both acidic and alkaline media was used as reducing agent.

2.4.3 (a) Preliminary studies using I^-/IO_3^- digestion

For the iodination reaction, 10 ml of hydrochloric acid (sp. gr, 1.18) was added to 5 ml of sample condensate and to condensate samples spiked with DPM and Conostan organometallic mercury compound (both 10 ng ml^{-1} as Hg) in a 50 ml volumetric flask. An aliquot, 5 ml (1:1) of iodide/iodate (0.05 M each) was added and the flask was shaken. The excess iodine was removed by the addition of 3 ml of ascorbic acid (10 % m/v). The lower aqueous layer was separated into a 50 ml volumetric flask and diluted to volume with Milli-Q water. A reagent blank was prepared by substituting toluene for condensate. Tin (II) chloride (5% m/v) in alkaline medium (4M NaOH) was used as the reducing agent.

2.4.3 (b) Further studies using I^-/IO_3^- digestion

The above procedure was extended to include DMM, DPM, EMC and PMC species in the spiking experiments.

2.4.4 Complexation with Dithizone, followed by extraction using thiosulphate and oxidative digestion with acid-persulfate

A 3 ml aliquot of citrate buffer [citric acid (21 g l^{-1}) and sodium hydroxide (8 g l^{-1}), adjusted to pH 2 with 0.1M hydrochloric acid] was added to 5 ml of condensate sample/condensate sample spiked individually with the organic mercury compounds DMM, DPM, EMC and PMC (10 ng ml^{-1} as Hg). The mixture was mixed with 5 ml dithizone in chloroform (1 mmol l^{-1}). The dithizone-mercury complexes were destroyed by shaking with 3 ml of a 1:1 (w/v) mixture of 5% of sodium nitrate and acid solution consisting of hydrochloric acid (0.1M), sulphuric acid (0.1M) and sodium chloride (0.1M) until the colour of the solution changed from green to yellow. The organomercurial complexes were extracted into the aqueous phase with 3 ml of sodium thiosulphate solution (2 mmol l^{-1}) buffered with ammonium acetate (0.05 mol l^{-1}). The aqueous layer was separated and

whilst shaking, 5 ml of oxidising solution consisting of sulphuric acid (0.25 mol l^{-1}), copper (II) sulphate (0.008 mol l^{-1}) and 2.5 % (m/v) potassium persulphate was added. The aqueous layer was diluted to volume (50 ml volumetric flask) with Milli-Q water. A reagent blank was prepared using the same procedure but without sample. Alkaline (4M NaOH) tin (II) chloride (5% m/v) was used as reducing agent.

2.4.5 Extraction with thiosulphate, followed by oxidative digestion with acid-persulphate

Samples of condensates (5 ml) spiked individually with organomercurial compounds; DMM, DPM, EMC and PMC (10 *ng* ml $^{-1}$ as Hg) were extracted into the aqueous phase with 3 ml of sodium thiosulphate solution (2 mmol l^{-1}) buffered with ammonium acetate (0.05 mol l^{-1}). The aqueous layer was separated and filtered into 50 ml volumetric flask. A 5 ml of oxidising solution consists of sulphuric acid (0.25 mol l^{-1}), copper (II) sulphate (0.008 mol l^{-1}) and 2.5 % (m/v) potassium persulphate was added in to the flask and shaken. The aqueous layer was separated 50 ml volumetric flask and make up to mark with Milli-Q water. A reagent blank was prepared with the same procedure but without sample. Tin (II) chloride (5% m/v) in alkaline medium was used as reducing agent.

2.4.6 Extraction using L-cysteine followed by oxidative digestion with acid-persulphate

Samples of condensates (5 ml) spiked individually with mercury compounds; Mercury (II) Chloride (MC), DMM, DPM, MMC, EMC and PMC (10 *ng* ml $^{-1}$ as Hg) were extracted into aqueous phase with 5 ml of L-cysteine solution (0.025 M). The aqueous layer was separated into 50 ml volumetric flask. A 10 ml portion of oxidising solution consisting of sulphuric acid (0.25 mol l^{-1}), copper (II) sulphate (0.008 mol l^{-1}) and 2.5 % (m/v) potassium persulphate was added to the flask and shaken. Excess oxidant in the samples

was removed by addition of 3 ml of hydroxyl ammonium chloride (12 % m/v). A reagent blank was prepared using the same procedure but without sample. Alkaline (4 M NaOH) tin (II) chloride (5% m/v) was used as reducing agent.

2.4.7 Mercury measurement

The treated samples were all measured for mercury using cold vapour atomic fluorescence spectrometry. The operating conditions for continuous flow mercury vapour generation are shown in Table 2.1

A summary of different digestion/extraction procedures are shown in Table 2.2

	Procedure 2.4.2 (9, 98)	Procedure 2.4.3	Procedure 2.4.4 (85)	Procedure 2.4.5	Procedure 2.4.6 (86)
step 1 :	Oxidation	Oxidation	Extraction:	Extraction	Extraction
	$K_2S_2O_8$ (0.1/0.2 g) 10 ml of HNO_3 (conc.) 2 hrs reflux	KI /KIO_3 (0.1M) 10 ml of HCl (conc.)	3 ml citrate buffer 5 ml Dithizone in chloroform	3 ml of thiosulpate (2 mmol/l) buffered with ammonium acetate (0.05 mol/l)	5 ml of L-cysteine (0.025M)
Step 2:			Destruction of complex	Oxidation	Oxidation
		3 ml ascorbic acid (10%) added to remove excess iodine	3 ml 1:1 of sodium nitrate (5%) and HCl (0.1M), H_2SO_4 (0.1M) and NaCl (0.1M)	5 ml of mixture of $K_2S_2O_8$ (2.5 % m/v), $CuSO_4$ (0.008 mol/l) and H_2SO_4 (0.05 mol/l)	5 ml of mixture of $K_2S_2O_8$ (2.5 % m/v), $CuSO_4$ (0.008 mol/l) and H_2SO_4 (0.05 mol/l)
Step 3:			Extraction:		
			3 ml of thiosulphate (2 mmol/l) buffered with ammonium acetate (0.05 mol/l)	3 ml hydroxyl ammonium chloride (12 % m/v)	3 ml hydroxyl ammonium chloride (12 % m/v)
Step 4:			Oxidation		
			5 ml of mixture of $K_2S_2O_8$ (2.5 % m/v), $CuSO_4$ (0.008 mol/l) and H_2SO_4 (0.05 mol/l)		
Reducing agent		Sn(II) Chloride (5% m/v) in acidic/alkaline medium			
Sample volume : 5ml					

Table 2.2 : Summary of digestion/extraction procedures for the determination of total mercury in gas condensate

2.5 RESULTS AND DISCUSSION

As five different digestion/extraction procedures were studied, the performance of each aqueous phase matrix upon mercury calibration required evaluation. For base line calibration, mercury (II) chloride was used. A series of 6 mercury (II) chloride standards was prepared (0 to 10 ng ml^{-1}) by diluting in Milli-Q water and the mercury concentration versus signal was recorded. Tin (II) chloride reductant was used to reduce the Hg(II) to its elemental form, prior to its determination by continuous mercury vapour generator AF Spectrometry. Five other calibration procedures involving the addition of persulphate, nitric acid, L-cysteine and various combinations were also performed. These were used to monitor performance and identify the suitability of the calibration sets for the five digestion/extraction procedures.

The result of the different calibration procedures indicates that when 'inorganic' mercury species is used for the calibration, the tin (II) chloride reductant efficiently released mercury. The overall performance (Figure 2.3) shows the consistency of the calibration procedures with r^2 greater than 0.99. The presence of various oxidants and extractants in the system does not significantly affect the performance of the calibration provided that excess oxidant had been destroyed with, for example, hydroxyl ammonium chloride, prior to the measurement step.

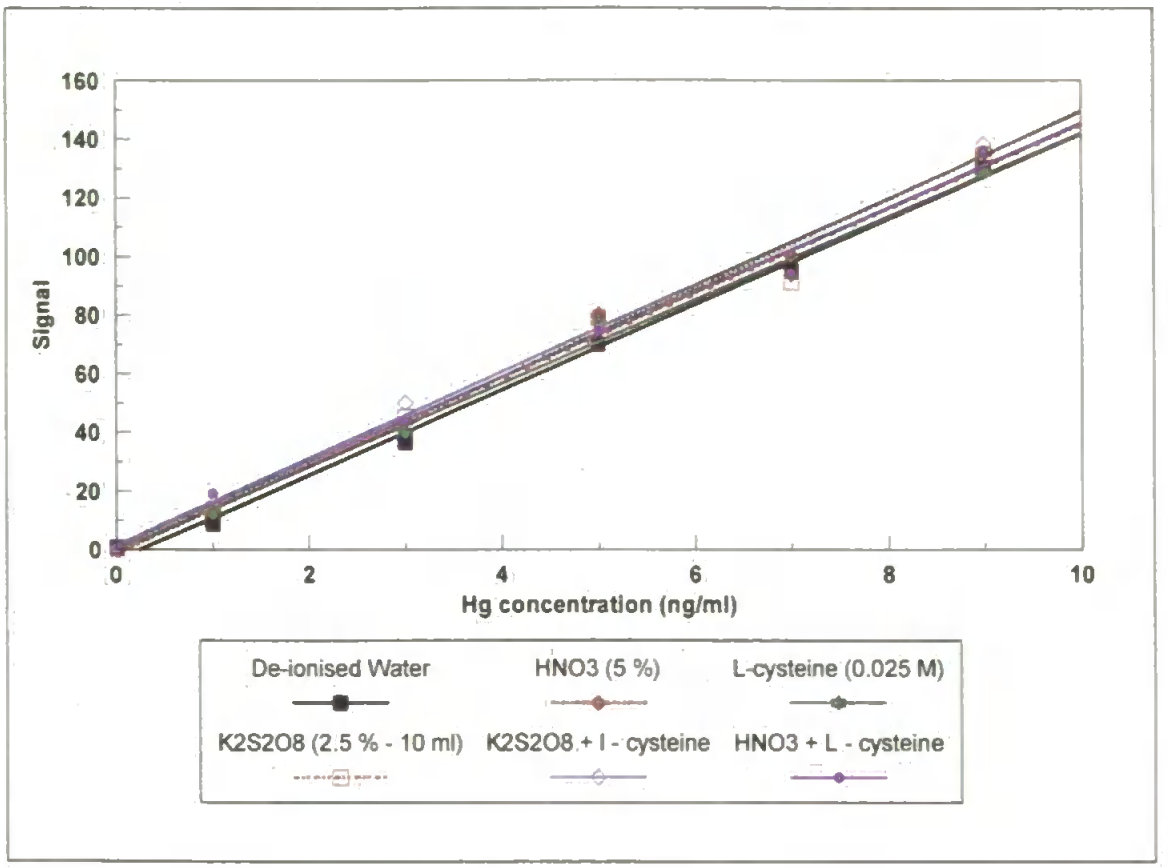


Figure 2.3 : Calibration graph for $HgCl_2$ using different digestion extraction procedures.

For the digestion/ extraction performance, the results of the study are as follows:

2.5.1 Acid-persulphate digestion

The results from this preliminary study are shown in Table 2.3. The recoveries for 'Conostan' mercury spiked (SBC) into base condensate (BC) are in the range of 4 to 29 percent.

Persulphate is a very strong oxidising agent. The indiscriminate nature of this compound (non targeting) was considered to be a problem. The low recoveries may be due to total consumption of the persulphate, by the sample matrix; This matrix comprises paraffins, naphthanes and aromatics compounds (carbon number of 4 to 10) .

Samples/ condensate	Hg added (Conostan) (*ng* ml $^{-1}$)	Hg found * (*ng* ml $^{-1}$)	% Recovery	Note
BC1	0	1.9 ± 0.4	-	0.1g $K_2S_2O_8$ added (acidic tin (II))
BC2	0	2.4 ± 0.8	-	0.2g $K_2S_2O_8$ added (acidic tin (II))
SBC1 *	10	2.8 ± 0.5	8.4	0.1g $K_2S_2O_8$ added (acidic tin (II))
SBC2 *	10	2.3 ± 0.6	3.7	0.1g $K_2S_2O_8$ added heat at (40 °C) (acidic tin (II))
SBC3 *	20	4.5 ± 0.9	13.8	0.1g $K_2S_2O_8$ added (acidic tin (II))
SBC4 *	20	3.6 ± 0.9	8.7	0.1g $K_2S_2O_8$ added heat at (40 °C) (acidic tin (II))
SBC5 *	20	7.6 ± 0.5	28.6	0.1g $K_2S_2O_8$ added heat at (40 °C - 2 hrs) (alkaline tin (II))
SBC6 *	20	6.3 ± 0.9	21.9	0.1g $K_2S_2O_8$ added heat at (40 °C - 4 hrs) (alkaline tin (II))

Note: Average results of four replicates analysis

* Recoveries corrected for base condensate mercury content

Table 2.3 : Recoveries of Conostan mercury compound spiked into condensates digested using persulphate

This exhaustion of persulphate was confirmed by experiment. A known excess of iodide was added to the aqueous layer after the digestion procedure was completed in order to reacts with any excess persulphate prior to quantification. The excess iodine formed can then be back titrated with standard thiosulphate. From this experiment no iodine was found indicating that all the persulphate was used up by the matrix.

From the above results, potassium persulphate although known to be a very strong oxidising agent, was considered not to be suitable for the direct digestion of the condensate sample.

2.5.2 (a) Digestion with I^-/IO_3^-

The results from this preliminary study (I^-/IO_3^-) are shown in Table 2.4. The recoveries (blank corrected) for mercury species added, DPM and Conostan spiked (SHC, SBC and SCHC, SCBC) in hydrocarbon (HC) and base condensate (BC) show the first indication of species dependance (DPM recovery ≥ 100 %, conostan ≤ 4 %. The hydrocarbon mixture use consisted of 5 components i.e., n-pentane (10 % v/v), n-hexane (25 % v/v), n- heptane (25 % v/v), cyclo hexane (25 % v/v), and toluene (15 % v/v) being similar to the major hydrocarbon range found in real condensate. Despite the simplification of the matrix little difference in terms of recovery was seen between HC and BC.

Sample	Hg added (ng ml $^{-1}$)	Hg found (ng ml $^{-1}$)		Recovery (%)		Note
		Acidic tin (5%)	Alkaline tin (5%)	Acidic tin (5%)	Alkaline tin (5%)	
HC	0	0.3 ± 0.09	0.1 + 0.03	-	-	
BC	0	0.2 ± 0.01	0.3 ± 0.02	-	-	
SHC	10	0.2 ± 0.02	13.4 ± 0.6	0	133.0 ± 6.1	Spiked with DPM
SBC	10	0.2 ± 0.0	10.7 ± 1.3	0	106.7 ± 13.0	
SCHC	10	0.2 ± 0.0	0.4 ± 0.09	0	4.0 ± 0.9	Spiked with Conostan
SCBC	10	0.2 ± 0.0	0.4 ± 0.07	0	4.0 ± 0.8	

Table 2.4: Recovery of DPM and Conostan organomercury compound spiked condensate and hydrocarbon samples after digestion with 5 ml of acidic iodide/iodate solution (0.05M)

The effect of quantity of oxidant upon mercury recovery was investigated using DPM. When the volume of I^-/IO_3^- (each 0.05 M) was varied from 1 ml to 5 ml, results from the experiment showed 1 ml gave 62 ± 11 % recovery, 3 ml gave 105 ± 4 % recovery and 5 ml gave 107 ± 13 % recovery.

2.5.2 (b) Extended experiment using above procedure

From the extended study of the previous digestion procedure, the recoveries of four mercury species used (DMM, DPM, EMC and PMC) are as shown in Table 2.5. The species dependence of the technique is seen clearly with the order of recovery being DPM > EMC> PMC > DMM (107, 48, 20 and 12 % respectively).

Samples	Species added	Amount added (ng ml $^{-1}$)	Hg Measured (ng ml $^{-1}$)	Hg Concentration (BlankCorrected) (ng ml $^{-1}$)	Recovery (%)	Replicates
BC	-	0	0.5 ± 0.2	0.5 ± 0.2	-	5
SBC 1	DMM	10.2	1.7 ± 0.9	1.2 ± 0.9	12 ± 9	5
SBC 2	DPM	10.0	11.2 ± 1.4	10.7 ± 1.3	107 ± 13	3
SBC 3	EMC	10.1	5.3 ± 0.9	4.8 ± 0.9	48 ± 9	5
SBC 4	PMC	10.0	2.5 ± 0.2	2.5 ± 0.2	20 ± 2	3

Table 2.5: Recoveries of mercury species spiked into condensate and digested with iodide/iodate

The digestion technique can be seen to target mainly two species, DPM and EMC, with very poor recoveries for DMM and PMC. The use of 1 hour ultrasonication (to increase intimacy) of aqueous oxidant/condensate samples did not improve upon the low recoveries. These were 16.9 ± 4.6 and 35.8 ± 3.4 *ng* ml $^{-1}$ (DMM and EMC) respectively.

2.5.3 Complexation with dithizone, followed by extraction with thiosulphate and oxidative digestion with acid-persulphate

The recoveries of DMM, DPM, EMC and PMC from spiked condensate, obtained from this complex are shown in Table 2.6. The low recoveries indicated that the efficient complexation of mercury with dithizone within the organic layer did not take place. This could be due to interference from the samples matrix which basically prevents the dithizone-mercury complex from being formed or the thiosulphate used to extract the mercury species into the aqueous phase after destruction of the complex not being efficient.

Sample	Species added	Amount added (ng ml $^{-1}$)	Hg Measured (ng ml $^{-1}$)	Hg Concentration (Blank Corrected) (ng ml $^{-1}$)	Recovery (%)
BC	-	0	1.1 ± 0.1	1.1 ± 0.1	-
SBC 1	DMM	10.2	0.8 ± 0.1	0	0
SBC 2	DPM	10.0	1.7 ± 0.2	0.6 ± 0.2	6 ± 2
SBC 3	EMC	10.1	2.9 ± 0.2	1.8 ± 0.2	18 ± 2
SBC 4	PMC	10.0	0.4 ± 0.1	0	0
Note : The results based on 4 replicate samples					

Table 2.6: Recoveries of DMM, DPM, EMC and PMC spiked into condensates - treatment with dithizone, thiosulphate and acid persulphate of aqueous phase.

2.5.4 Extraction with thiosulphate, followed by oxidative digestion with acid-persulphate

The recoveries of DMM, DPM, EMC and PMC spiked into condensates using the technique are shown in Table 2.7. The recoveries are seen to be very poor (< 2%).

An experiment where sodium diethyldithiocarbamate (NaDDC, 0.5 % w/v) prepared by dissolution of an appropriate amount in a pH 9 solution made of 0.02 ammonium hydroxide + 0.01 M acetic acid) was replaced thiosulphate in the above procedure gave, similar result (very poor recoveries)

Sample	Species added	Amount added (ng ml $^{-1}$)	Hg Measured (ng ml $^{-1}$)	Hg Concentration (Blank Corrected) (ng ml $^{-1}$)	Recovery (%)	Replicates
BC	-	0	0.8 ± 0.1	0.8 ± 0.1	-	3
SBC 1	DMM	10.2	0.3 ± 0.1	0	0	3
SBC 2	DPM	10.0	0.2 ± 0.0	0	0	3
SBC 3	EMC	10.1	1.1 ± 0.1	0.2 ± 0.1	2	3
SBC 4	PMC	10.0	0.2 ± 0.1	0	0	3

Table 2.7 : Recoveries of DMM, DPM, EMC and PMC - treated with thiosulphate followed by oxidative digestion with acid-persulphate

2.5.5 Extraction with L-cysteine

The recoveries of five mercury species i.e. MC, DMM, EMC, PMC and DPM spiked individually into the condensate samples are shown in Table 2.8. These values show that the above procedure is more effective in the extraction of certain mercury species compared with previous procedures. The recoveries for DPM, EMC and MC were 100 % in spiked base condensate (SBC). However the recovery of DMM, MMC and PMC were 15 %, 15 % and 33 % respectively. As DMM is an important species, likely to be present in condensates **(78, 178)**, the procedure could not be considered.

Sample	Species added	Amount added (ng ml $^{-1}$)	Hg Measured (ng ml $^{-1}$)	Hg Concentration (Blank Corrected) (ng ml $^{-1}$)	Recovery (%)	Replicates
BC	-	0	2.7 ± 0.3	2.7 ± 0.3	-	6
SBC 1	DMM	10.2	4.2 ± 0.1	1.5 ± 0.1	15 ± 1	5
SBC 2	DPM	10.0	12.6 ± 1.0	9.9 ± 0.9	99 ± 9	5
SBC 3	EMC	10.1	13.7 ± 1.4	11.0 ± 1.3	110 ± 13	5
SBC 4	PMC	10.0	6.1 ± 0.2	3.3 ± 0.2	33 ± 2	5
SBC 5	MC	10.0	12.9 ± 1.8	10.2 ± 1.7	102 ± 17	5
SBC 6	MMC	10.0	4.2 ± 0.2	1.5 ± 0.2	15 ± 2	7

Table 2.8 : Recoveries of mercury species spiked into condensate - treated with L- cysteine

As stated, gas condensate samples are complex mixtures of hydrocarbons, their contents comprising paraffins, naphthanes, olefins and aromatics. To simplify the matrix problem, the condensate sample was replaced by toluene. The toluene was spiked with PMC and DMM (two distinctive boiling ranges of alkyl mercury compounds) and subjected to the same extraction treatment as before. The recoveries results are shown in Table 2.9.

Sample	Mercury added (ng ml $^{-1}$)	Hg Concentration (ng ml $^{-1}$) (Mean ± S.D.) (n = 4)	Hg Concentration (Blank Corrected) (ng ml $^{-1}$)	Recovery (%) (Mean ± S.D.)
Toluene	0	1.1 ± 0.2	1.1 ± 0.2	-
ST 1	DMM (10.0)	3.8 ± 1.9	2.7 ± 1.9	27.0 ± 6.3
ST 2	PMC (10.0)	10.4 ± 1.7	9.3 ± 1.7	93.0 ± 16.5

Table 2.9: Recoveries of DMM and PMC spiked into Toluene

2.5.5.1 Concentration of DMM

As stated earlier, the DMM species is an important species and likely be present in condensate sample. The recoveries for DMM spiked in toluene at different concentration (10, 20 and 50 ng ml^{-1}) were measured in order to observe the effect, if any, of the volatility on the recovery of DMM. The results obtained highlighted that the increase of concentration did not improve the recovery.

2.5.5.2 Factorial design

An attempt to improve the recovery of DMM was undertaken using a 'factorial design' experiment. A two levels factorial designed experiment was conducted. The variable used in the experiment were L-cysteine (0.001 to 0.05 M), persulphate (0.1 to 2.5 %) and tin (II) chloride (1 to 5 %) concentrations. Toluene spiked with 20 ng ml^{-1} DMM was used as a sample. The results from the experiment did not identify any one of the three variables as the more influential upon recoveries. No improvement upon previous recoveries was obtained.

2.5.5.3 Effect of pH of L-cysteine

Series of L-cysteine solutions at different pH's were used to extract a mercury species (DMM) spiked into toluene (10 ng ml^{-1} as Hg). The effect of pH upon the concentration of the different ionic forms of L-cysteine is shown in Table 2.10 **(159).** Sodium hydroxide (0.01M) was used to adjust the L-cysteine pH. Four different pH were selected accordingly:

pH	Ionic forms
12	$^{-}S\ R\ NH_2$ (95%)
9.5	$^{-}S\ R\ HH_3^{+}$ (60%) $HS\ R\ NH_2$ (20 %)
< 8.0	$HS\ R\ NH_3^{+}$ (95 %)

Table 2.10 : Ionic form of L-cysteine solution at different pH's

The recovery for DMM at different pH were measured and the results are shown in Table 2.11. While the pH is shown to be important, the maximum recoveries was still limited to 34 % (pH 8.65).

pH of L-cysteine	% recovery
5.97	0
7.95	19.0 ± 3.5
8.65	33.7 ± 5.2
11.95	22.0 ± 5.0

Note:
Sample used : 5 ml
L-cysteine (0.025M) : 5 ml
Persulphate (2.5% m/v) : 10 ml
Alkaline tin (II) : 5%

Table 2.11 : Recoveries study at different pH

The study also highlighted the batch to batch variation (variable mercury content) of unspiked base condensate. Different batches of condensate analysis gave different results, i.e. batches 1, 2 and 3 gave respectively 2.8 ± 0.3 , 1.0 ± 0.1 and 8.3 ± 0.9 ng ml^{-1}. This may be due to the 'base' condensate containing some particulate matter-with adsorbed mercury, sediment sludge etc.,. To minimise variation in analytical results, filtration or centrifugal may be considered in obtaining a homogenous sample. However, it would be preferred if the minimum of sample pre-treatment/ handling was employed to avoid losses.

2.6 CONCLUSIONS

The recoveries for various organic and inorganic mercury species, spiked into synthetic and real condensate samples using different digestion and/or extraction techniques from was studied. These procedures have previously been employed for the determination of various inorganic and organomercury halides, present in mainly aqueous systems.

The five digestion and/or extraction techniques used were (i) acid-persulphate digestion, (ii) digestion with iodine, liberated *in-situ* with I^-/IO_3^-, (iii) complexation with dithizone followed by extraction with thiosulphate and oxidative digestion with acid-persulphate, (iv) extraction with thiosulphate, followed by an oxidative digestion with acid-persulphate and (v) extraction using L-cysteine.

The results of the study showed that the efficiency of some of the digestion and/or extraction procedures carried out was dependent upon the speciation.

The recovery of a 'Conostan' mercury standard (mercury diethyl dithiocarbamate) from the persulphate digestion technique was in the range 4 to 29 %. Further experiments indicated that the persulphate added for the digestion step had been consumed by the sample matrix rather than targeting mercury species.

A 100 % recovery of di-phenyl mercury was achieved using the acidic iodine digestion technique. For other mercury species, i.e. ethyl mercury chloride, phenyl mercury chloride and di-methyl mercury, the recoveries by the same technique were 48 %, 20 % and 12 % respectively.

The two extraction procedures involving thiosulphate, i.e. with and without a complexation step using dithizone, were both found to be unsuitable for gas condensate samples since they yielded low recoveries of various mercury species. With the complexation step using dithizone, recoveries of the DMM, DPM, EMC and PMC were 0 %, 6 %, 18 % and 0 % respectively. The recoveries obtained with extraction by thiosulphate alone were less than 2 %.

Extraction using L-cysteine (0.025M) followed by oxidation with potassium persulphate (2.5% m/v) showed very encouraging results. The recoveries of the DPM, EMC and MC species were 100 %. While, the recovery of PMC was also high (over 90 %), that of DMM was only 15 %. This latter species is considered to be a major contributor to the total mercury in condensate samples. Only a procedure which would bring about a significant improvement in DMM recoveries (> 90 %) could be considered useful.

There was no improvement in the recovery values, obtained from the spiking of increasing concentrations of DMM into toluene, using the above extraction technique.

The results from a 'factorial design' experiment did not identify any one variable i.e. concentration of L-cysteine, persulphate and tin (II) chloride, as being the most influential upon recoveries of DMM. No improvement upon previous recovery values was obtained.

Experiments performed to change the concentration of different ionic forms of L-cysteine available for complexation using different pH values showed that recoveries for DMM were still limited to a maximum of 34 % at pH 8.65.

Overall, it was concluded that the favoured procedures used for digestion and/or extraction of mercury species from water and sediment samples, were of limited application to samples such as gas condensate.

Recovery problems encountered in the extraction and/or digestion of mercury species in gas condensate may arise because of the following:

- A natural gas condensate sample is unique in its properties and these depend upon its origin, and its processing and treatment steps.
- The complex matrix of a gas condensate can lead to various interferences during the digestion and/or extraction procedure. One example is the effect from a 10^4 : 1 ratio of unsaturated matrix to mercury species which limits the efficiency of certain procedures.
- The highly volatile nature of both the condensate and the mercury species can result in mercury loss of analytes during the determination. Heating during a procedure can also induce losses.

It is important to note that, to date, no fully validated, certified reference material is available for mercury species in a hydrocarbon-based sample. The absence of a CRM, needed to serve the analytical requirements of a large and environmentally important industry, is a reflection of the difficulty this sample-type offers. This absence also results in a plethora of techniques available for mercury species measurement in hydrocarbon-based samples, many of which are poorly designed, poorly tested and poorly presented.

CHAPTER 3

THE DETERMINATION OF TOTAL MERCURY IN LIQUID HYDROCARBONS AND GAS CONDENSATE BY VAPORISATION AND TRAPPING AT ELEVATED TEMPERATURES TOGETHER WITH ATOMIC FLUORESCENCE SPECTROMETRY

CHAPTER 3

THE DETERMINATION OF TOTAL MERCURY IN LIQUID HYDROCARBONS AND CONDENSATE BY VAPORISATION AND TRAPPING WITH ATOMIC FLUORESCENCE DETECTION.

3.1 INTRODUCTION

It was seen in Chapter 2 that digestion/extraction techniques **(8, 9, 12, 77, 78, 96 -100)** used for the determination of total mercury in gas condensate samples are inefficient, with the efficiency being dependent upon the species present and the complexity of the matrix. It is known however, that mercury species are efficiently adsorbed onto gold, gold-coated materials and the platinum group metals (amalgamation) **(66, 77)**. The possibility of utilising this characteristic as a means of removing the interferent matrix prior to release and measurement was investigated.

Unlike condensate samples, the determination of total mercury in natural gas can be carried out accurately and to very low limit of detection by collecting the species onto special gold coated sand traps at room temperature. The trapped/adsorbed mercury is released when heated to a high temperature (~ 900 °C) and swept through into the atomic fluorescence detector by argon gas for measurement **(161-162)**.

Depending upon the type of trap system, the adsorption technique can have some restrictions. In the presence of heavier hydrocarbons and/or 'wet' conditions, the adsorbent collection efficiencies are affected. It was reported that using Au/Pt coated *wire,* kept at 80°C to prevent matrix condensation, adsorption efficiency of 100 % for elemental mercury is achievable. However only 50% of dimethyl mercury is recovered from the same gas

matrix **(8,9,77)**. The trap system therefore displays species dependency, under the conditions used.

The performance of different adsorbents in collecting mercury species, such as activated charcoal, silver and gold coated *sand* has been studied by Dumarey *et al.* **(66)**. Elemental mercury, inorganic mercury ($HgCl_2$), organomercury halides (MMC and EMC) and the di-alkyl mercury compounds (DMM and DEM) generated in a stream of air (vapour form) were 100% collected when using gold coated sand. The study also reported that activated charcoal and silver coated sand was not recommended as the collection is not quantitative and depends on the sampling flow rate, the 'ageing time' of the collector, the mercury species used and the interferent nature of the matrix. In general the gold sand trap capable is capable of collecting various species provided the gas or the sample is dry and contains minimum interferents.

Recently, the performance of a newly developed gold impregnated silica (Amasil) trap indicated that the efficiency of the trap or collector was not affected by sampling in humid air (relative humidity of 95%) **(163)**.

Prior to the determination of mercury by an element specific detector such as AFS or AAS, the collector or trap is required to be heated to a temperature high enough to ensure decomposition of the compounds and the release of mercury in its elemental form. The thermal desorption behaviour of several mercury species released from a gold trap, as elemental mercury is controlled by the decomposition process **(164)**. To obtain full desorption and decomposition, the collector or trap must be heated to at least 500 °C **(66, 164-166)**. Mercury species will not be decomposed or released from the gold collector/trap if a temperature of 250 °C **(93)** is not reached. At 345 °C, 60 % of elemental mercury is

released if oxygen is used as carrier but for argon or nitrogen, a temperature of 250°C is sufficient. At 267 °C the recovery of DMM is 0 % , and at 345 °C the recovery for MMC is also 0 %. For DPM a temperature as high as 557 °C is required for complete decomposition **(164)**. This would suggest that the trapping mechanism does not produce elemental mercury directly during the adsorption process.

The aim of this study was to develop a simple, accurate, rapid and precise technique for the determination of total mercury in condensate samples. The excellent sensitivity of atomic fluorescence spectrometry has been utilised in this study, using a commercially available system, for the determination of total mercury. To address the matrix interference and species-dependent recovery problem obtained using conventional digestion and/or extraction techniques, a new trapping technique was designed and constructed.

The technique is based on vaporisation of the sample and trapping of mercury at an elevated temperature prior to its determination by atomic fluorescence spectrometry. The performance of the technique was evaluated from recovery data for total mercury using various known species from spiking experiments. The use of real condensate samples for analysis was carried out.

3.2 PRELIMINARY STUDY USING A SAMPLE VAPORISATION TECHNIQUE WITH ELEVATED TEMPERATURE TRAPPING OF MERCURY

3.2.1 EXPERIMENTAL

In this preliminary investigation, n-pentane was employed as a 'synthetic' condensate. A known amount of DMM and DPM, 20 to 50 ng ml^{-1} were spiked into the n-pentane. A one millilitre sample (spiked n-pentane) was injected into a 3 necked round bottom flask, at room temperature and heated slowly (approximately 20°C min^{-1}) in an oven to 200 °C. This temperature was maintained for about 10 minutes to ensure the sample vaporised completely. The sample vapour generated was swept by argon gas through a gold coated silica (Amasil) trap maintained at 200 °C by a resistance wire heater jacket. The flow rate of the argon was set to between 300 and 400 ml min^{-1}. To avoid losses of analyte, a minimum amount of tubing was used for the connection of glassware.

After sample vaporisation, the gold-coated silica trap was disconnected and transferred to a commercial mercury analyser unit (Sir Galahard Mk II, PS Analytical), for the determination of mercury. After samples had been collected using the method described above (remote sampling), the trap was placed into a heating module, where it was flushed with argon to ensure that no traces of air or any matrix vapour remain. The module then heated up and vaporised the mercury, which was carried by a stream of argon to a second permanent gold sand trap, where it was adsorbed. The second permanent trap then went through its heating cycle, releasing the mercury at 800 to 900 °C which was swept into the fluorescence detector where a response was measured. A detailed description of the instrument system has been described elsewhere **(161, 162)**. A schematic diagram of the preliminary instrumental arrangement is shown in Figure 3.2.

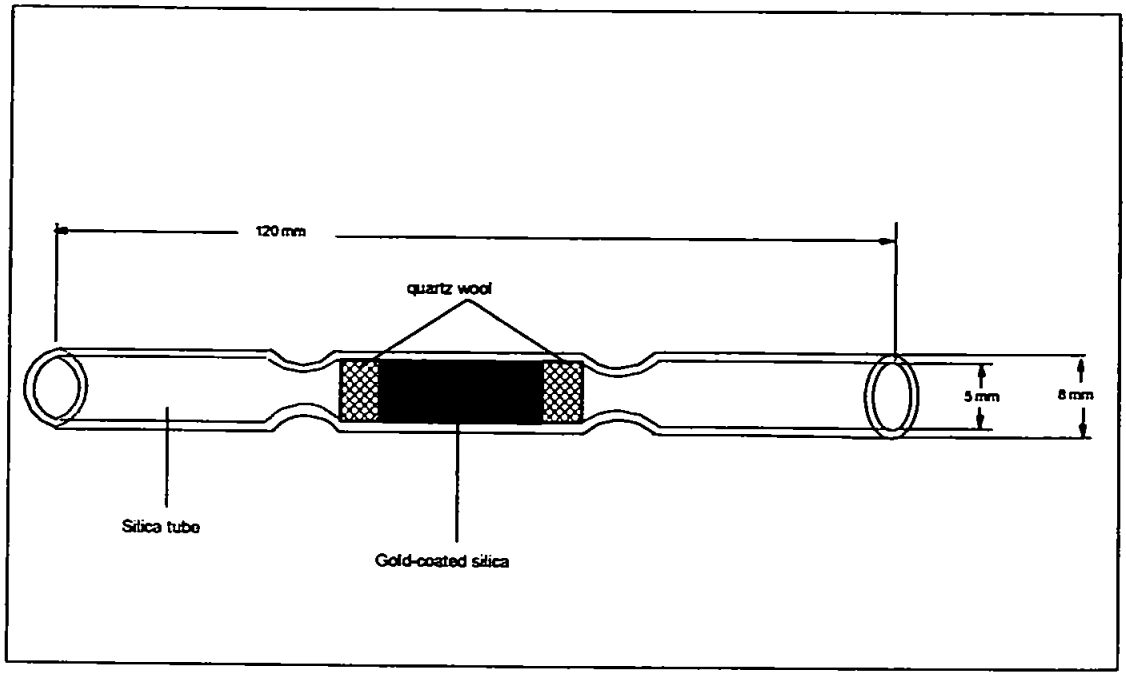


Figure 3.1 : Schematic diagram of gold-coated silica trap

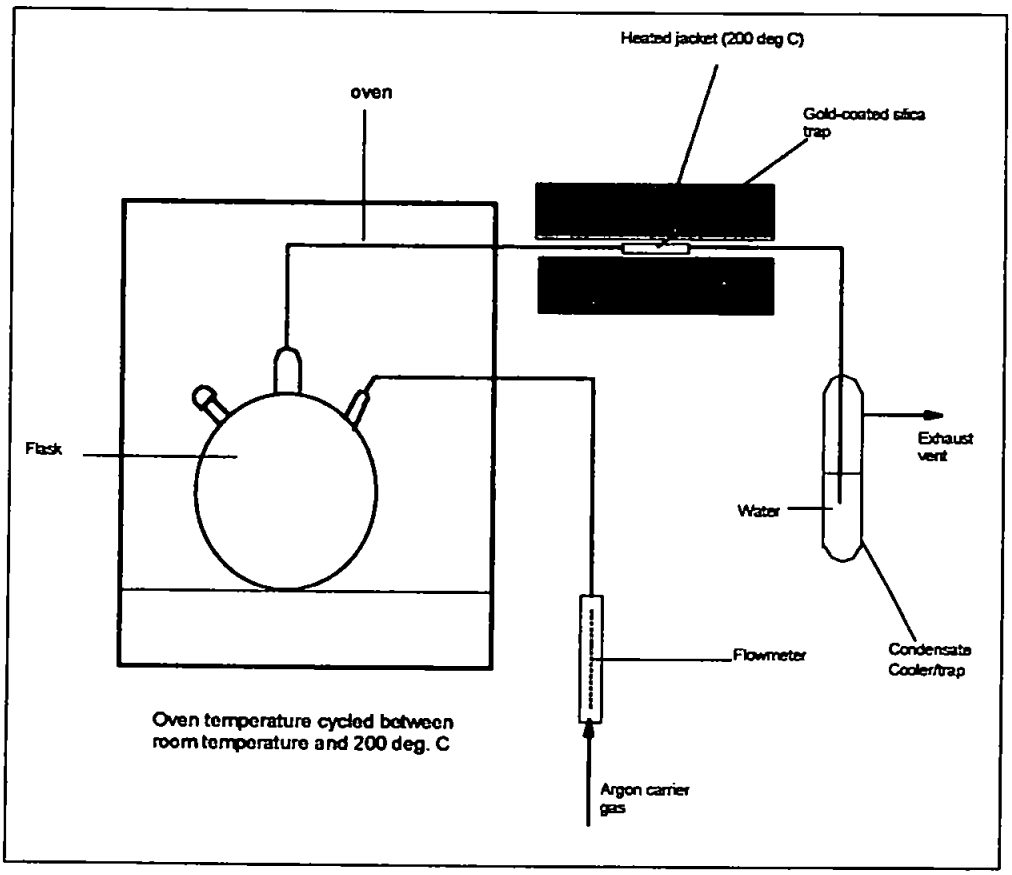


Figure 3.2 : Schematic diagram of vaporisation set-up used in the preliminary study for the determination of total mercury in condensate

3.2.2 Results and Discussion

3.2.2.1 Preliminary study using the sample vaporisation technique with an off-line detection system

From the results of the preliminary study, it was found that the determination of total mercury in both a simple (n-pentane) and a complex liquid hydrocarbon mixture such as gas condensate, can be carried out using a sample vaporisation procedure with trapping of two mercury species at an elevated temperature of 200 °C. Based on these findings, the potential of this new technique is evident. The recovery of DMM was some 100 % but DPM only yielded 75 % recovery when spiked into n-pentane. These results are shown in Table 3.1 and Figure 3.3. The low recovery of DPM is considered to be due to a low vaporisation temperature (boiling point of DPM is 352.1°C @ 760 mm Hg). The temperature used to volatilise the samples was limited to 200 °C to prevent the Teflon connection/tubing from degrading rapidly.

Some inconsistency in the results arose which was considered to be due to difficulty in controlling the heating rate of the oven used to vaporise the sample. The highly volatile nature of the sample in the warm oven leads to some problems through losses during the transfer of sample to the vaporisation vessel. The determination of mercury by off-line procedures is also time consuming especially as a cooling period is required before removing the trap and cooling of the oven before injection of the next sample.

To improve both the recovery and precision of this new technique, the sample introduction system had to be improved to eliminate losses during injection of volatile samples. Efficient and precisely controlled heating and cooling of the oven must be considered in order to regulate the heating temperature.

A re-design of both the heating chamber, used to vaporise samples, and the trapping module, held at 200 °C, was required so that connection and fitting do not limit the operating temperature to below that required for vaporisation of the higher boiling point mercury species. Also, an on-line fluorescence detector was required to avoid losses and to simplify the procedure thereby improving recoveries and precision.

No	Sample	Hg Species spiked	Amount spiked (ng ml $^{-1}$)	Total mercury measured (ng ml $^{-1}$) Mean ± s.d.	Recovery % Mean ± s.d.
1	PENTANE	-	-	0.0	0.0
2	PENTANE	DMM	20	21.2 ± 5.5	106 ± 27
3	PENTANE		40	40.22 ± 2.2	101 ± 6
4	PENTANE		50	57.7 ± 8.1	115 ± 16
5	PENTANE	DPM	20	10.3 ± 5.5	54 ± 64
6	PENTANE		50	37.9 ± 6.2	76 ± 12
7	Condensate	-	-	29.1 + 1.8 RSD = 6 %	-
Based on 4 replicate samples					

Table 3.1 : Recoveries of DMM and DPM spiked into n-pentane

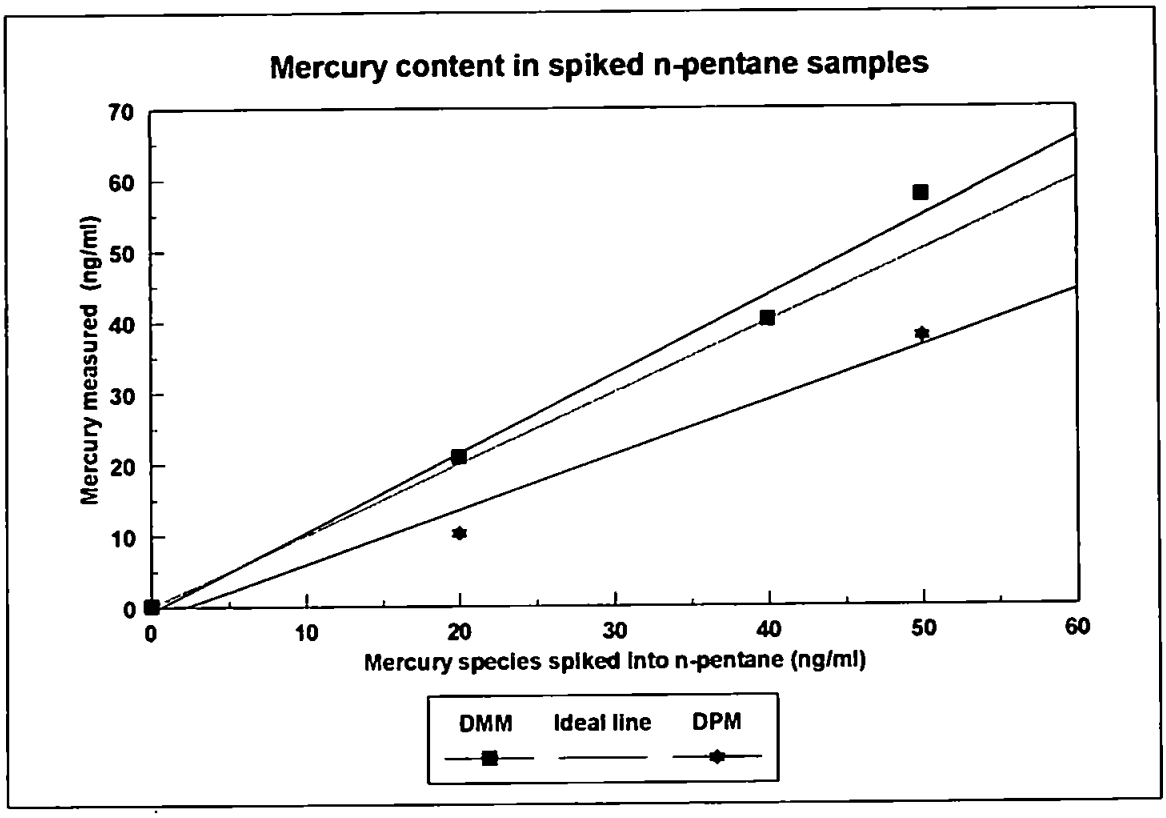


Figure 3.3 : Concentration of mercury species measured in spiked n-pentane

3.3 DEVELOPMENT OF AN EFFICIENT VAPORISATION AND TRAPPING INSTRUMENT FOR MERCURY DETERMINATION WITH ON-LINE FLUORESCENCE DETECTION.

3.3.1 EXPERIMENTAL

3.3.1.1 Reagents

Eight mercury species were used in the spiking experiments of both toluene and a real gas condensate sample to study the efficiency of the vaporisation and trapping of the new designed instrument. The species used were DMM, DPM, MMC, EMC, PMC, MC, Conostan metallo-organic mercury standard (CONO) and the two species diethyl mercury (DEM) and dibutyl- mercury (DBM)(Strem Chemical, Massachusetts, USA). All reagents were of analytical grade.

The organomercury stock solutions DMM, DEM, DPM and Conostan Metallo-Organic Mercury standard were prepared by dissolving the compounds in toluene. To prepare the stock solutions (1000 μg ml^{-1}) for MMC, EMC, PMC and MC, the species were initially dissolved in a small quantity of propanol prior to dilution in toluene. All stock solutions were stored in a dark bottle and kept in a refrigerator at 4 °C. The stock solutions were prepared freshly every two weeks. Working analytical solutions were prepared freshly for each daily set of experiments.

3.3.2 Instrumentation

A photograph of the layout is shown in Figure 3.5 and a schematic diagram of the instrumentation is shown in Figure 3.6

3.3.2.1 Vaporisation chamber.

The chamber consists of a 250 ml three necked round bottom flask which was maintained at 400 °C ± 10 °C using an electrothermal heating mantle. The separate necks were connected to the heated trap line and an argon purge gas line while the third neck was fitted with a double septum for sample introduction by an injection technique. The top part of the chamber was insulated with aluminium foil to reduce heat loss. The tubing from the chamber to the gold-coated silica trap was maintained at 200 °C by heating tape and a variac supply. The latter prevented condensation of the vaporised sample before it reached the heated trap.

3.3.2.2 Adsorption trap module

The new adsorption trap module (Figure 3.4) consisted of a gold-coated silica (Amasil, 30 mg) bounded by Quartz wool within a silica tube and surrounded by a nichrome heating wire (to release mercury at 900 °C). This tube was retained within a specially designed

cooling chamber (flushed using air to return the inner silica tube to 200 °C from 900 °C). The trap was positioned within a small oven (Kenwood, Hants, UK) maintained at 200 °C ± 5 °C.

3.3.2.3 Valve switching sequences

Control switching of the purging, cooling and carrier gas lines was performed by a computer driven 'Galahad' system (P.S. Analytical, Kent, UK). A schematic diagram of the switching arrangement for the sampling mode (pre-concentration) and for the measurement mode (detection) is shown in Figure 3.7.

3.3.2.4 Filter

To improve baseline stability and prevent trace organic material entering the detector system, a filter was inserted into the gas line prior to the detector. This filter which comprises two ashless, No. 1 filter papers in a 2 cm diameter demountable holder (Whatman Int. Ltd., Maidstone, UK) did not affect the performance of the calibration or any subsequent analyses. This was changed every fifty run or earlier if shown to be necessary.

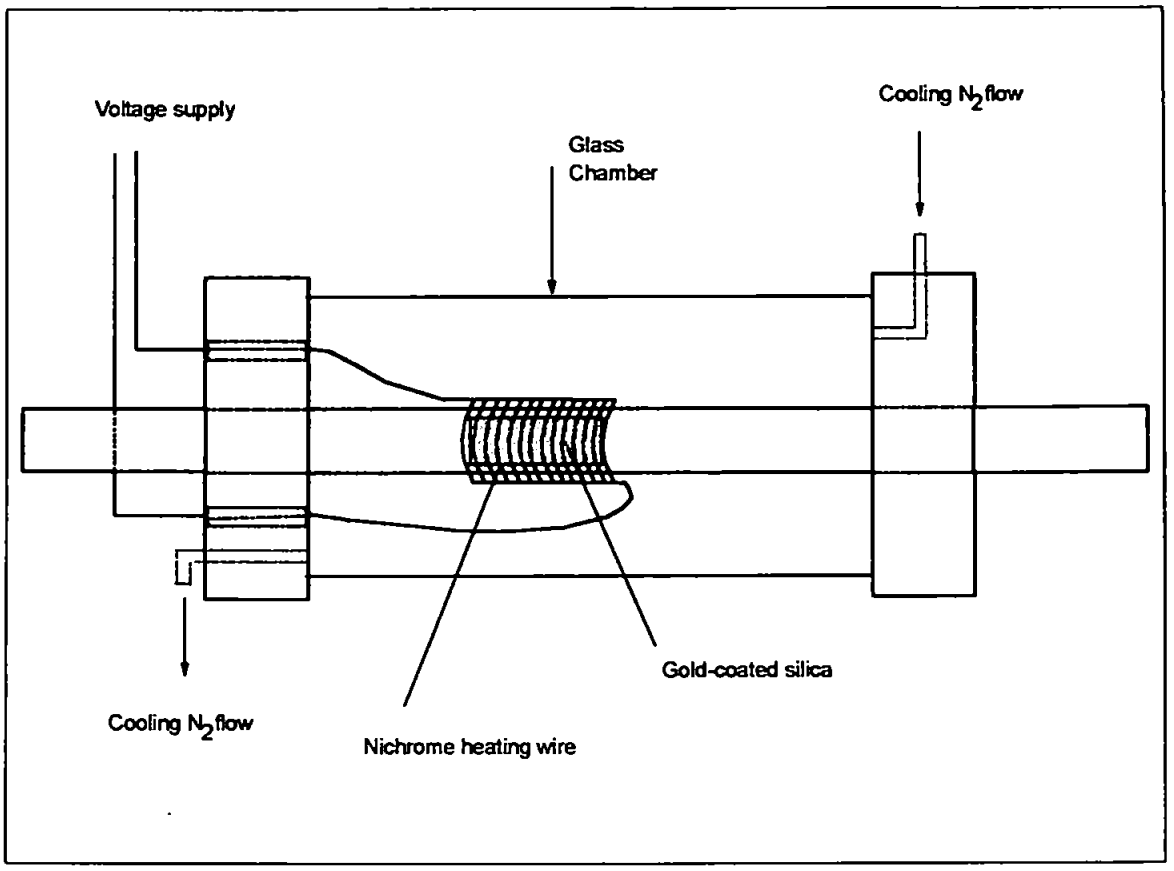


Figure 3. 4 : Schematic diagram for the adsorption trap module

3.3.3 Experimental procedure

Known mercury species were spiked individually at different concentrations (measured as mercury) in condensate and control samples (condensate or toluene). An accurately measured volume of sample (usually 0.25 ml) was injected using a gas-tight syringe (Dynatech Precision, Baton Rouge, Louisiana, USA) into the three necked a vaporisation chamber now held at a temperature of 400 °C. Normally some 5 to 10 minutes were required to vaporise the sample completely; a parameter which was studied later. The sample vapour generated was continuously swept by argon gas, at between 300 and 400ml per minute, through to the gold-coated silica trap maintained at 200 °C within the small oven. The sample matrix (paraffins, aromatics, naphthanes) was consequently carried in its vapour phase away from the trap and directed to a waste collector. The mercury species

which were first adsorbed on the gold coated silica trap, were subsequently released (as elemental mercury) by heating to a temperature of 900 °C and swept through to an Atomic fluorescence detector (Merlin, P.S. Analytical, Orpington, Kent, UK). Recovery experiments based upon the standard additions technique, together with condensate sample analyses (various condensate fractions, oils etc.) were performed.

In order to acquire the 'optimum' conditions for use, a number of instrumental operating parameters were varied and their effects investigated. In particular the effects of sample volume, argon gas sweep rate, temperature of trapping and the size of trap used, upon recovery were studied. In addition, the retention efficiency for different species and their bleed-off effects were studied.

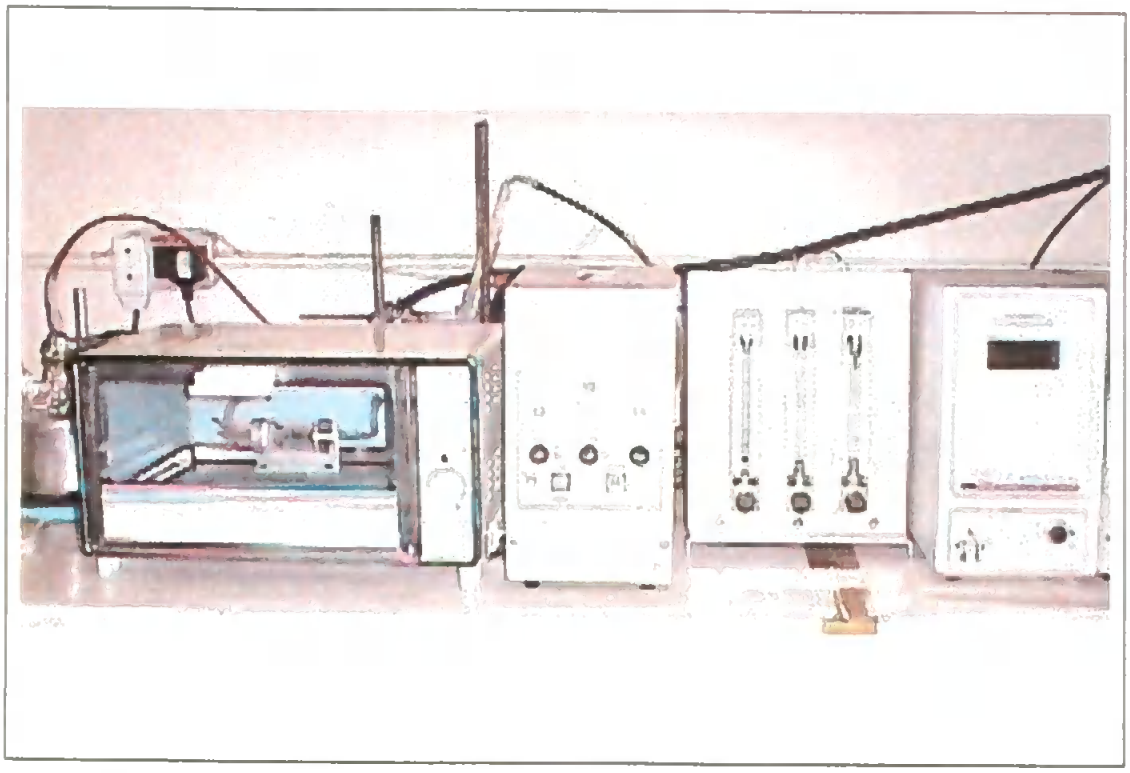


Figure 3.5 : Set-up for determination of total mercury in condensate

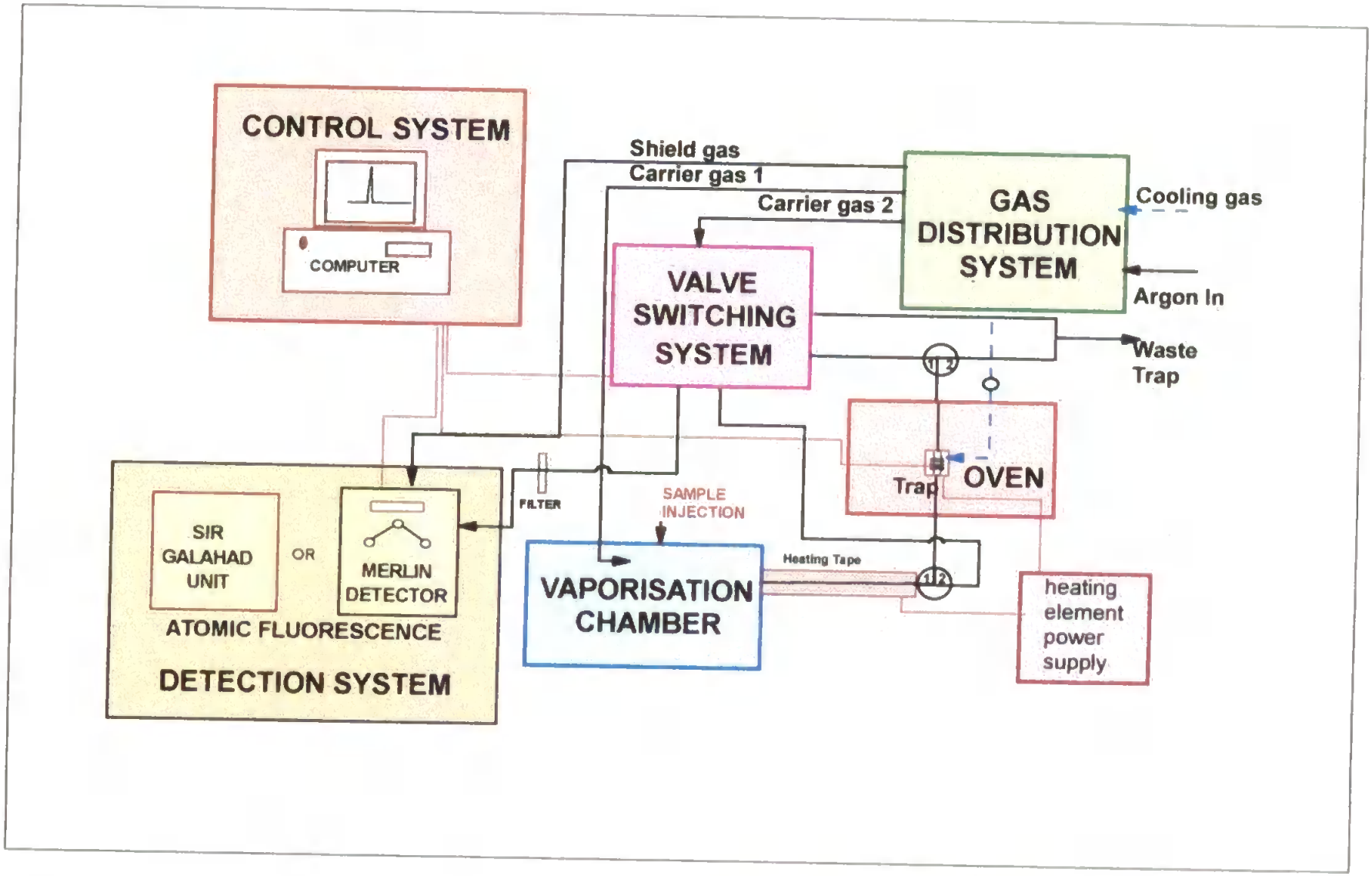


Figure 3.6 : Schematic diagram of modular system for the determination of mercury in gas condensate by vaporisation technique

3.3.3.1 Calibration procedure.

Calibrations were based against elemental mercury for all species. The Calibrations relies upon the knowledge that at a fixed temperature, the saturated vapour pressure of mercury is known and a fixed volume of vapour will contain a known quantity of mercury. This volume is injected and adsorbed onto the gold sand trap and then re-vaporised into the detector where the peak response is measured **(167)**. Once the values of temperature and volume are known, the absolute quantity of mercury adsorbed onto the trap can be calculated.

The mercury saturation concentration can be calculated using the formula as follows **(168)**:

$$C = \frac{3216522.61}{T} \times 10^{-(A + B/T)}$$

where:

C = Mercury Concentration in air (ng ml^{-1})

A = - 8.134459741

B = 3240.871534

T = Absolute temperature (K)

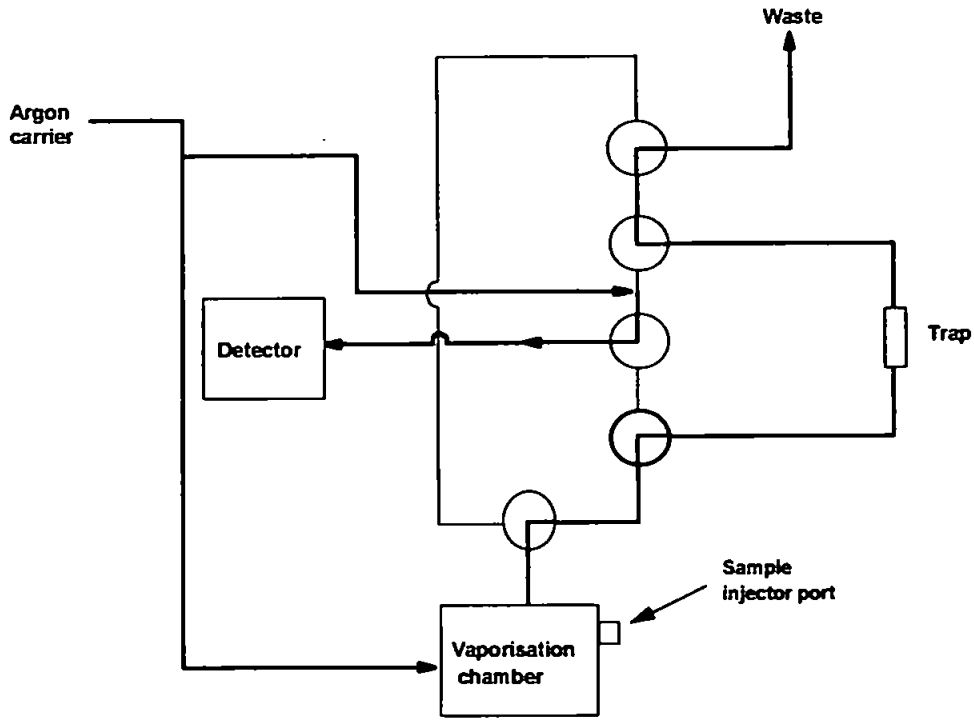
The use of elemental mercury to calibrate also served as another species which can be present in gas condensate.

A Summary of the general operating conditions used in all mercury determinations is given in Table 3.2.

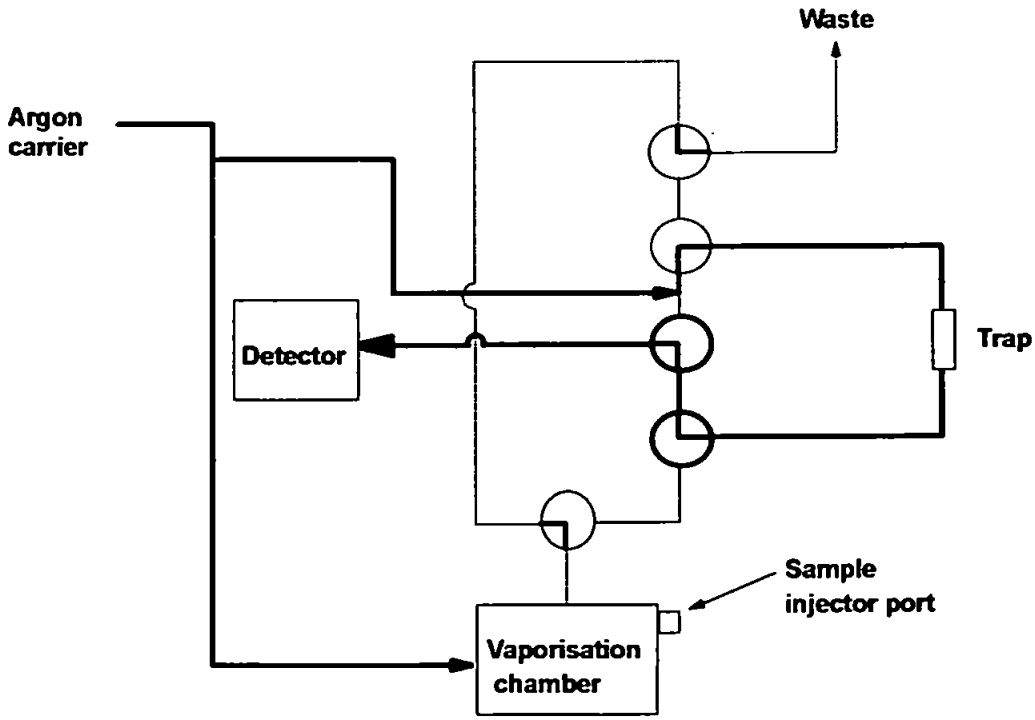
Conditions	Values
Vaporisation Chamber Temperature (° C)	400
Vaporisation Time (min.)	5 - 10 *
Argon carrier for Vaporisation (ml min $^{-1}$)	300 - 400
Argon flow rate for the detector (ml min $^{-1}$)	500
Detector Sheath gas flow rate (ml min $^{-1}$)	250
Gold Trap Flushing time (sec.)	30
Gold Trap Vaporisation time (sec.)	15
Gold Trap vaporisation temperature (° C)	900
Gold Trap Cooling period (min)	2

Note : * *Longer vaporisation times may be required if the samples are heavier than typical condensate*

Table 3.2: Summary of operating conditions



(A) Sampling Mode



(B) Measurement Mode

Figure 3.7 : Valve switching sequence between (A) sampling mode (pre-concentration) and (B) measurement mode

3.3.4 RESULTS AND DISCUSSION

3.3.4.1 Performance characteristics of the trap system

The stability of mercury adsorbed onto the gold coated silica trap was evaluated by carrying out calibrations at room temperature and at 200 °C. The results, shown in Figure 3.8 indicate that at 200 °C the mercury calibration is both stable and quantitative. It is also noted that an improvement in sensitivity is obtained over collection of species at room temperature.

The performance of the trap in holding the mercury species (bleed-off effects) at 200 °C was investigated. The sample (0.25 ml), containing 20 ng ml^{-1} of a mercury species was vaporised and swept through the trap by argon gas (350 ml min^{-1}) at different time settings from 5 minutes to 1 hour. The results, summarised in Figure 3.9, show that no significant bleeding occurred up to 30 minutes (96 % to 103 % recovery) and that the trap was efficient in holding the mercury species at 200 °C. Longer time periods (> 30 minutes) gave slightly increased recoveries due to contribution from the very low mercury content of argon carrier gas being trapped. It was observed that traps did not suffer from memory effects and that the life time of a trap was also improved because of the higher trapping temperatures employed (200 °C).

Calibration procedures using several species of mercury in hexane indicated that the same performance and accuracy obtained with reference to elemental mercury was achieved. The comparison shows that the trap is capable of trapping efficiently several species (DMM, DEM, DBM and DPM) vaporised through the trapping module at elevated temperature. Calibration using elemental mercury is recommended since it is simple and eliminated any chemical preparation. The comparison of all species is shown in Figure 3.10. The higher temperature of the vaporisation chamber (400 °C compared with 200 °C previously)

resulted in the higher boiling point species being vaporised efficiently and retained within time period set for trapping.

Examples of volatogram from the calibration comparison for 10 ng ml^{-1} DMM, DEM, DBM, and DBM spiked into hexane are as shown in Figure 3.11 together with a calibration for the single species DMM in toluene.

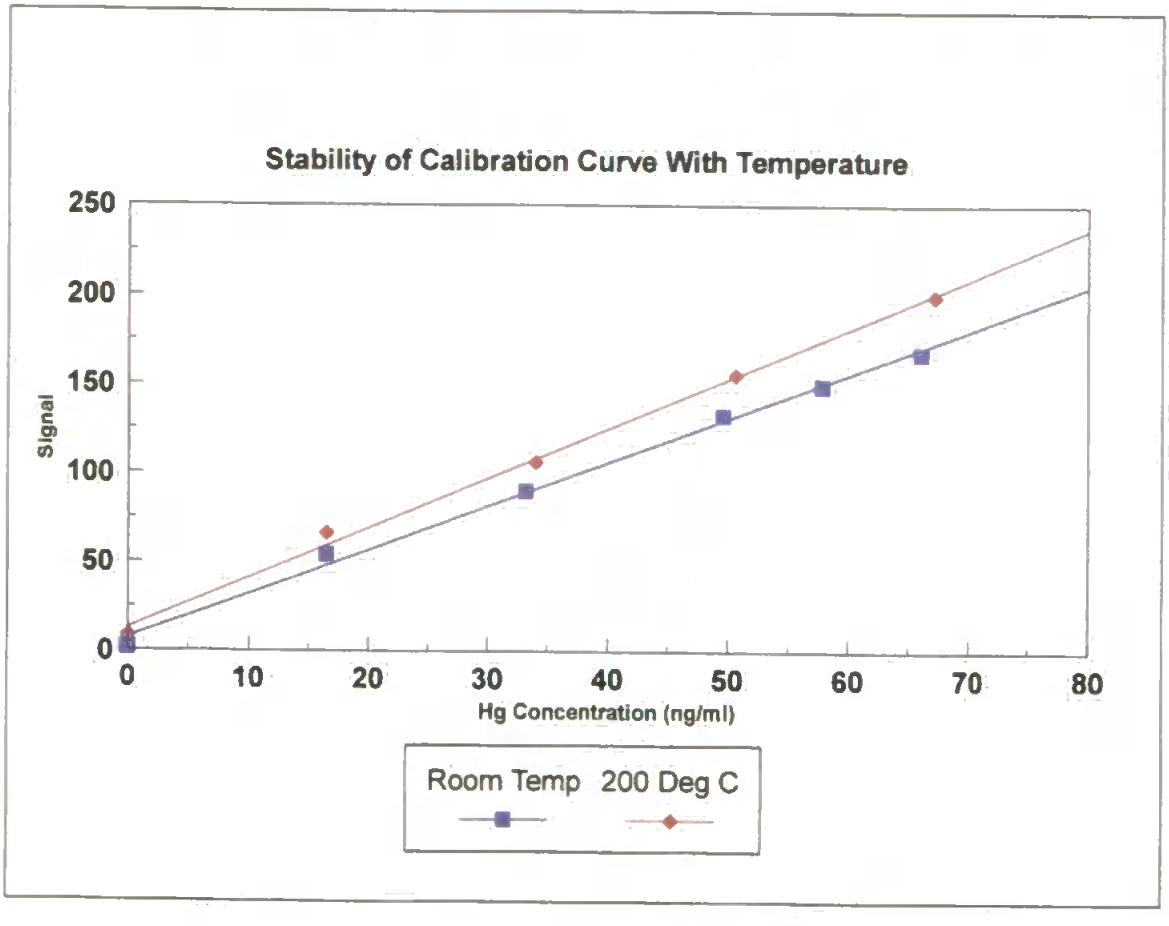


Figure 3.8: Calibration graphs for the gold coated silica traps at room temperature and at 200 °C

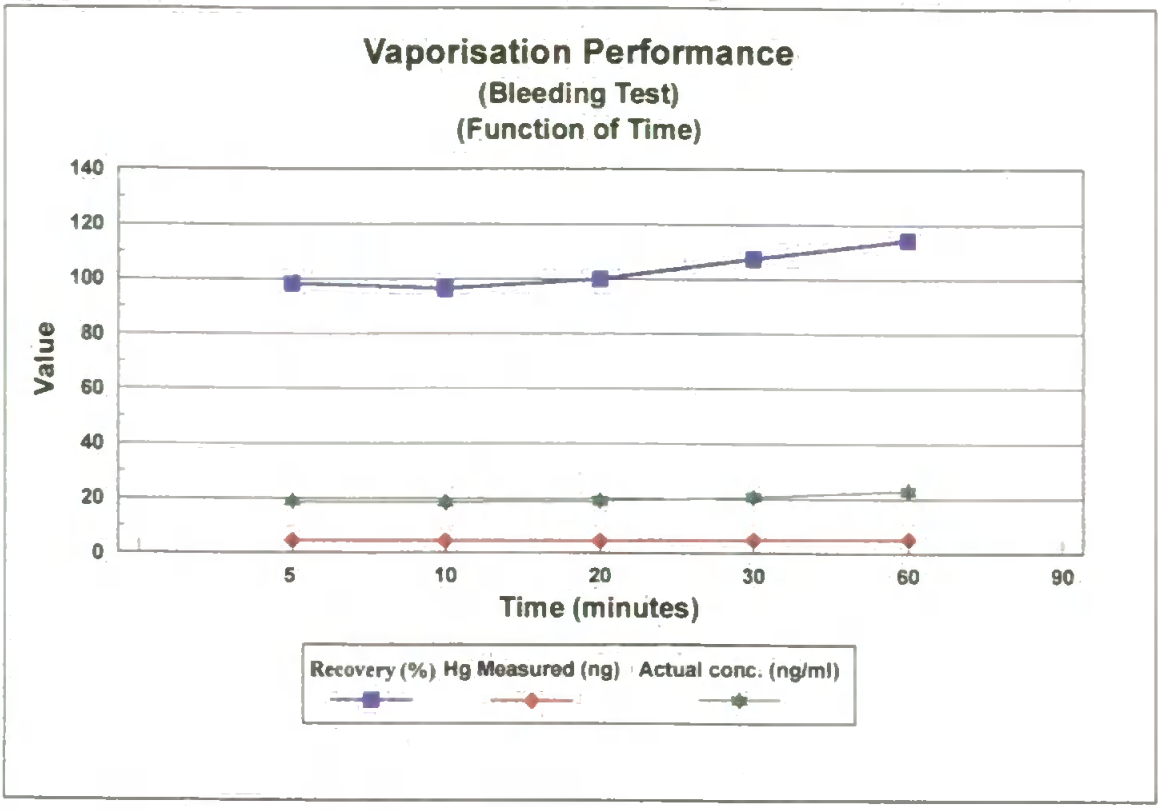


Figure 3.9 : Stability of the trap in holding mercury species at 200 °C

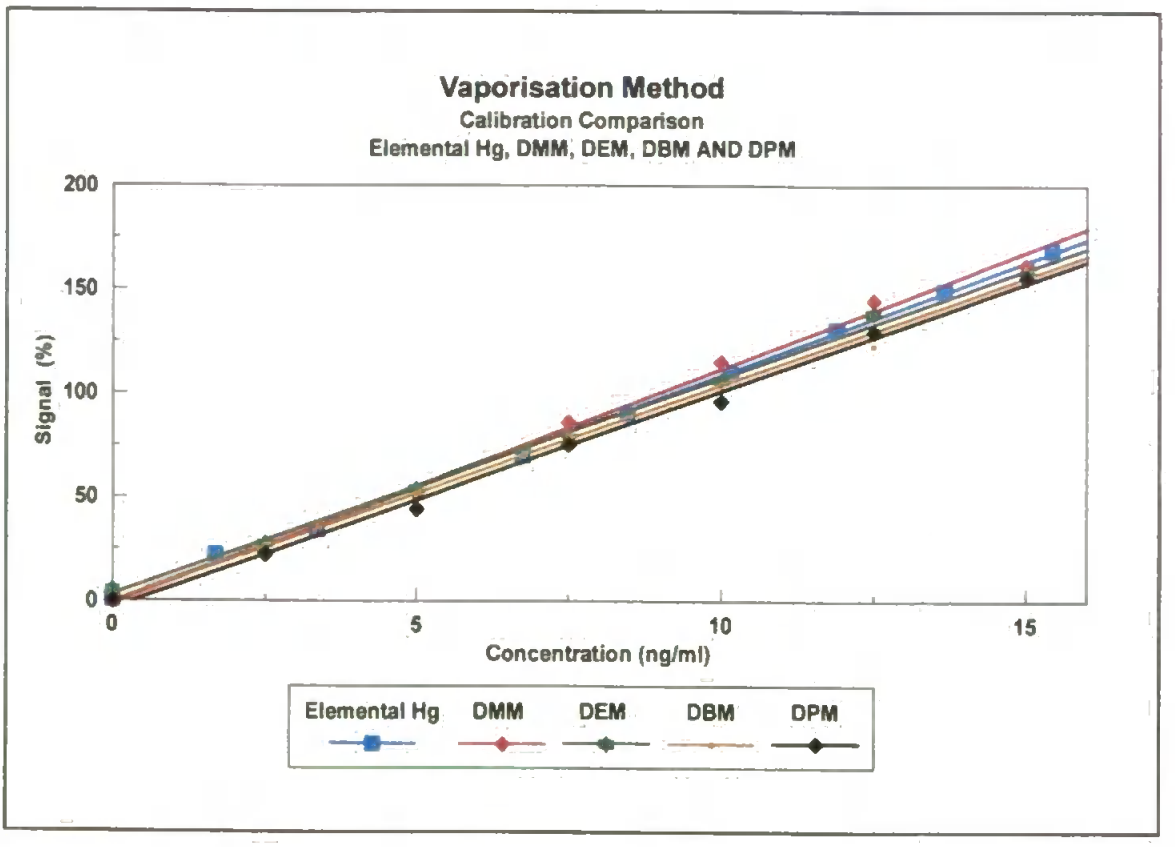


Figure 3.10 : Calibration comparison for several dialkyl mercury compounds and elemental mercury

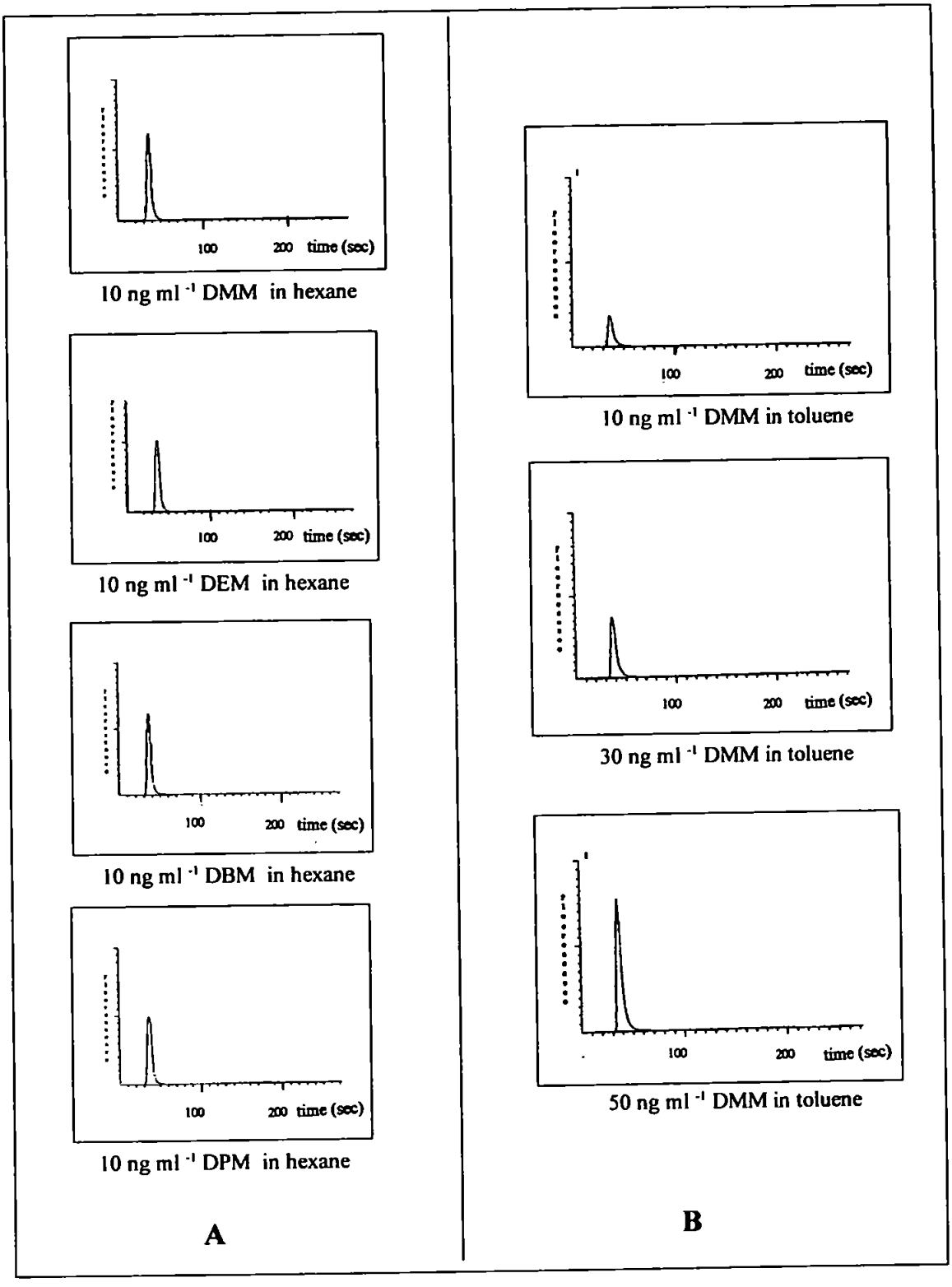


Figure 3.11 : A - Example of volatograms for 10 ng ml $^{-1}$ DMM, DEM, DBM and DPM and
B - Volatograms of DMM (10, 30 and 50 ng ml $^{-1}$)

Note : X axis = Time (seconds) and Y axis = Fluorescence signal

3.3.4.2 Effect of argon sweep gas flow rate

The argon flow rate that sweeps the vaporised sample to the gold-coated silica trap was varied from 100 ml min $^{-1}$ to 500 ml min $^{-1}$. For each flow rate set-up, 0.25 ml of n-hexane spiked with 10 ng ml $^{-1}$ DEM was injected. The fluorescence signal from the mercury measurement was monitored for each flow rate. The results indicated that, there was little difference in the sensitivity of the signal for the flow rates up to 400 ml min^{-1} of argon carrier gas. However the sensitivity of the signal decreased when the flow rate increase to 500 ml min $^{-1}$ and above (less contact time or resident time). Correlation between argon sweep gas flow rate and signal is shown in Figure 3.12.

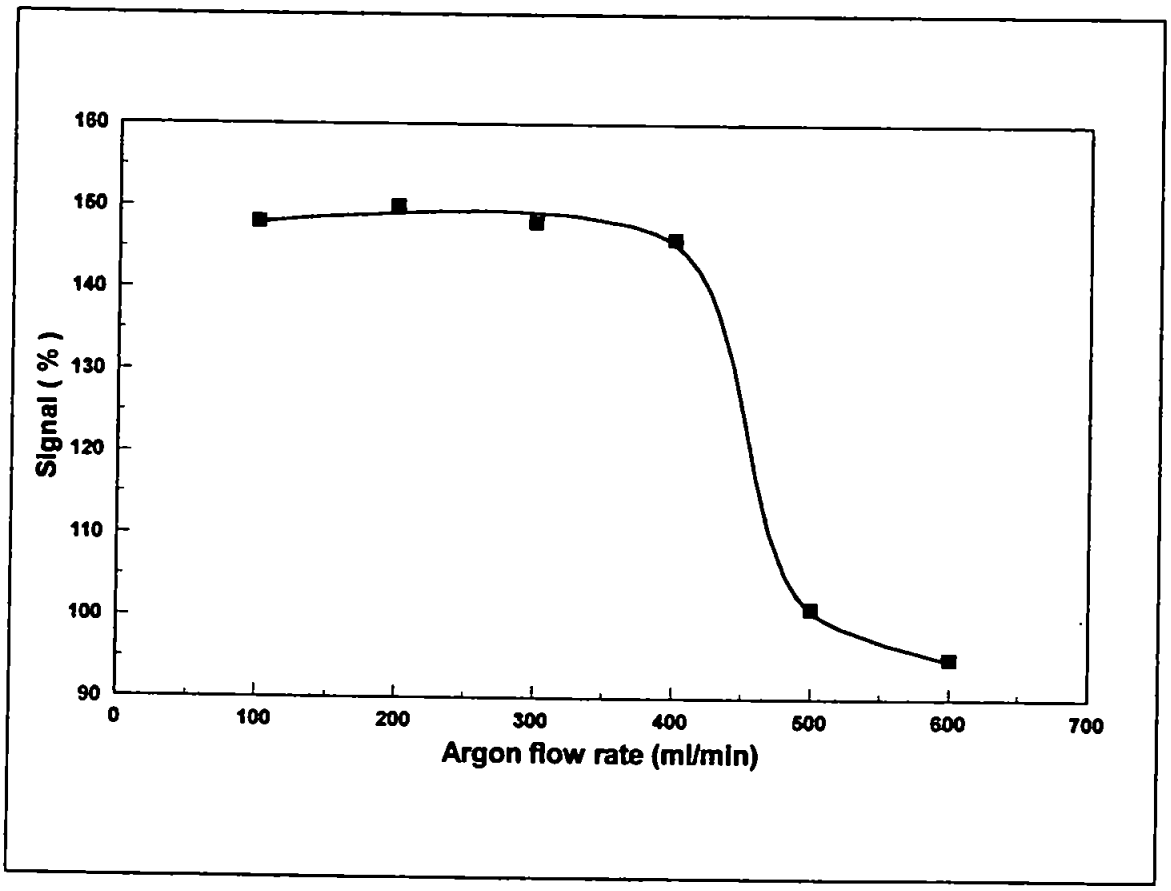


Figure 3.12 : Effects of argon sweep gas flow rate upon signal response

3.3.4.3 Effect of volume of sample injected upon recovery

The total mercury content of a toluene sample (control) was determined. The sample was vaporised at 400 °C and the vapour trapped at 200 °C prior to desorption for mercury determination by the AF detector. The analyses were conducted by injecting different sample volumes (0.1 to 1.0 ml) via the septum to the vaporisation chamber. The mercury content in the toluene was found to be 2.0 $\pm$ 0.3 ng ml^{-1}, 2.4 $\pm$ 0.2 ng ml^{-1} and 3.4 $\pm$ 0.4 ng ml^{-1} for the volumes 0.1 ml, 0.25 ml and 0.5 ml respectively (not gas blank corrected). The vaporisation time was increased slightly when the volume injected increased. For the above volumes, the times correspond to 7, 9 and 11 minutes respectively. When DMM and DPM (50 ng ml^{-1} as Hg) were spiked into toluene and the different volumes injected, the recovery values showed a 20 % reduction for an increase in volume of sample from 0.25 to 0.5 ml. These recovery value continued to decrease slowly as the volume was increased to 1.0 ml. The detailed results are shown in Table 3.3. All values are corrected for toluene and gas blanks.

A volume of 0.25 ml was chosen for three reasons:

(i) this volume allows representative sampling and showed improved precision, (ii) 85 to 90 % recovery for species was obtained and (iii) to introduce the maximum of sample injected to the system without saturating the gold-coated silica trap with matrix during the adsorption process (to reduce competitive exclusion effects).

Sample	Hg species spiked (ng ml^{-1})	Volume of Sample (ml)	Concentration measured (ng ml^{-1}) Mean ± s.d.	Recovery (%) Mean ± s.d.
Toluene	-	0.1	2.0 ± 0.3	-
Toluene		0.25	2.4 ± 0.2	-
Toluene		0.5	3.4 ± 0.4	-
Toluene		1	3.5 ± 0.3	-
Tol 50 DMM	DMM 50	0.1	44.9 ± 2.2	86 ± 5
Tol 50 DMM		0.25	43.3 ± 0.4	82 ± 1
Tol 50 DMM		0.5	36.5 ± 0.5	66 ± 1
Tol 50 DMM		1	29.6 ± 0.2	54 + 0
Tol 50 DPM	DPM 50	0.1	66.3 ± 1.9	129 ± 4
Tol 50 DPM		0.25	45.9 ± 0.8	87 ± 2
Tol 50 DPM		0.5	34.5 ± 2.3	62 ± 5
Tol 50 DPM		1	27.0 ± 2.5	49 ± 5

Table 3.3 : Recoveries of DMM and DPM added into toluene - Effect of volume injected **(single size trap)**

3.3.4.4 Double size trap

In order to reduce competitive effects within the trapping module by the matrix and mercury species while increasing the capability to improve efficiency of collection in absolute terms, the effect of increasing the quantity of trapping material upon recoveries was investigated. To this end a double sized trap (60 mg trapping material) was chosen.

The effect of trap size upon recoveries was much reduced when a double size gold-coated silica trap was employed. Up to 1.0 ml of sample gave the same recovery for the species as that of a 0.25 ml injection. This recovery data is shown graphically in Figure 3.13.

It is important to note that the increase in sample volume requires a longer vaporisation period, hence a longer trapping time is needed. A correction for the mercury present in the argon carrier must therefore be made alongside any solvent blank contribution.

A comparison of calibrations using elemental mercury as species for single size trap and double size trap indicated that the performance was almost identical at very low concentration but the double size trap was more efficient when the concentration increased. The calibration comparison of these two traps are as shown in Figure 3.14.

Sample	**Hg species spiked (ng ml $^{-1}$)**	**Volume of Sample (ml)**	**Concentration measured (ng ml $^{-1}$) Mean ± s.d.**	**Recovery (%) Mean ± s.d.**
Toluene	-	0.25	0.38 ± 0.01	-
Toluene		0.5	0.65 ± 0.05	-
Toluene		1	1.07 ± 0.03	-
Tol 50 DMM	DMM 50	0.25	45.5 ± 1.3	90 ± 2
Tol 50 DMM		0.5	44.9 ± 0.7	89 ± 1
Tol 50 DMM		1	44.8 ± 0.5	88 ± 1
Tol 50 DPM	DPM 50	0.25	42.8 ± 2.5	85 ± 5
Tol 50 DPM		0.5	43.4 ± 0.9	86 ± 2
Tol 50 DPM		1	45.1 ± 1.0	88 ± 2

Table 3.4 : Recoveries of DMM and DPM added into toluene - Effect of volume injected **(Double size trap)**

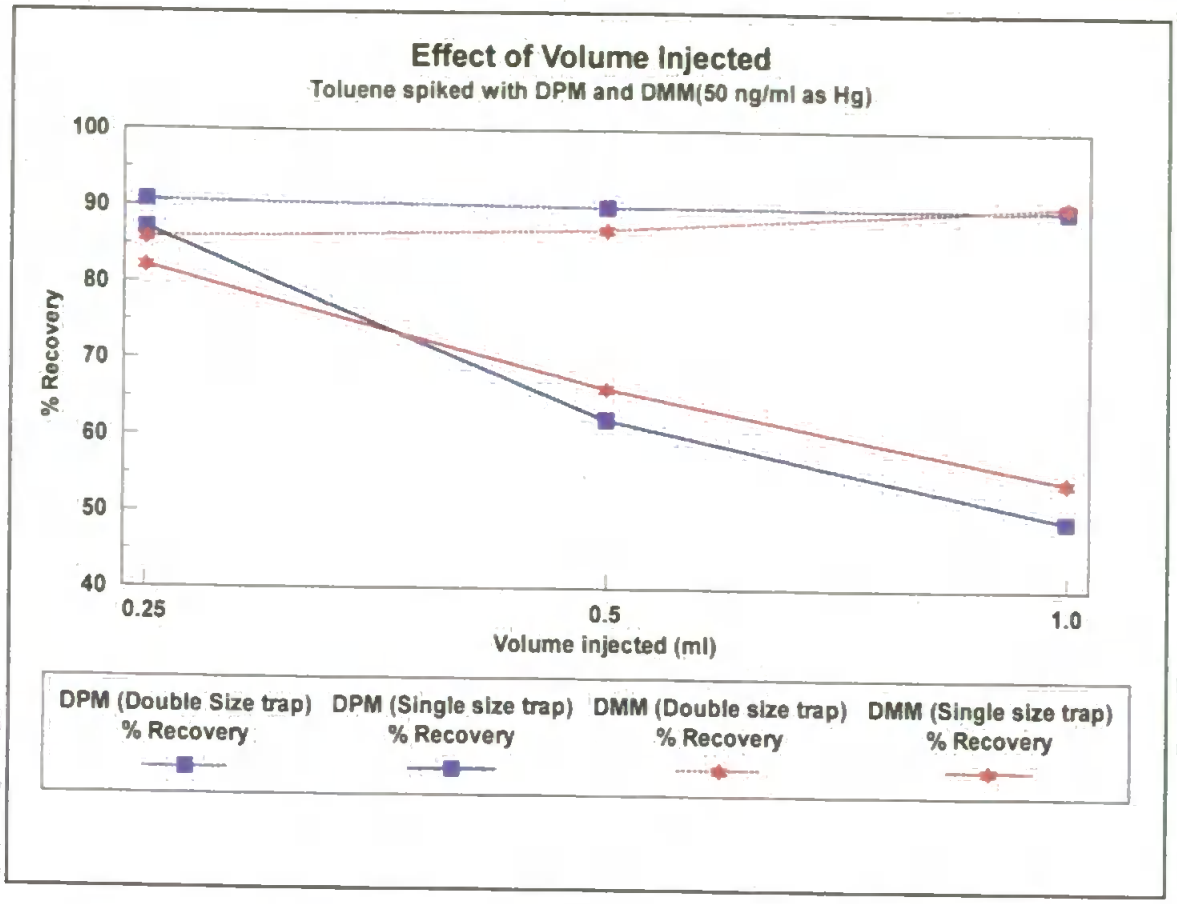


Figure 3.13 : Summary of recovery performance of DMM and DPM added in toluene - Effect of volume injected between single and double size traps

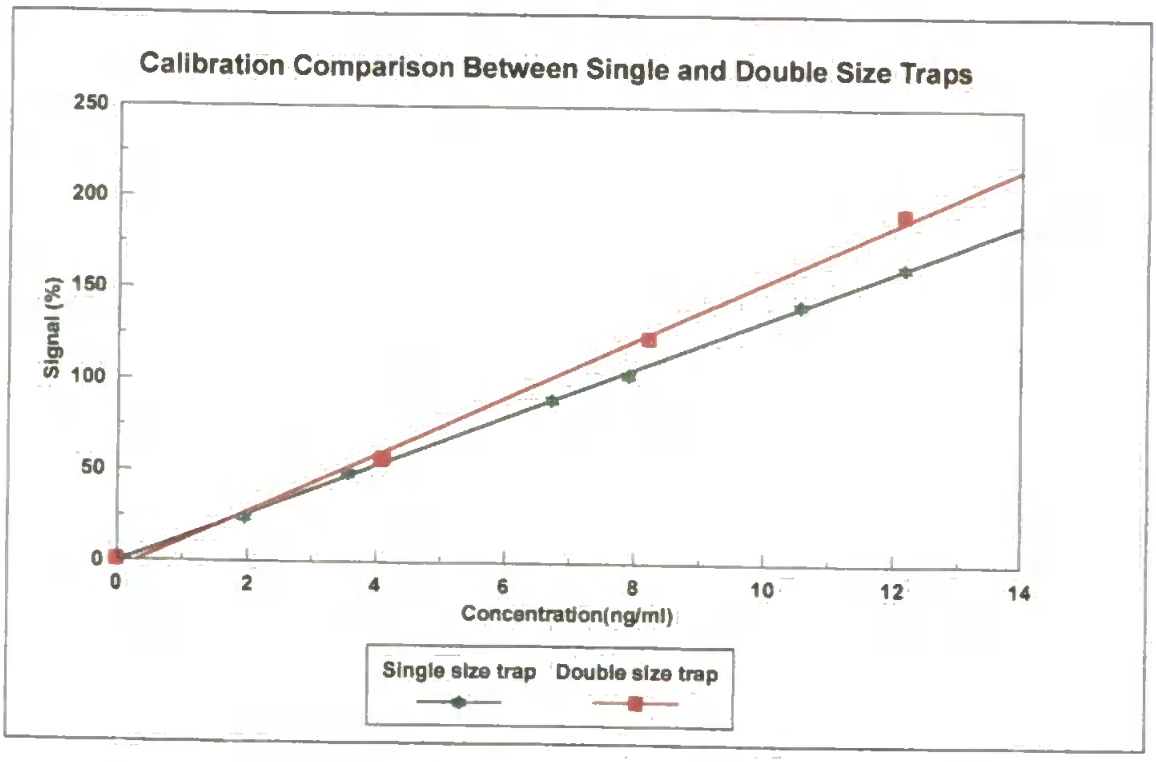


Figure 3.14 : Calibration comparison between single and double size traps

3.3.4.5 Recoveries for mercury species added into 'real' condensate samples

The recovery of mercury species spiked into 'real' gas condensate samples was evaluated. Two commercial gas condensate samples labelled as BSTB 1/2 and BSTB 3/4, light gas condensates from different sites were used as a base condensate. The vaporisation temperature used was 400 °C and was sufficient to vaporise the samples completely in 10 minutes.

Using the American Standard Testing Material (ASTM) method D86, distillation of hydrocarbon mixtures, the volatility properties were investigated. The distillation curves are shown in Figure 3.15. This shows that the condensate has an Initial Boiling Point (IBP) of about 30 °C and a Final Boiling Point (FBP) of almost 300 °C. The two condensates composition, determined using gas chromatography (high performance cross linked dimethyl siloxane fused silica capillary column, PONA analysis-ASTM D 5134) was found to consist of about 80 isomers/components for the sample BSTB 1/2 and 100 components for sample BSTB 3/4; with the following ratio; Paraffins - 58 % wt (C_3 to C_{15}), Naphthanes - 23 % wt (C_5 to C_9) and Aromatics- 19 % wt (C_6 to C_{12}). The chromatogram for BSTB 1/2, as an example, is shown in Figure 3.16. The calculation using HYSIS engineering simulation software estimates that the dew point for a condensate with the above compositions at pressure of 101.325 kPa (1 atmosphere), and a temperature of 82.49 °C is sufficient to maintain the condensate matrix in the vapour phase (Figure 3.17). The choice of a trap temperature of 200 °C ensures an absence of condensate matrix in the liquid phase, a reduction in blinding of the gold-coated silica active sites by the matrix and a subsequent increase in efficiency of mercury retention.

Seven species of mercury i.e. DMM, DEM, MMC, EMC, DPM, PMC and MC were spiked individually at different concentrations i.e. 10, 30 and 50 ng ml^{-1} (as Hg), into real

gas condensates (BSTB). In each experiment, the total mercury content of a condensate sample was determined and then blank corrected to give the recovery value.

A summary of the results is shown in Table 3.5. Considering the nature of the condensates, which are a very complex mixture of volatile hydrocarbons, full and near to full recoveries were obtained for five out of the seven species (average values >95 %). One of the two remaining species gave a reduced but reproduce value, DPM, of 74 to 77 % while the other species, PMC, ranged between 77 and 85 %. For each given species, the linearity of the recovery data, in the concentration range covered, was better than $r^2 = 0.99$. The total mercury recoveries for mixtures of the seven species added in equal quantities i.e. all 10, or 30, or 50 ng ml^{-1}, are also shown in Table 3.5 and Figure 3.18. These percentage recoveries were in the range 88 to 97 %.

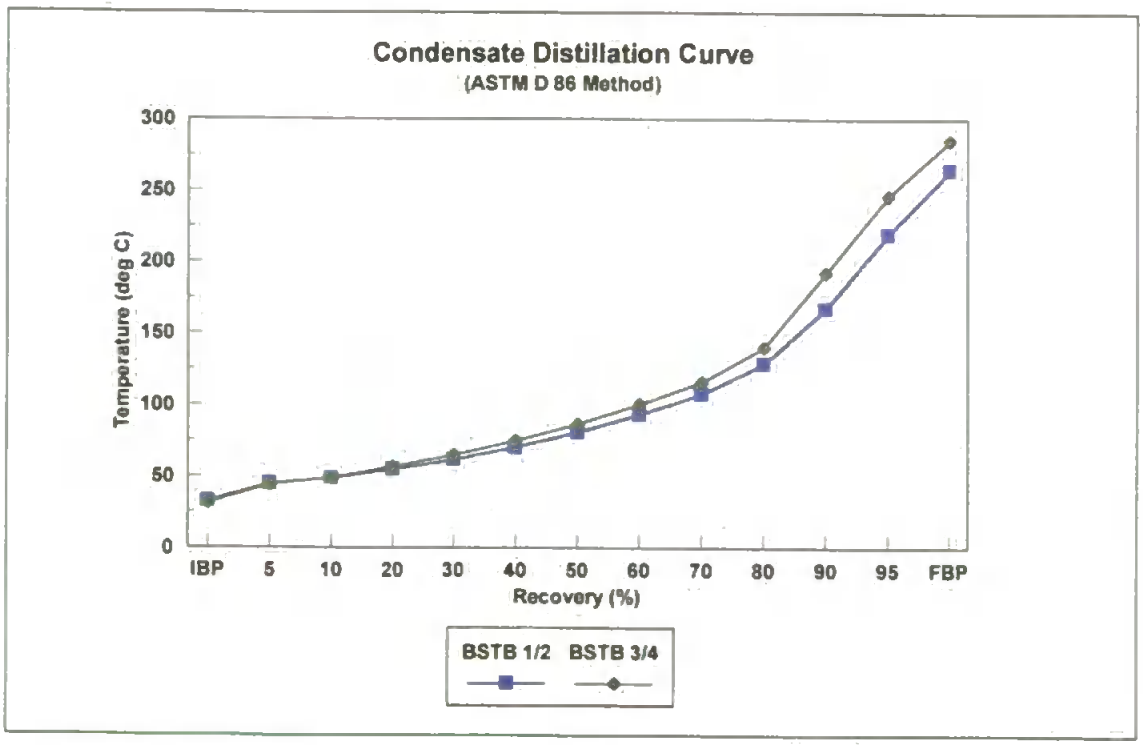
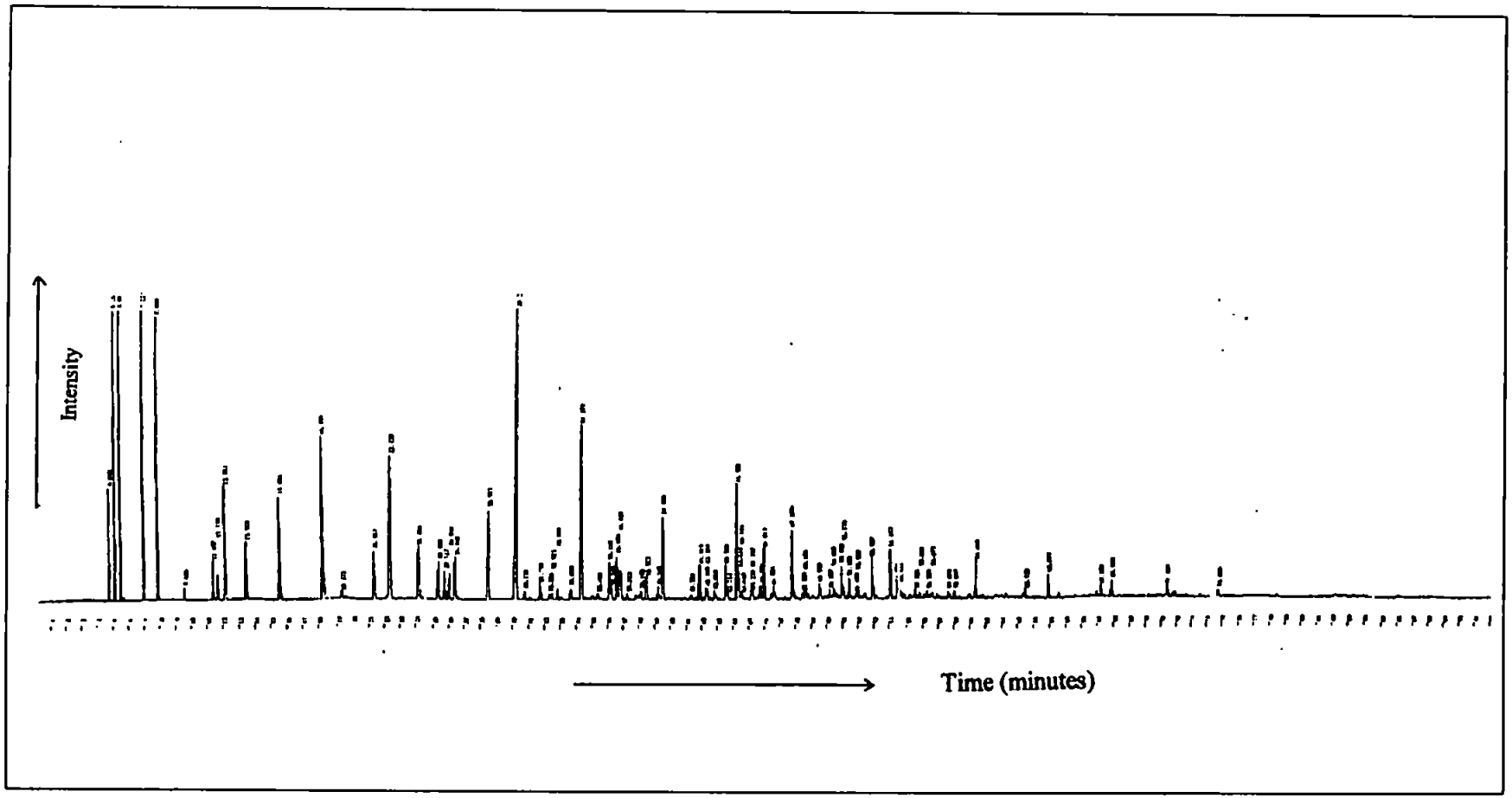


Figure 3.15 : Distillation curves (ASTM D 86) of BSTB condensates


Intensity
Time (minutes)

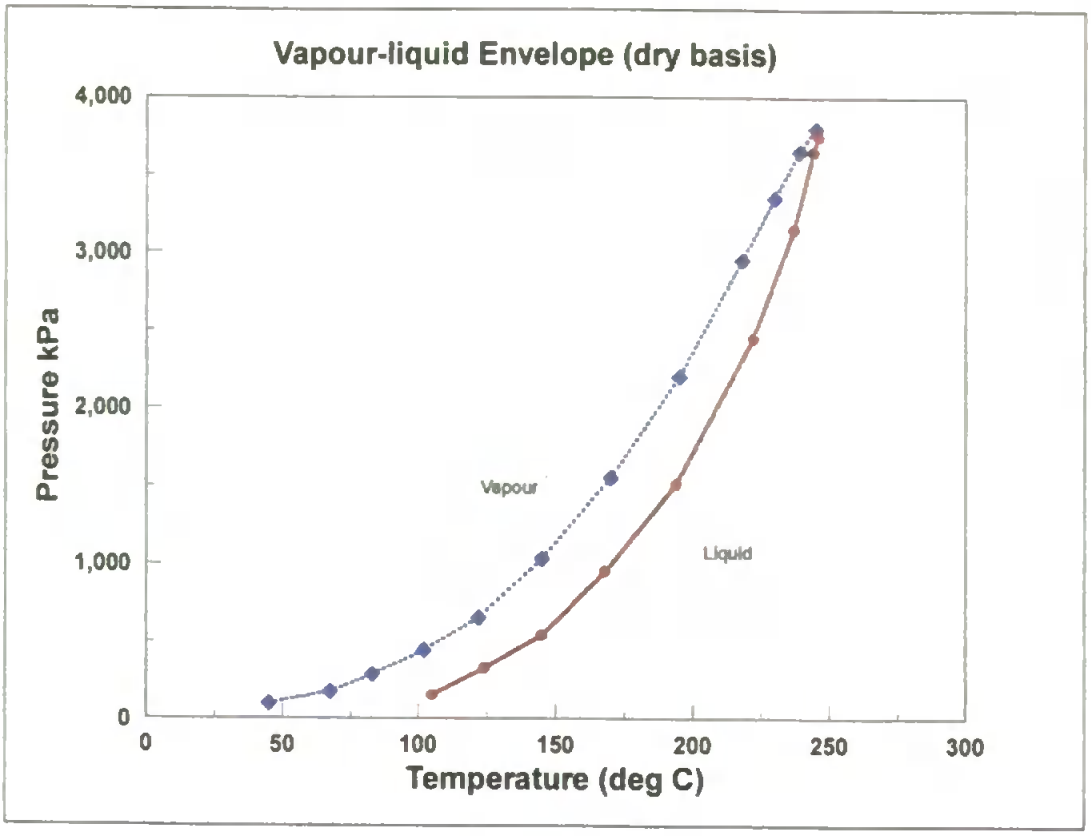


Figure 3.17 : Vapour- liquid phase envelope for BSTB condensate.

No	Mercury species added	% Recovery ± S.D.		
		Concentration		
		10 ng ml $^{-1}$	30 ng ml $^{-1}$	50 ng ml $^{-1}$
1	DMM	111 ± 13	119 ± 14	105 ± 9
2	DEM	113 ± 8	92 ± 6	99 ± 5
3	DPM	74 ± 12	74 ± 2	77 ± 5
4	MMC	102 ± 4	92 ± 5	92 ± 8
5	EMC	97 ± 19	99 ± 3	98 ± 5
6	PMC	77 ± 13	78 ± 5	85 ± 6
7	MC	102 ± 13	98 ± 15	94 ± 6
8	Equal mixture	90 ± 5 *	88 ± 2 *	97 ± 1 *
* *Total mercury where concentration stated is for each component*				

Table 3.5 : Summary of recovery performance

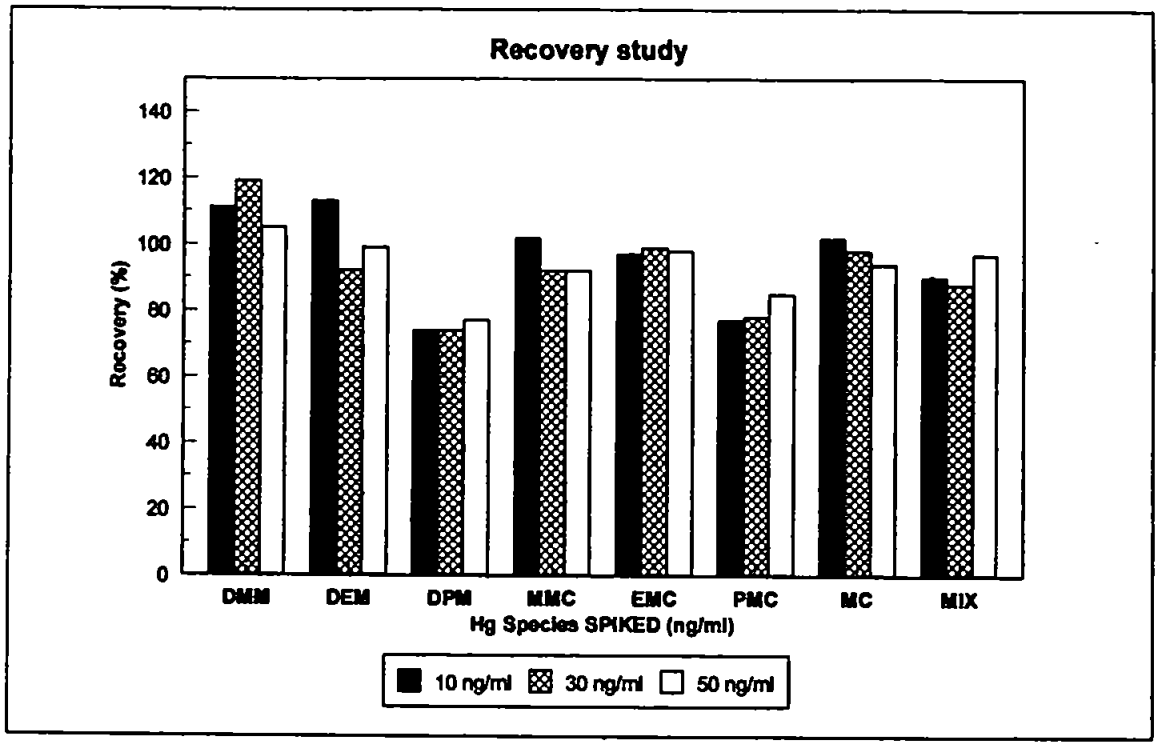


Figure 3.18: Summary of Recoveries study

3.3.4.6 Precision of the experimental technique

To determine the precision of the experimental set-up, the total mercury content was measured 10 times in (i) toluene, (ii) a commercial condensate (TC123) and (iii) a condensate (TC123) with three different type of mercury compound, each added at the 10ng ml^{-1} Hg level. The three types of mercury compound were based upon organohalide, di-alkyl and inorganic species. These were represented by EMC, DEM and MC.

The mercury content for the toluene (0.25 ml injected) was 6.4 $\pm$ 0.2 ng ml^{-1}. For the condensate TC123 alone, the mercury value was 7.45 $\pm$ 0.34 ng ml^{-1}. The relative standard deviation (RSD) for the analyses were 3.7 % and 4.8 % respectively. The consistency of the analyses i.e. toluene and condensate alone are shown in Figure 3.19.

For the condensate TC123 spiked with 10 ng ml $^{-1}$ (as Hg) of the three species, the total mercury content was determined as 17.55 $\pm$ 0.35 ng ml $^{-1}$ (EMC), 17.28 $\pm$ 0.62 ng ml $^{-1}$ (DEM) and 18.04 $\pm$ 0.86 ng ml $^{-1}$ (MC) showing the RSD to be between 2 and 5 %. It is of note that the recovery values for these spiking experiments with condensate were 105, 101 and 98 % respectively (RSD between 4 and 7 %). A summary of the recoveries for the three types of mercury species added to TC 123 condensate is as shown in Figure 3.20.

3.3.4.7 Conostan mercury standard for oil analyses

For the determination of mercury in higher boiling point oils and similar petroleum products, a suitable mercury standard is required which can be used for the standard addition technique. Conostan mercury standard is employed in oil analysis and is a mercury dialkyldithiocarbamate compound (Hg-S bonded) dissolved in white base (paraffin) oil. This species was spiked 10 times into condensate at the 10 ng ml $^{-1}$ level. These results are shown in Figure 3.21 and demonstrate that the recovery was 88 $\pm$ 5 %.

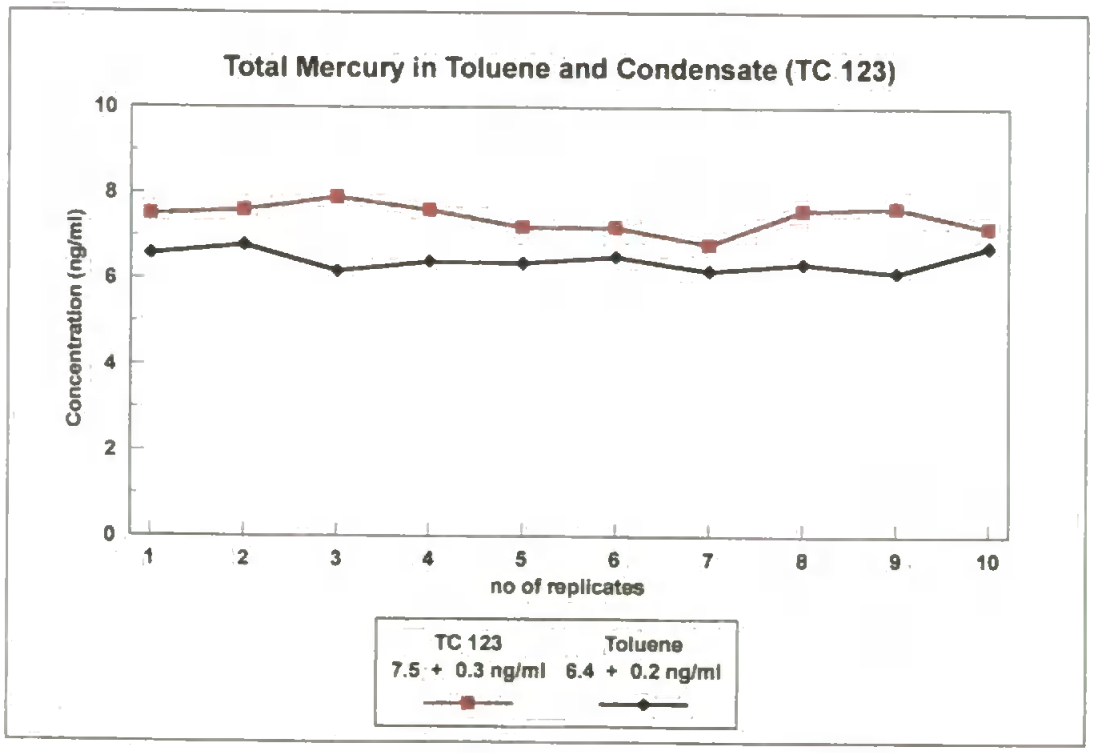


Figure 3.19 : Total mercury content in Toluene and TC123 Condensate

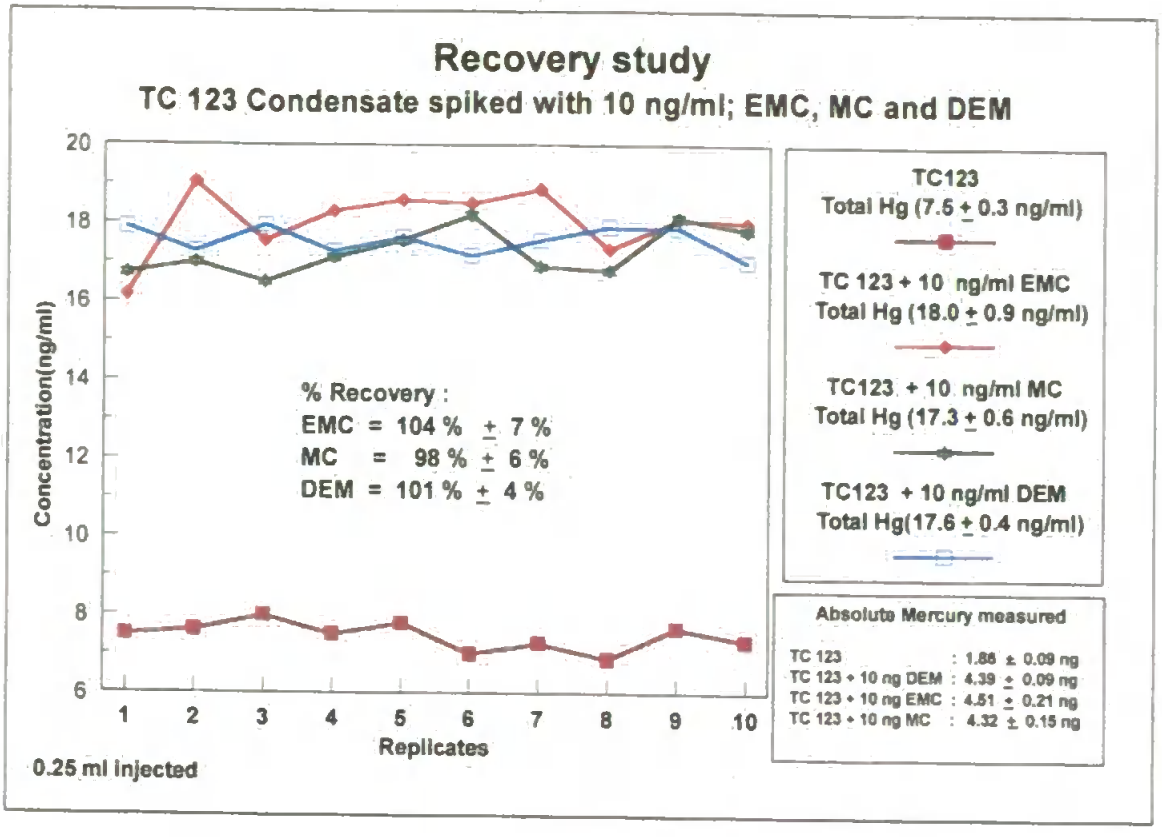


Figure 3.20 : Recovery of DEM, MC and EMC in Condensate

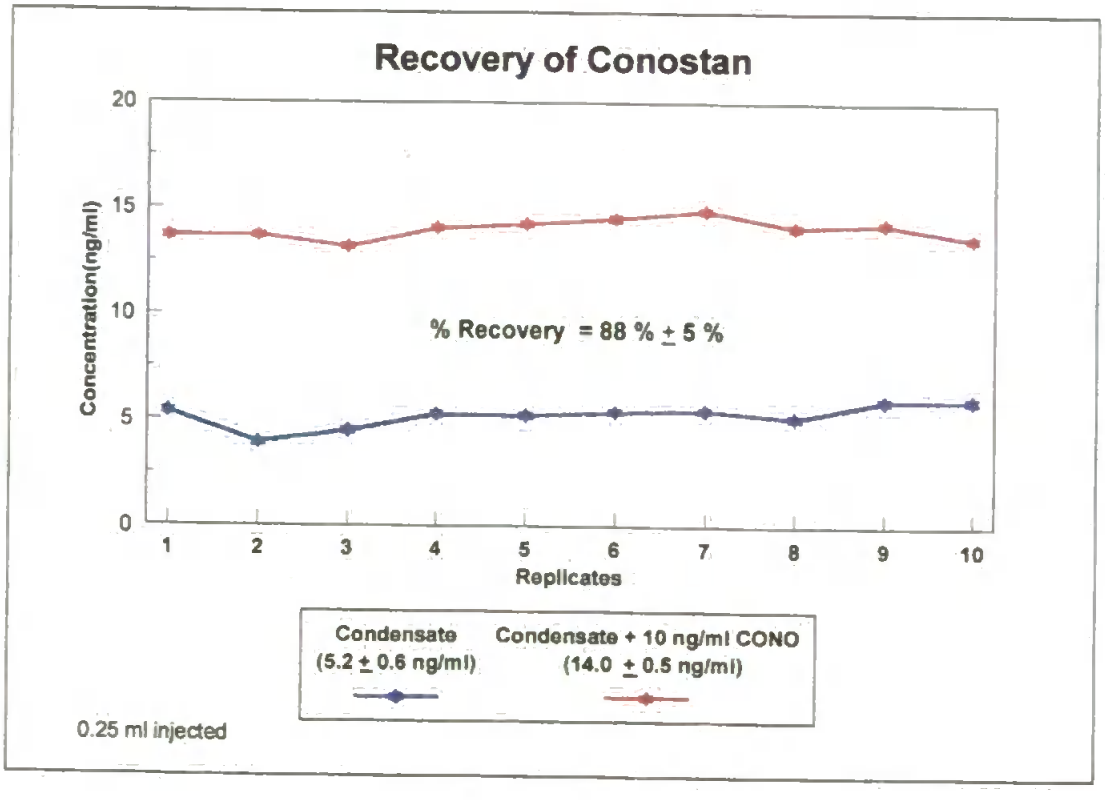


Figure 3.21 : Recovery of Conostan in condensate

3.3.4.8 Detection limits

The detection limits that can be obtained from the current method depend to some extent upon the complexity of the condensate sample i.e. the volatility of both the condensate and the mercury species in the sample, together with the effect of any sample matrix interacting with the trap. From recovery data given in Figure 3.20, the absolute detection limits for the method (based on three times the standard deviation) were 180 pg for toluene and 270 pg for TC123 condensate. For three different mercury species added to the TC 123 condensate, the absolute detection limits were 270 pg for DEM, 450 pg for MC and 630 pg for EMC. When based on the system alone, without sample introduction but monitoring the carrier gas (argon) the absolute limit of detection is reduced to 11 pg (n = 6).

3.3.4.9 Total mercury content in commercial condensate

Five types of natural gas condensate, obtained from several sources were analysed for total mercury. The results indicated that the concentration of the mercury is independent of 'location' and 'type' of condensate. The total mercury concentrations of the condensate samples BSTB 1/2, BSTB 3/4, TC 123, TC 604 and TC 102 are shown in Table 3.6. The relative standard deviation for the analyses are in the range 4 to 7 % for a 0.25 ml manual sample injection. The consistency of the determinations are shown in Figure 3.22.

Condensate	Mean ± s.d. (ng ml $^{-1}$)
BSTB 1/2	22.3 ± 1.4 ; RSD = 6 % ; n = 10
BSTB 3/4	49.7 ± 2.6 ; RSD = 5 % ; n = 10
TC 123	7.5 ± 0.3 ; RSD = 4% ; n = 10
TC 604	12.8 ± 0.9 ; RSD = 7 % ; n = 6
TC 102	43.3 ± 1.7 ; RSD = 4 % ; n = 7

Table 3.6 : Total mercury content in commercial condensates

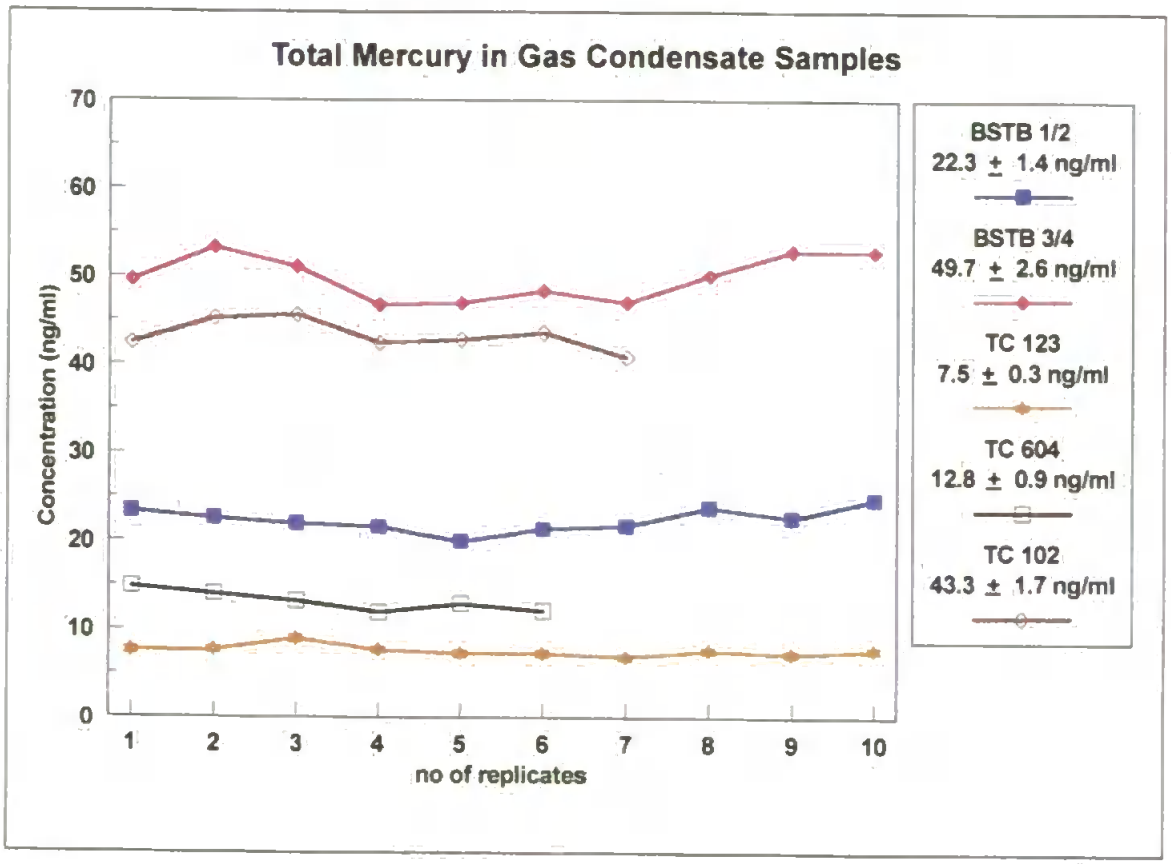


Figure 3.22 : Total mercury content in commercial condensates

3.4 THE DETERMINATION OF TOTAL MERCURY IN REAL CONDENSATE AND HYDROCARBON SAMPLES BY THE VAPORISATION TECHNIQUE

3.4.1 TOTAL MERCURY IN CONDENSATE SAMPLES

A total of four condensate samples were received from a United Kingdom multinational company. Samples 1 and 2 were observed to be typical in appearance to a commercial condensate, while samples 3 and 4 were observed to be quite heavy with the smell of *kerosene*. The density for samples 1 and 2 was of the order 0.70 g ml^{-1} while samples 3 and 4 were around 0.77 g ml^{-1}.

For samples 1 and 2, 0.5 ml of sample (no dilution) were used for the preliminary determination of total mercury. A 1.0 ml injection of sample 1 was also performed for comparison of the precision of the analysis. The mercury content of sample 1 was 3.1 $\pm$ 0.1 ng ml^{-1} (RSD = 4.5 %, n = 7) and for sample 2 it was 0.6 $\pm$ 0.1 ng ml^{-1}. For samples 3 and 4, the mercury contents were 27.5 $\pm$ 1.5 and 29.0 $\pm$ 2.4 ng ml^{-1} respectively. For sample 3, a dilution of one to one with a very low mercury-containing gasoline was made. For sample 4 the dilution performed was 1 to 2 with gasoline. The detailed results are shown in Table 3.7

For samples 3 and 4, 0.25 ml and 0.5 ml direct injection were used for the analysis. However, for these samples, a delay in the release of mercury was observed (Figures 3.23-3.25). The volatograms consist of two peaks; one sharp and normal of around 8 to10 seconds in width followed by one broad and relatively flat, around 50 to 90 seconds in width. This effect was previously observed, to a marked degree, in heavy fuel oil samples

and is often associated with samples with a higher range of boiling points and viscosities (see section 3.5.3).

Sample	Sample labelled	Volume injected (ml)	Total mercury concentration mean ± s.d. (ng ml $^{-1}$)	Replicates
Sample 1	RT97/131/1	1	2.92 ± 0.11	n = 6
		0.5	3.05 ± 0.14	n = 7
Sample 2	RT97/131/2	0.5	0.64 ± 0.10	n = 6
Sample 3	RT97/131/3	0.25 Dilution (1:1)	27.52 ± 1.51	n = 6
		0.5 Dilution (1:1)	26.51 ± 0.93	n = 6
Sample 4	RT97/131/4	0.25 Dilution (2 :1)	29.04 ± 2.4	n = 6

Table 3.7 : Total mercury content for condensate samples 1 to 4

To eliminate the multipeak problem a dilution of the sample with a much lighter fraction of condensate with very low and known mercury content was performed. For samples 3 and 4, a 1 to 1 mix with light gasoline (Hg < 50 pg ml $^{-1}$) was used to lower the boiling point and viscosity of the sample (Figures 3.26-3.28). However, for sample 4, a 1 : 2 mixture with the a 'light' gasoline was required to produce the volatogram shown in Figure 3.29 which displayed the improved baseline.

One possible reason for this effect is a result of the delayed mercury release and retarded flow caused by the presence of a higher portion of the high boiling point fraction which may condense on/interact with the trap even at 200 °C. An alternative cause might be attributed to delayed scattering effects from minor carbonisation products formed from condensate remaining on the trap during the high temperature (900 °C) mercury release step which are swept to the detector.

It is important to note that dilution of the matrix effect to obtain the correct total mercury value also results in a degradation of the limit of detection/precision for the method.

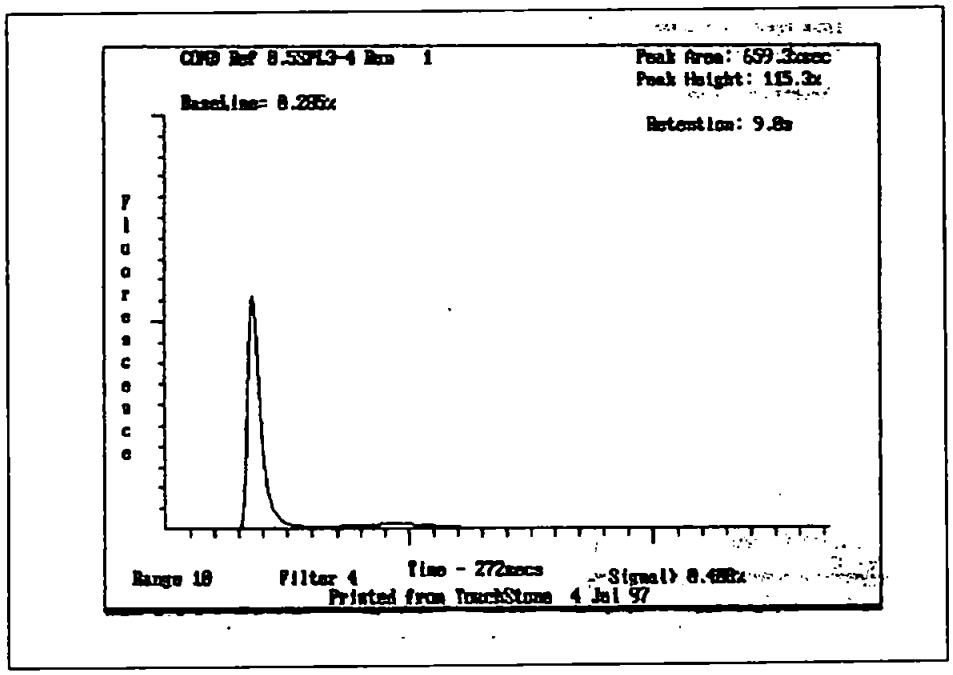


Figure 3.23: Example of volatogram for sample 3 (0.5 ml injected)

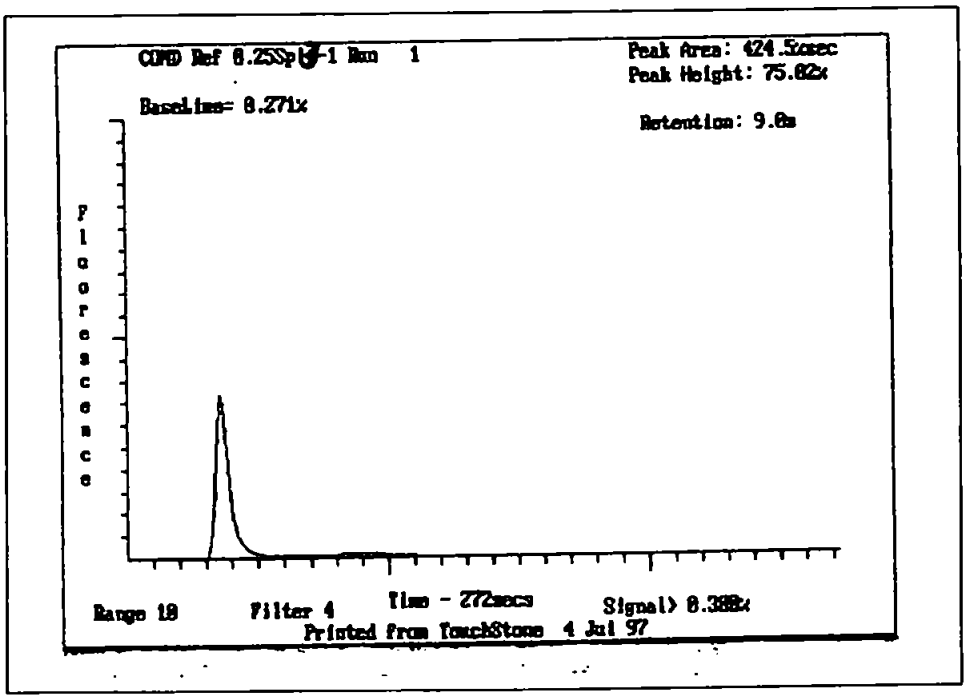


Figure 3.24: Example of volatogram for sample 3 (0.25 ml injected)

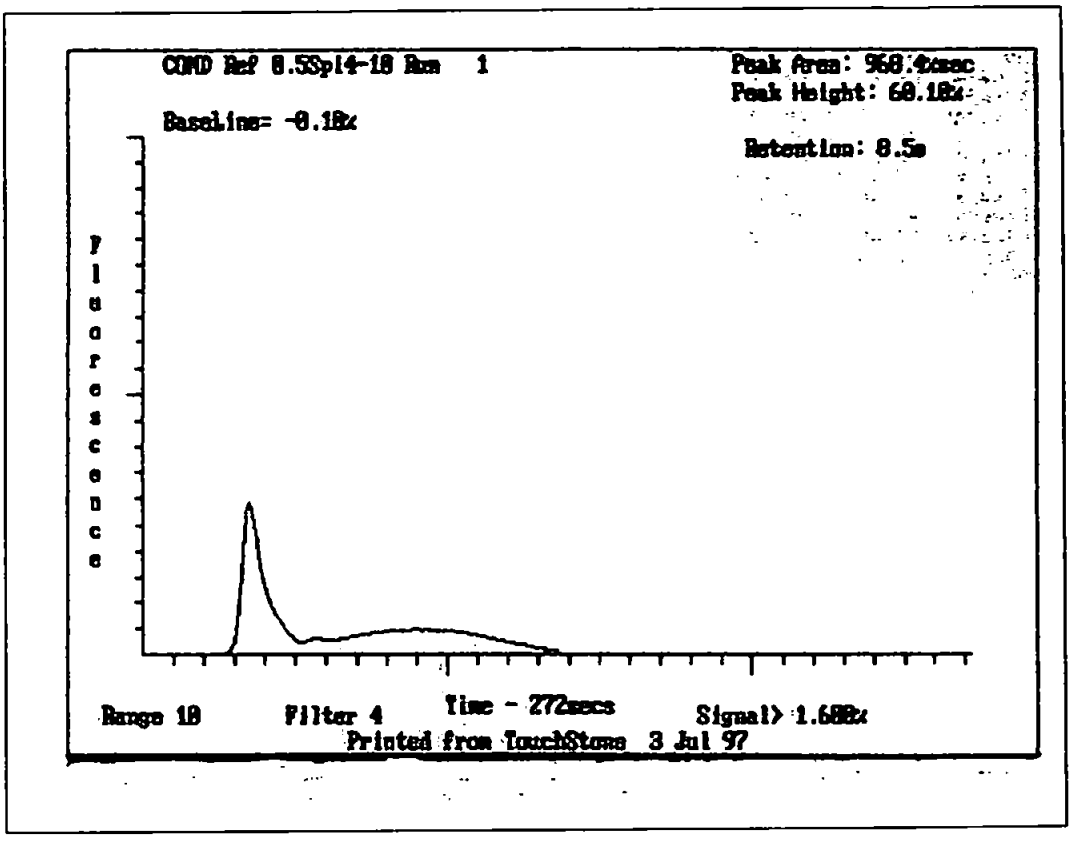


Figure 3.25 : Example of volatogram for sample 4 (0.5 ml injected)- no dilution

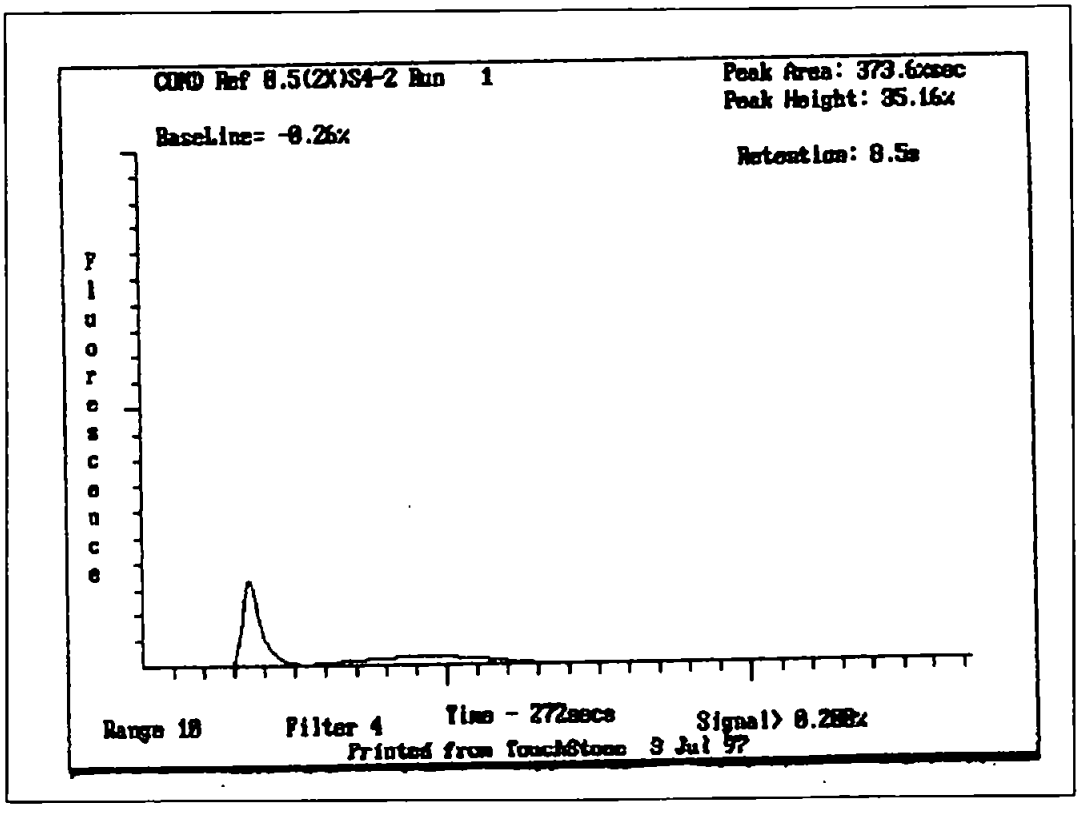


Figure 3.26 : Example of volatogram for sample 4 (0.5 ml injected) - dilution 1 : 1

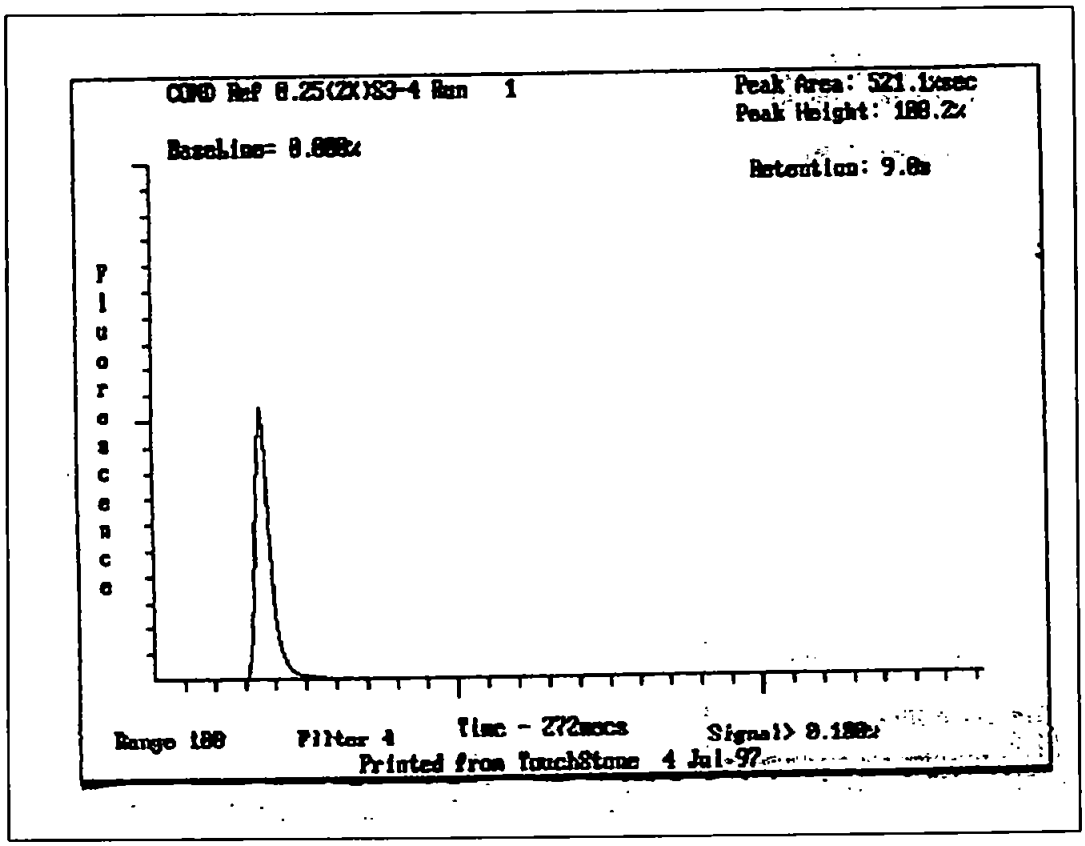


Figure 3.27: Example of volatogram for sample 3 (0.25 ml injected) - dilution 1 : 1

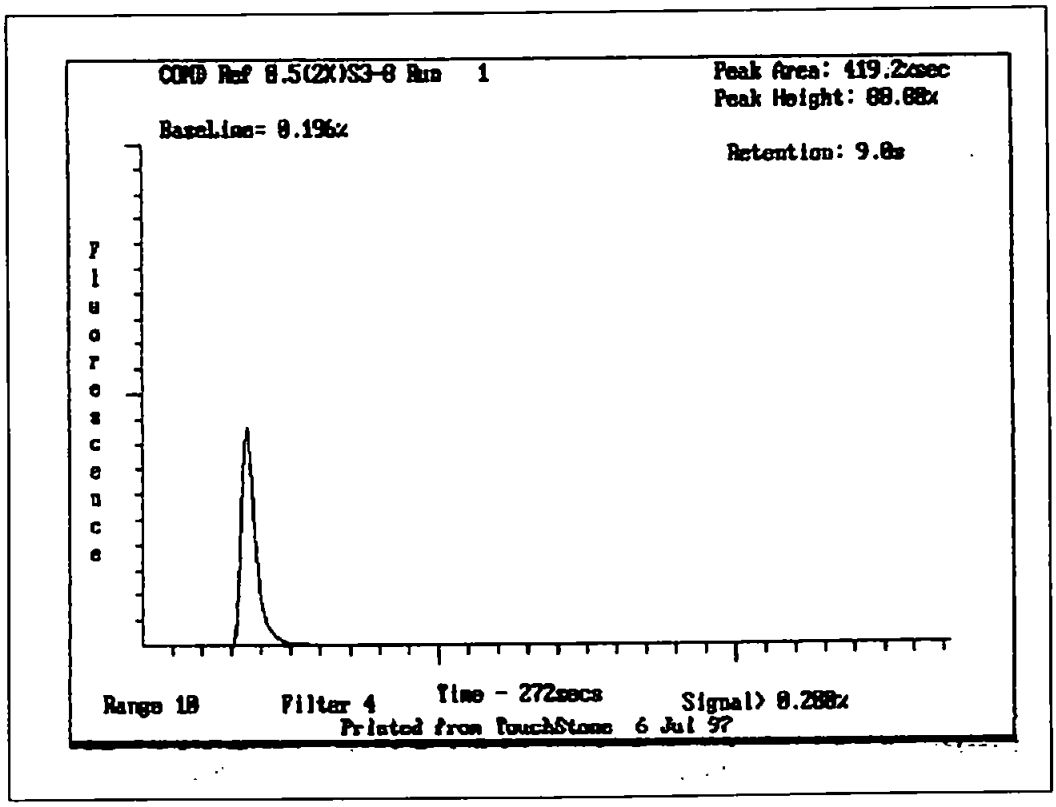


Figure 3.28: Example of volatogram for sample 3 (0.5 ml injected)

(dilution 1 : 1)

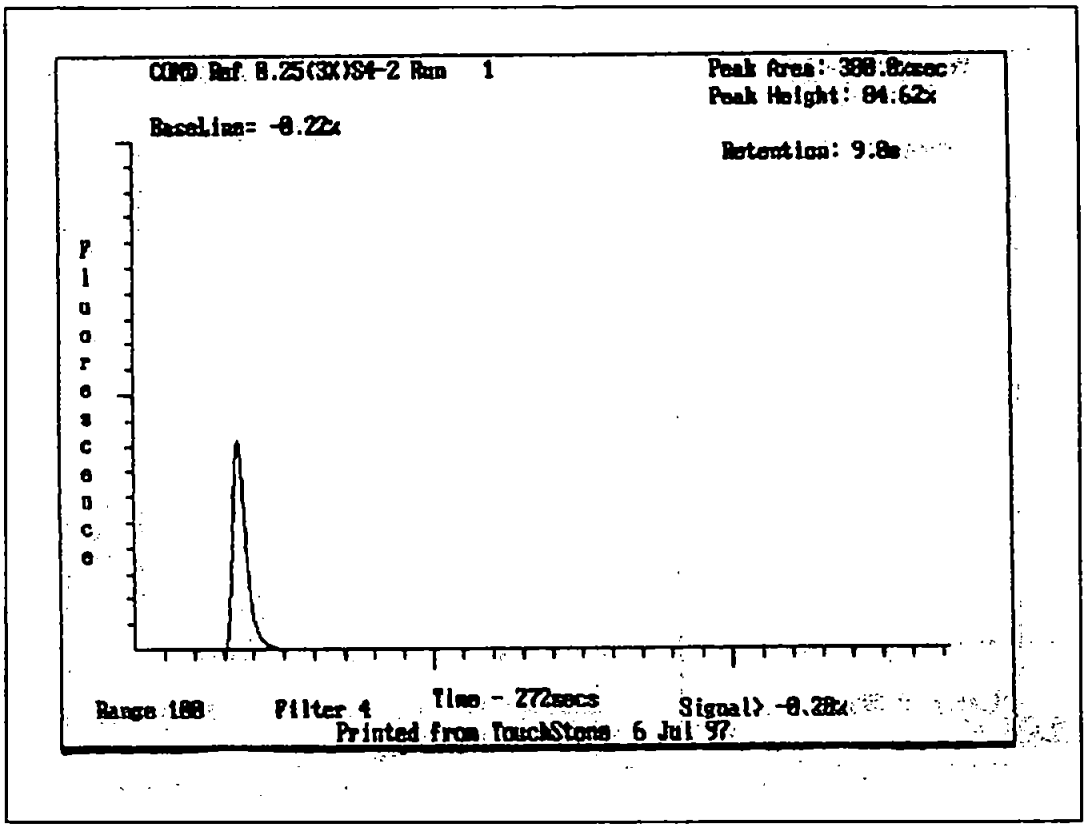


Figure 3.29: Example of volatogram for sample 4 (0.25 ml injected)

(dilution 1: 2)

3.4.2 GASOLINE WITH ULTRA TRACE MERCURY CONTENT

Two gasoline (light naphtha) samples from a European refinery that are known to contain ultra trace levels of mercury have also been determined by the vaporisation method. The total mercury content for the samples are 42.3 $\pm$ 6.5 and 87.2 $\pm$ 4.7 pg ml^{-1} respectively (Table 3.8).

In comparison with gas condensate samples analysed previously, the levels of mercury measured in the gasoline samples is considerably lower. The maximum sensitivity setting together with a 1.0 ml sample volume injection was required to obtain the value shown in Table 3.8. The gas blank corrected values indicate a limit of detection for this type of sample, between 15 and 20 pg ml^{-1} (close to the carrier gas limit).

Sample	Mercury contents (pg ml $^{-1}$)	Limit of detection (pg ml $^{-1}$)	Replicates
Gasoline 1	42.3 $\pm$ 6.5	19.5	10
Gasoline 2	87.2 $\pm$ 4.7	14.1	7

Table 3.8 : Total mercury in gasoline samples

3.4.3 TOTAL MERCURY CONTENT IN HEAVY OILS

3.4.3.1 Effect of matrix on the precision

As a study to investigate whether a heavier fraction oil sample could also be analysed for its mercury content with this system, two commercial 'heavy gas oil' samples, A and B, with boiling points of between 260 °C and 538 °C were obtained.

The samples were found to be of the very heavy dark coloured fuel oil type. Severe matrix effects were evident when direct injection and low ratio dilution (1 : 4) injections with toluene of the oil was performed. This resulted in multipeaked, mercury-delayed volatograms. Hence for this analysis, several dilution ratios with toluene were carried out i.e. factors of 5, 20 and 50. Sample B was chosen for the above dilution exercise. For sample A, a dilution of 100 times was used (since this sample was found to be more viscous than sample B). In each case 0.25 ml of sample was used.

The results show that for the 5 times dilution, the measurement suffered from poor peak shape, a raised tail and base line. The total mercury measured was relatively higher than normally encountered, in the μg ml $^{-1}$ range. This result is shown in Table 3.9 and an example of the peak signal for a 5 times dilution is as shown in Figure 3.30.

Further dilution was therefore carried out (20 times). Although greater sensitivity and accuracy was obtained, the unstable base line effect still occurred and the peak signal was split on the top. The complex mixture which constitutes the oil samples give rise to a high proportion of high boiling point fractions which, like previous samples, interact/condense on the trap even at 200 °C and delay mercury release. The total mercury concentration obtained from this analysis was greater than the 5 times dilution value by a factor of 1.4 (40% greater). This result and an example of the peak signal are shown in Table 3.9 and Figure 3.31 respectively.

Finally, a much improved baseline and peak shape was achieved by diluting the sample 50 times. The total mercury measured was greater again than the 20 times dilution value by a factor of 1.3 (30% greater). This result is shown in Table 3.9 and an example of the improved peak signal is shown in Figure 3.32. The precision is also noted to improve, with the 50 times dilution value giving 3 % RSD.

For sample A, a dilution of 100 times was made. The total mercury measured was 22.19 $\pm$ 0.62 $\mu g\ ml^{-1}$, RSD was 3 % (n = 4). The base line of the measurement and peak shape was good and at this dilution it is assumed that the matrix interference is reduced substantially (i.e light enough to obtain complete vaporisation of the sample). This result is shown in Table 3.9 and an example of peak signal is shown in Figure 3.33. The results indicated that heavier oil fractions can also be analysed using this technique, provided that the samples be diluted with a suitable solvent/s to a suitable concentration range.

Sample	Vol. injected (ml)	Dilution factor ('X)	Concentration Mean ± s.d. (μg ml $^{-1}$)*	RSD (%)	Replicates
A	0.1	100	22.19 ± 0.62	2.8	n = 4
B	0.25	5	1.19 ± 0.13	10.9	n = 3
		0	1.68 ± 0.12	7.1	n = 7
		50	2.23 ± 0.07	3.1	n = 7

* *Blank corrected (toluene as blank/solvent)*

Table 3.9: Total mercury content of heavy oil A and B

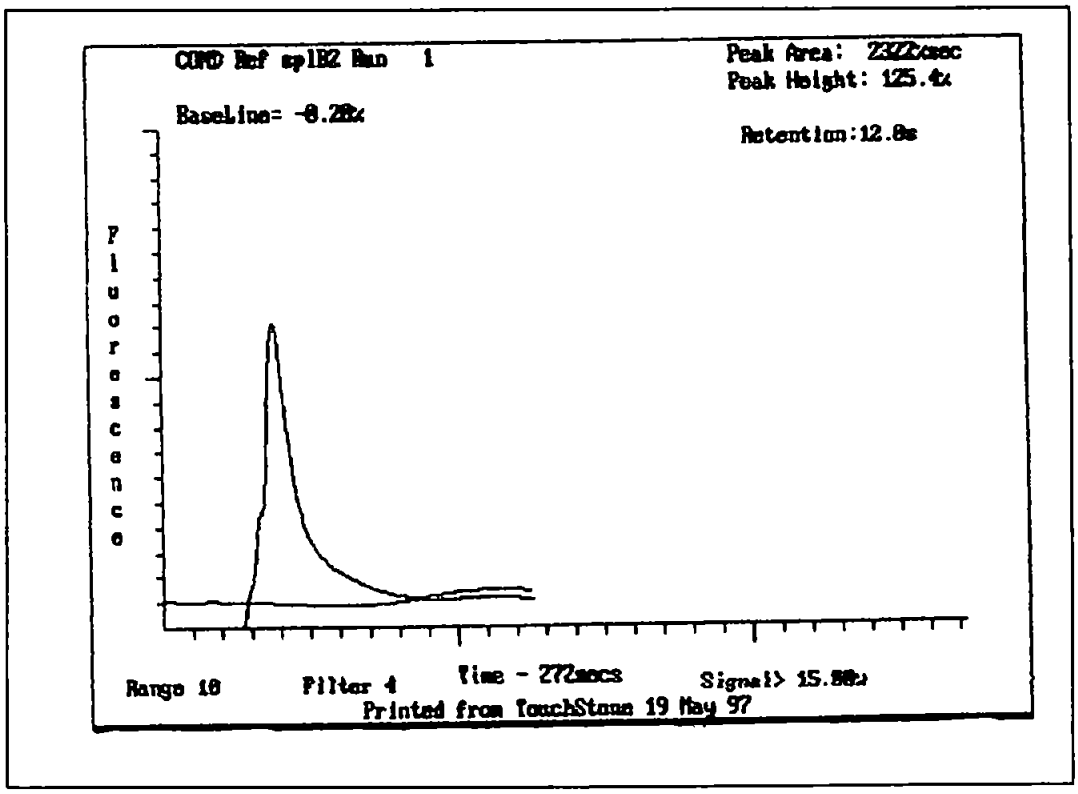


Figure 3.30: Volatogrm for sample B , 5 X dilution

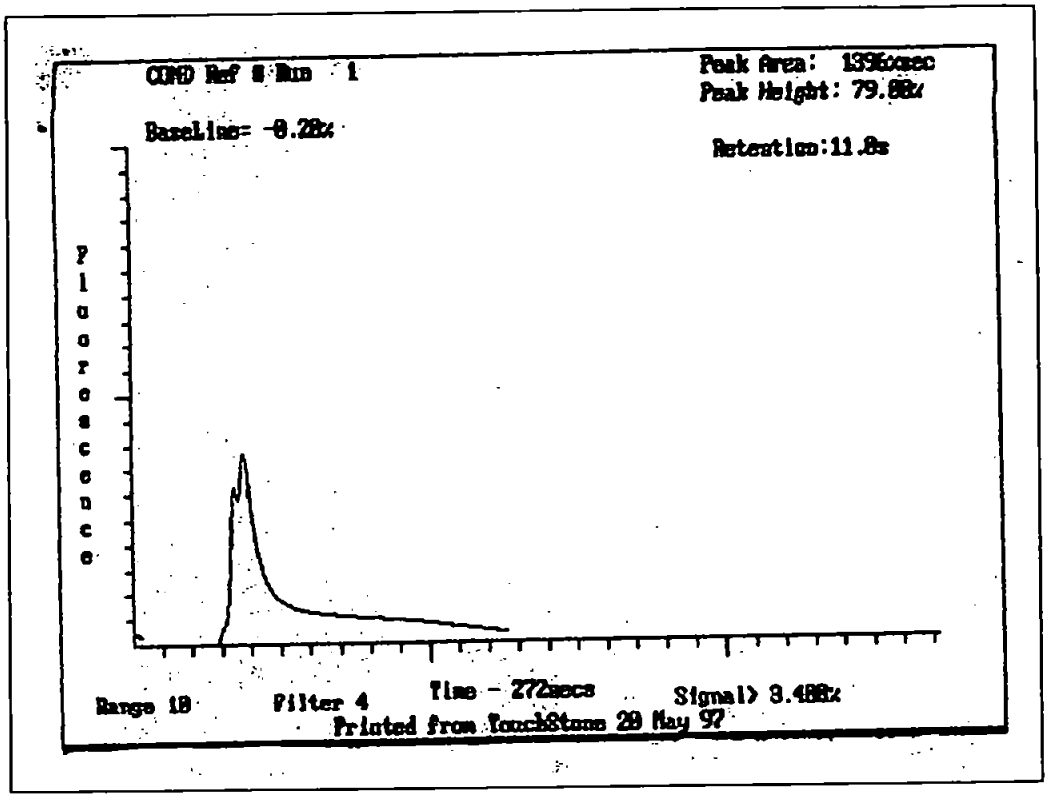


Figure 3.31: Volatogram for sample B , 20 X dilution

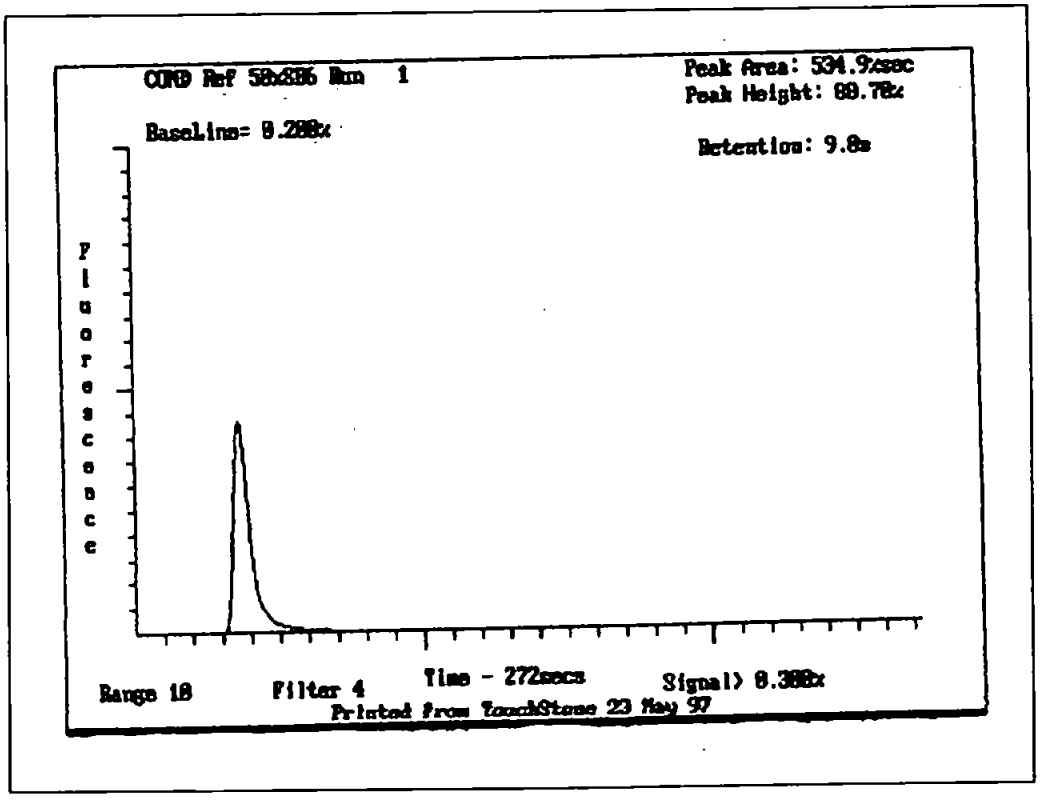


Figure 3.32: Volatogram for sample B , 50 X dilution

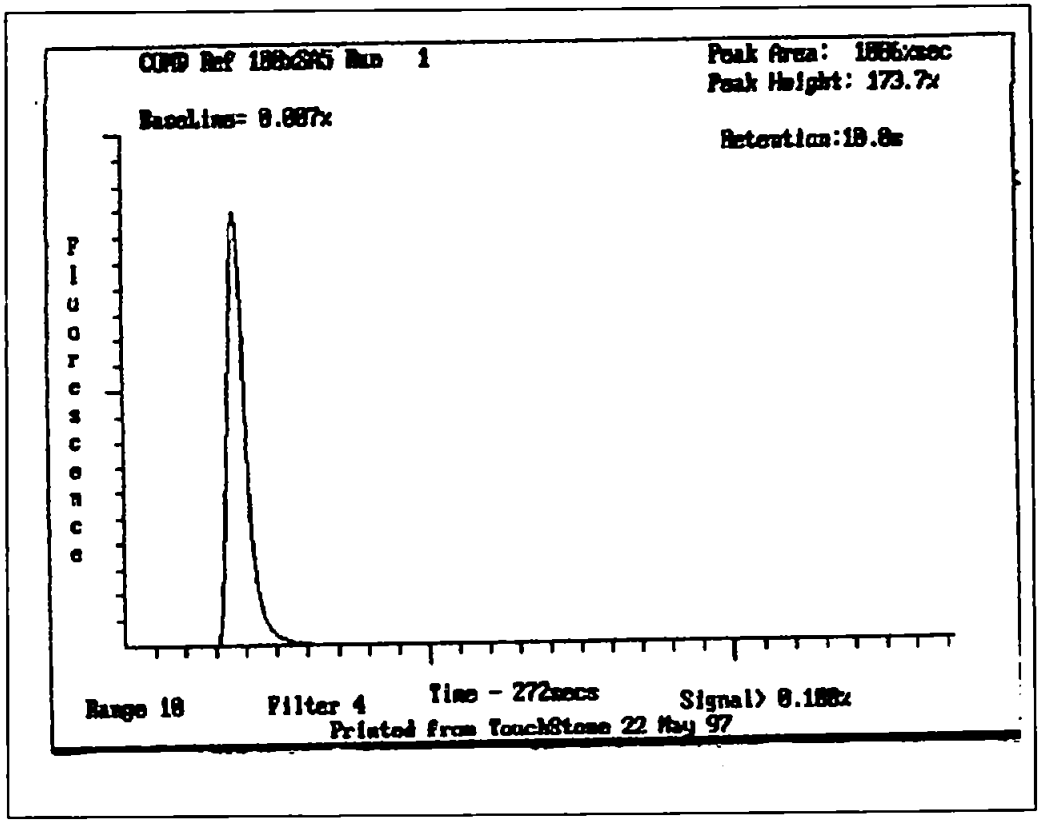


Figure 3.33: Volatogram for sample A , 100 X dilution

3.5 CONCLUSIONS

A relatively rapid, simple accurate and precise technique has been developed for the determination of total mercury in gas condensates and other liquid hydrocarbons. The technique comprised a 250 ml glass vaporisation vessel, held at 400 °C into which a sample was injected (0.1 to 1.0 ml). The sample vapour was directed with argon carrier gas *via* a heated transfer line, to a gold-coated silica trap maintained at 200 °C. it was shown that all nine mercury species used in the study were adsorbed efficiently and retained on the trap, while the complex hydrocarbon matrix was carried away to waste. When the trap temperature was raised to 900 °C, elemental mercury was rapidly released and carried, with argon gas, to the atomic fluorescence detector for measurement.

For the high efficiencies of species adsorption to be maintained when higher sample volumes were used (>0.25 ml), a double-sized trap was required together with longer vaporisation times (5 to 10 minutes). Despite scavenger tubes being on-line for all argon gas flows, mercury blanks in the gas had to be considered on a time factor basis. An argon carrier flow rate of less than 400 ml min^{-1} was found to be necessary.

Recovery values of over 90 % were generally obtained for eight mercury species spiked into toluene and 'real' condensate in the 10 to 50 ng ml^{-1} range. These species were DMM, DEM, DPM, MMC, EMC, PMC, MC and CONO. Precision studies using spiked condensate (DEM) gave a limit of detection of 270 *pg* (absolute) equivalent to 1 ng ml^{-1} (0.25 ml sample).

Five samples of 'real' gas condensate gave total mercury values in the range 7.5 to 50 ng ml^{-1}. The technique was extended to look at mercury content of the 'light fraction' of

gasolines at the ultra-trace level (< ng ml^{-1}). Sample volumes of 1.0 ml were required and values for total mercury in the two samples ranged from 42 to 87 pg ml^{-1}.

It was noted that when 'higher fraction' oils were introduced directly as samples to the vaporisation chamber, the high boiling point components could cause interferences in the release of mercury from the trap later on in the cycle. Dilution of 20 to 100 times with a suitable solvent such as toluene was necessary to increase the volatility of the sample and to reduce the high mercury content of the sample to the range required. The heavy gas oil samples gave values of 2 to 22 μg ml^{-1} for total mercury content, approximately 22,000 times higher than the gas condensate samples and some 4×10^{6} times higher than the gasoline samples. This displays the wide range in concentration and flexibility of sample that the technique can tolerate.

CHAPTER 4

MERCURY SPECIATION IN NATURAL GAS CONDENSATE BY GAS CHROMATOGRAPHY COUPLED WITH ATOMIC FLUORESCENCE SPECTROMETRY.

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MERCURY SPECIATION IN NATURAL GAS CONDENSATE BY GAS CHROMATOGRAPHY COUPLED WITH ATOMIC FLUORESCENCE SPECTROMETRY

4.1 INTRODUCTION

Knowledge of total mercury content and the different species present in natural gas condensate is extremely important. Mercury in most forms is highly toxic and, particularly when present as the organomercury species, is a cause of great environmental concern. The types of mercury species in environmental samples are in the forms of inorganic mercury, organomercury halide and dialkyl- and diaryl-mercury.

The damage caused to industrial plants particularly petrochemical plants by the presence of certain mercury species can be financially crippling especially when unscheduled shut-downs are forced. Information on the species content is vital for the development, improvements and monitoring of the performance of newly developed or commercially available mercury removal systems. This is due to the mercury species content being unique to each condensate, i.e. the species contents depend very much on the origin of the condensate and stage of process.

The effect from mercury in petroleum products upon the industry was first reported in 1973 in Algeria. The implications were discussed in detail in chapter 1, sections 1.2.1 and 1.2.2.

Mercury may be present in natural gas condensate in its metallic form and/or as organometallic compounds with boiling point comparable to that of the range of the

condensate (**7, 12**) shown in Table 1.4, Chapter 1. The elemental mercury content in liquid hydrocarbon or gas condensate may be in the range of about 10 % or less of the total mercury in the samples due to the high volatility and the low solubility of elemental mercury (**12**).

Other species such as organomercury halide and inorganic salts (polar compounds) may also be present but at a lower concentration in the non-polar condensate matrix. The presence of these species is likely to be associated with impurities, such as particulate matter (which are likely to adsorb mercury species) or the moisture or free water in the sample.

To date, a complete and rapid technique for the identification and quantification of all the mercury species content in natural gas condensate is not well established. Various papers report the speciation of mercury in hydrocarbons and gas condensate but most are targeted at single or a few species of interest (**9, 77,78**).

The majority of papers are focused on aqueous-based and related environmental samples rather than the complex and hydrophobic, liquid hydrocarbon sample type. For separation of the species, chromatographic techniques are most commonly used including gas chromatography, high performance liquid chromatography and ion chromatography. For detection of mercury, the detection systems used are either electron captured detector (ECD), microwave induced plasma-atomic emission spectrometry (MIP-AES), atomic absorption spectrometry (AAS) or atomic fluorescence spectrometry (AFS). The analytical technique most commonly used in earlier studies for determination of organomercury compounds in environmental samples was gas chromatography using electron capture detection (GC-ECD) (**169-174**). Speciation techniques have involved derivatization by

butylation (175-176), aqueous phase ethylation (93, 172, 182) or hydridization (180) prior to chromatographic separation and coupled with microwave-induced plasma (MIP), GC-MS, GC-ICP-MS, GC-MIP-AES, CVAAS and CVAFS, for mercury detection. These procedures can be time consuming, can lead to contamination of analytes and losses during the procedure and the derivatized products may not necessarily reflect the actual concentration of the various organic mercury species native to the samples.

The determination of methyl mercury and ethyl mercury compounds in sediments by capillary GC-AFS that eliminates any derivatization techniques was reported. The procedure was a direct solvent extraction of organomercury compounds from sediments with dichloromethane after digestion with acidic potassium bromide and copper sulphate followed by GC -AFS (177). Atomic fluorescence offers the potential of greater accuracy, reliability and simplicity of operation compared with the other detection techniques mentioned above (93, 170, 181).

Other examples of the utilisation of gas chromatography include, the determination of mercury species in air by GC coupled with AFS using a carbotrap column (93) and the determination of mercury species in humic rich water by GC-MIP-AES after complexation with diethyldithiocarbamate and butylation with a grignard reagent (89).

Speciation through separation using liquid chromatography (LC) or high performance liquid chromatography (HPLC) before determination of mercury by cold vapour AAS has been a preferred method used in environmental and water samples. Examples include the speciation of MC, MMC and EMC in waste water using a STR-ODS-H (5μm) column after preconcentration with Develosil-ODS and elution with cysteine-acetic acid (185); speciation of inorganic and methyl-mercury^{+} by on-line preconcentration by silica C_{18}

column after complexation with chelate forming reagents (diethyldithiocarbamate, pyrolidin-1-yl-dithioformate and diphenyl thiocarbazone) coupled with CVAAS **(186)** and LC coupled with CVAAS with continuous flow reduction for alkanes thiolates and $NaBH_4$ reduction of inorganic, methyl and ethyl mercuric compounds **(91)**. A HPLC-CV-AAS for the separation of methyl-, ethyl-, phenyl- and inorganic mercury in water after complexion with cysteine on LiChro-CART RP-18 column also has been reported **(86)**.

Many coupled chromatographic-atomic spectrometric methods have been applied to the detection and determination of organomercurial compounds mostly in environmental samples of aqueous base and origin **(72, 87, 93, 172, 178, 181 - 185)**. Few in depth investigations have been carried out for speciation of mercury in petroleum based samples A method for determination of mercury species in gas condensate by on-line coupled high-performance liquid chromatography and cold-vapor atomic absorption spectrometry has been reported **(9)**. Various organo- mercury species were first separated by reversed-phase HPLC using an aqueous-based gradient elution. Before the final measurement, the organic ligands and the matrix were destroyed by oxidation with $K_2Cr_2O_7$. Mercury was detected with cold-vapour atomic absorption spectrometry. However, when applied to natural gas condensate, only inorganic mercury (II) was detected and severe matrix interference was reported. Chemical rearrangements between the mercury species was also observed.

The determination of dimethyl mercury species in natural gas condensate was reported **(78)** that used an on-line amalgam trap or solid phase micro extraction with capillary GC-MIP-AES detection. This procedure eliminated background interference from carbon compounds passing through the plasma that occur when a direct measurement approach is carried out. Monomethyl mercury and inorganic mercury require derivatization (butylation)

prior to the determination. More recently mercury speciation in natural gas condensate using GC-ICP-MS has been achieved, using a treated DB-1701 capillary column **(187)**. The condensate samples analysed contained Hg^{o}, $HgCl_2$, DMM, methyl-ethyl mercury (MEM) and DEM. Little or no organomercury halide was detected.

The aim of the study is to develop a simple and rapid procedure for the accurate determination of all mercury species that may be present in natural gas condensate. This chapter describes the determination of mercury species in natural gas condensate by using gas chromatography coupled via a pyrolysis unit with atomic fluorescence detection. The technique utilised the advantages of gas chromatography as the separation method and the highly sensitive and easy operation of atomic fluorescence detection for mercury speciation work. The utilisation of a single gas (argon) to replace the dual type carrier gas **(177)** i.e. helium and argon, was studied. Direct injection, without any pre-treatment, derivatization or extraction of the sample, has been used. This was to avoid problems associated with the sample types and species having a relatively low boiling point (< 250 °C) and stability.

This chapter also investigates the optimisation of parameters of the method, the ability of the method to identify all species that may be present in the gas condensate, evaluates the efficiency of certain capillary columns, and compares data for a mass balance of the total concentrations of mercury obtained from the speciation analysis of condensate samples with the total mercury content determined by the vaporisation method discussed, in detail, in Chapter 3 **(188)**.

4.2 EXPERIMENTAL

4.2.1 Instrumentation and optimisation study

The set-up of the instrument system, and the construction of the injector assembly and pyrolysis unit are as shown in Figures 4.1 to 4.3.

The GC unit was a PYE Unicam model 104 gas chromatograph. The Injection system was constructed with a deactivated silica-lined adapter for splitless injection. Two columns were used, (i) a 30 metres x 0.53 mm i.d. megabore fused silica column coated with 1 micron non-polar crossed link poly dimethyl siloxane stationary phase (RTx-1) (Benner Circle, Bellefonte, Pennsylvania, USA) and (ii) 1 micron Carbowax 20M, 25 metres x 0.53 mm i.d. Cp-wax 52CB column (Chrompac, Middleburg, The Netherland).

The column was inserted through a pyrolysis unit (Model CAL 9900, PS Analytical, Orpington, Kent, UK) which was maintained at 800 °C and the outlet connected to the atomic fluorescence detector (Merlin, PS Analytical, UK) using 1.65 mm and 3.18 mm i.d. Teflon tubing. In between the heating block of the pyrolysis unit and the GC oven, a 6.35 mm i.d. copper tubing fitted with a heater was installed to prevent a cold spot and hence avoid any condensation of eluted species. The copper column also acted as a support for the fragile column link. A single gas, argon was used as column carrier gas, make-up gas and shield gas for the detector. The signals from the detector were recorded by an integrator HP 3395 (Hewlett Packard, Willmington, DE, USA).

For the study 1 microlitre volumes of sample were injected. The same volume was used throughout the study.

In order to acquire the optimum conditions for use, a number of instrumental operating parameters were varied and their effects investigated. In particular, the effect of injector temperature, column flow rate, make-up gas, resolution of species using polar and non-polar columns, calibration using individual species (including Hg^{o}), and a comparison of their response comparison and limits of detection. The speciation of real condensate samples by direct injection, with and without spiking were investigated.

The oven temperatures profile for the chromatographic separation of the mercury was based on the operating programme used in the determination of hydrocarbon-types in naphtha or gas condensate (ASTM D5134, PONA analysis). By using an established method for separation of the hydrocarbons components in condensate, any problem related to resolution and separation (chromatographic problem) of the sample matrix can be reduced.

4.2.2 Chemicals and Reagents

Di-methyl mercury (DMM), diethyl mercury (DEM), dibutyl mercury (DBM) (Strem Chemical, Massachusetts, USA), methyl mercury chloride (MMC), ethyl mercury chloride (EMC), phenyl mercury chloride (PMC) (Johnson Matthey, Royston, Herts, UK), di-phenyl mercury (DPM) (Sigma Aldrich, Dorset, UK), and mercury (II) chloride (MC) (BDH, Dorset, England) were used in the experimental procedures for calibration and for spiking into AnalaR n-hexane and toluene solvents (Merck, Poole, Dorset, UK) and ' real ' condensate samples.

4.2.3 Gas condensate samples

Six condensate samples were injected directly into the optimised column systems to determine their mercury species contents. The samples originated from a number of

different Far East sources and stages of production and have been designated TC 102, TC 123, BS 1/2, BS 3/4, TBHN 1 and TX1.

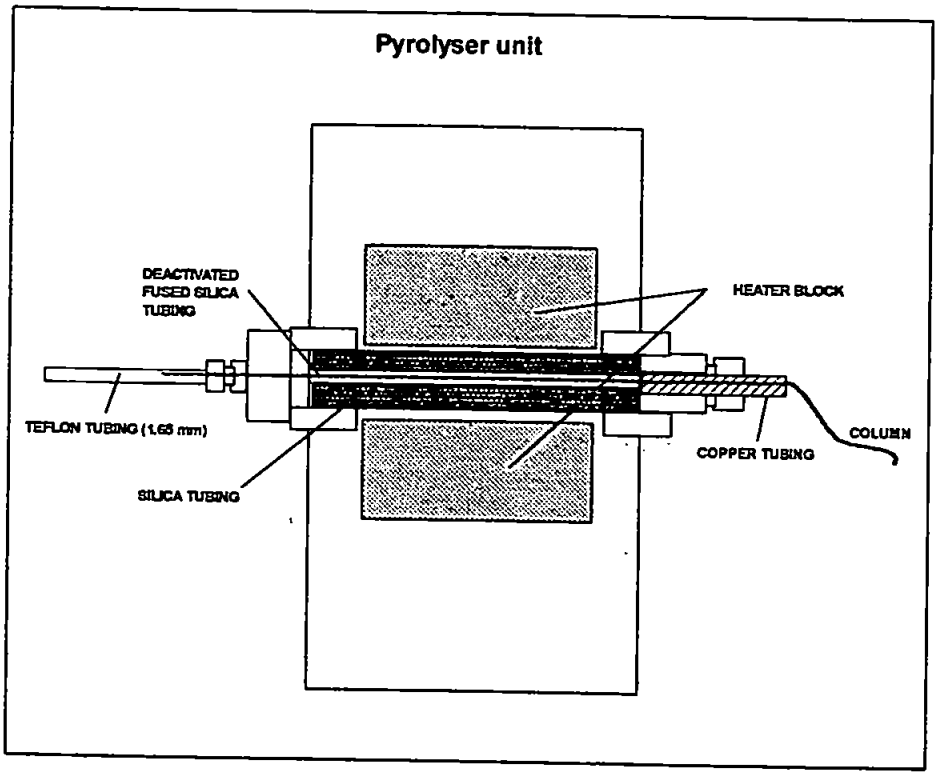


Figure 4.1: A diagram of the pyrolysis unit

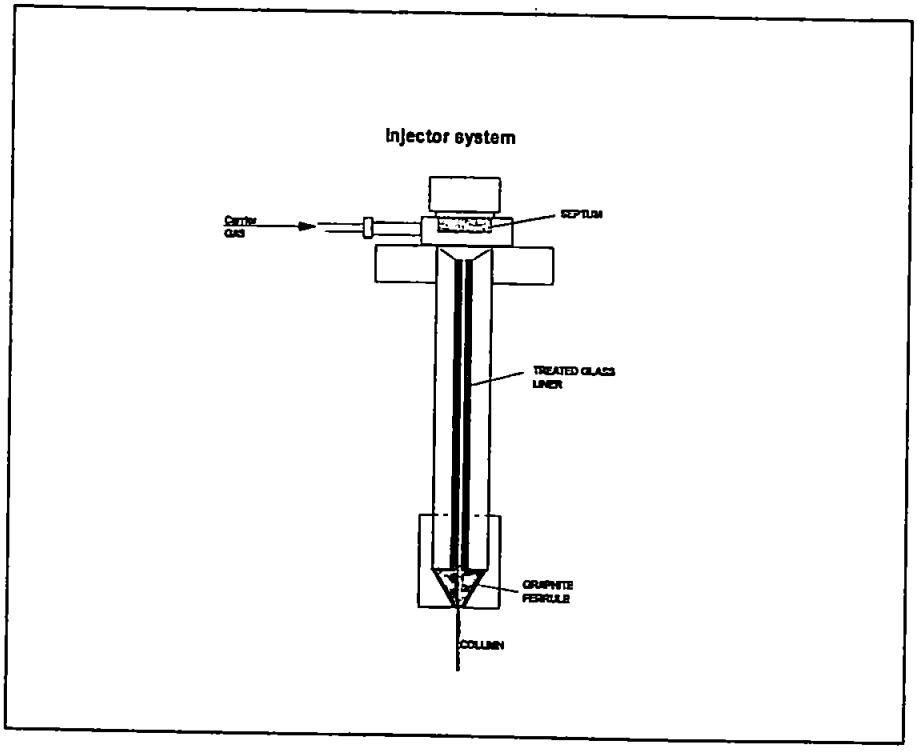


Figure 4.2 : A diagram of the injector system

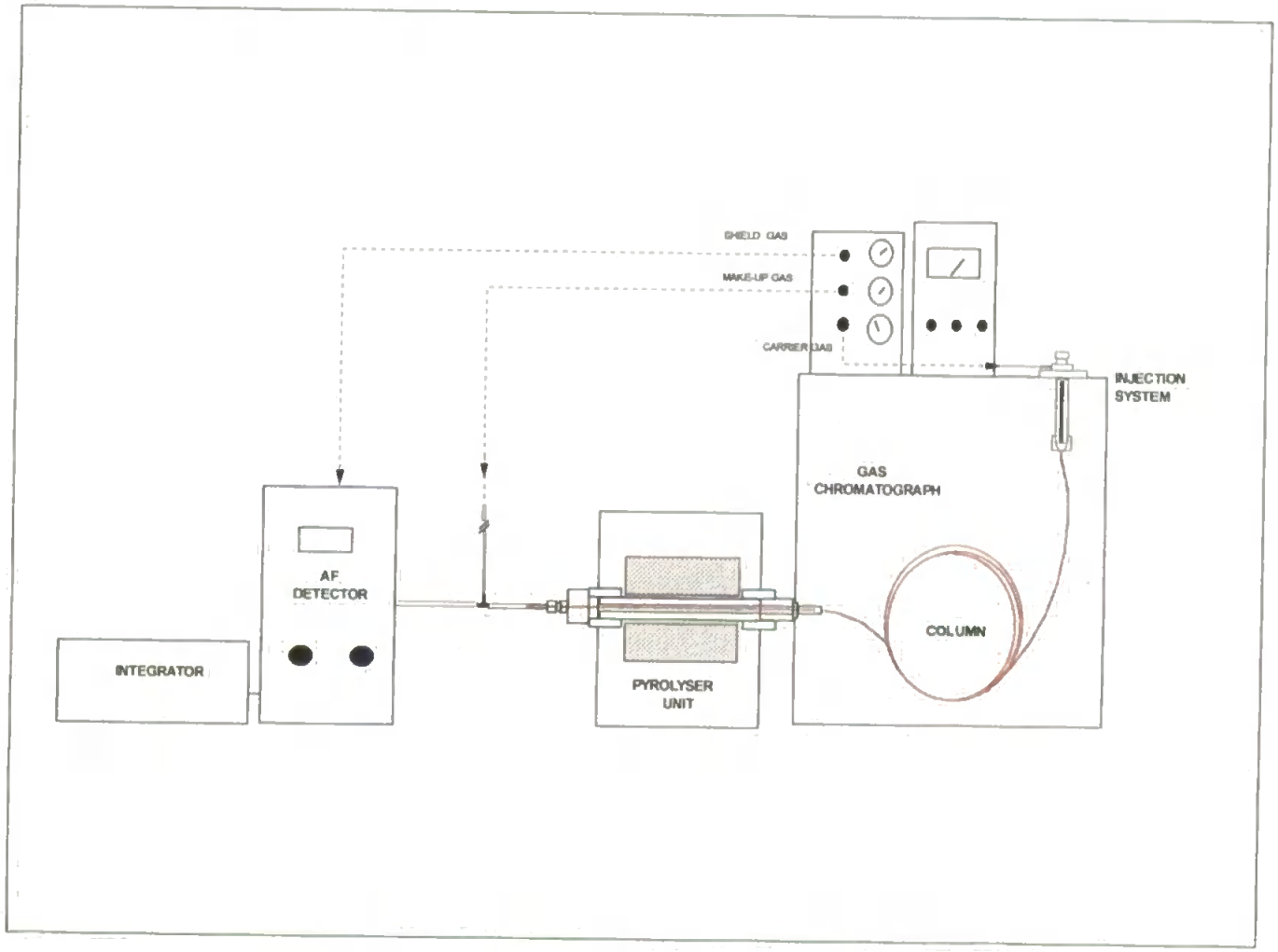


Figure 4.3 : Instrumental set-up for mercury speciation in natural gas condensate

4.3 RESULTS AND DISCUSSION

4.3.1 The effects of injector temperature

The effects of injector temperature were investigated. An equal mixture of three organo mercury species DMM, DEM and DPM 10 pg μl^{-1} each as Hg in n-hexane was used for the study. The area, area percentage, peak width and retention times were monitored. The dialkyl mercury species were chosen for the study because those species are most likely to be present in the non-polar hydrocarbon matrix. Other species, such as elemental mercury and the organomercury halides were also tested but after the optimisation studies. The latter polar species may also be present in the sample however, their solubilities are low in non-polar hydrocarbon liquid/condensate. If present, they are most likely to be associated with any moisture or free water in the sample matrix and/or any particulate or suspended impurities.

A mixture of the three organomercury species (10 pg μl^{-1} each as Hg) in n-hexane were injected (volume 1 μl) at several different temperatures. The oven temperature profile was set at an initial temperature of 40 °C (10 min. hold time) and final oven temperature of 300°C (20 minutes) with a ramp rate of 4 °C min^{-1}. For an injector temperature of 220 °C, 4 peaks were obtained in the chromatogram instead of three. The extra peak was confirmed as elemental mercury from comparisons with mercury vapour injections. It's presence was due to the degradation of certain mercury species, especially the DEM whose area changed the most, to form elemental mercury when introduced through the heated splitless injector liner. The formation of free mercury from degradation of organomercury species was reduced when the injector temperature was reduced, and was totally eliminated when the injector temperature was set at 125 °C. The effect of the injector temperature on the formation of elemental mercury is shown in Figure 4.4. The chromatograms from the series of experiments are shown in Figure 4.5.

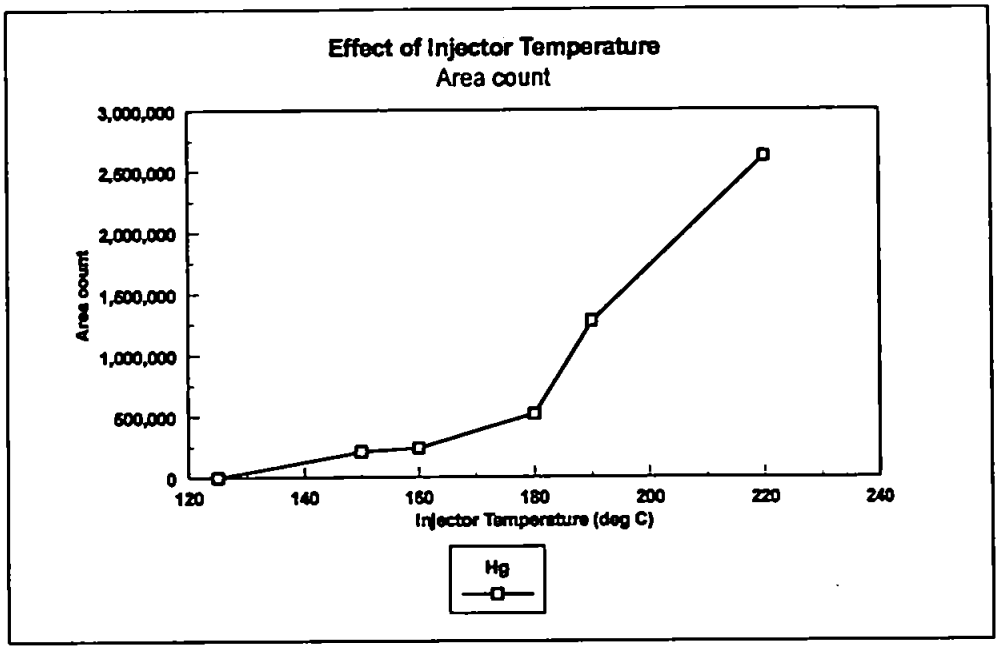


Figure 4.4 : Effect of injector temperature on elemental mercury formation from dialkyl mercury

4.3.2 Optimisation of column gas flow rate

Different column gas flow rate settings of 3, 6, 10, 15 and 20 ml min^{-1} argon were investigated. The results show that there were no significant effects on the area or area percentage or peak shape/width. The retention times of the peaks were reduced when the higher flow rates were applied. These results are displayed in the chromatograms, Figure 4.6 and graphically in Figure 4.7.

To obtain the optimum column gas flow, the chromatography of three species (DMM, DEM and DPM species (10 pg μl^{-1} as Hg) were monitored at different linear velocities. The theoretical plates number (N) was calculated using equation 4.1. Plate height (HETP) values were obtained from the equation 4.2 for the species. The Van Deemter plot for each species indicated that the optimum gas velocity and hence flow for the three organomercury species, of widely differing boiling point, was in the range of 23 to 45.4 cm sec^{-1} or 3 to 6 ml min^{-1} for argon. The Van Deemter plot is shown in Figure 4.8.

$$N = 5.54 \left(t_r / W_{1/2}\right)^2 \qquad \text{..... 4.1}$$

where,

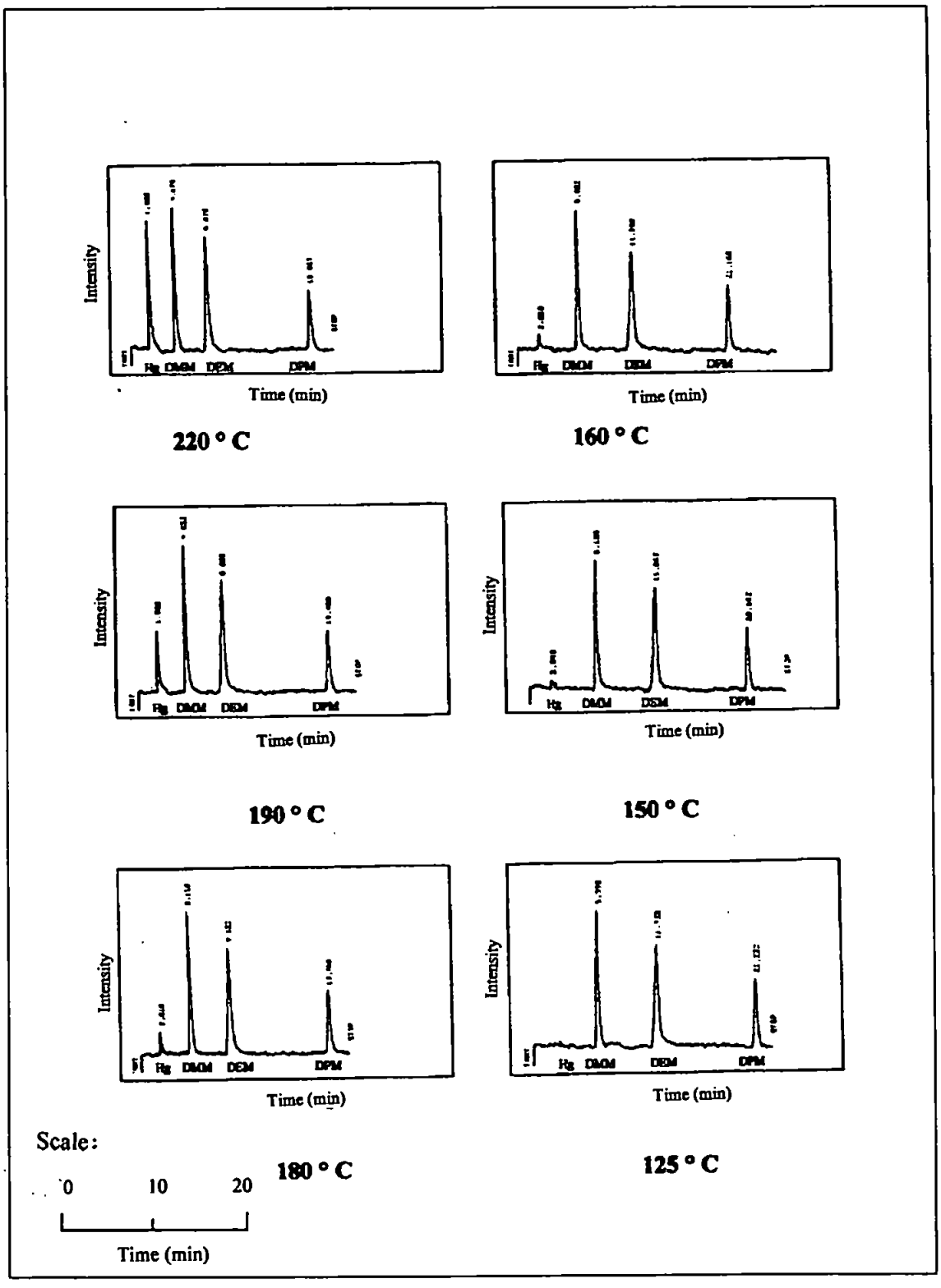
N	=	theoretical plates number
t_r	=	retention time of the compound (s)
$W_{1/2}$	=	peak width at half height of the peak (s)

$$HETP = L / N \qquad \text{..... 4.2}$$

where,

HETP	=	plate height
L	=	length of column (metres)
N	=	theoretical plate number

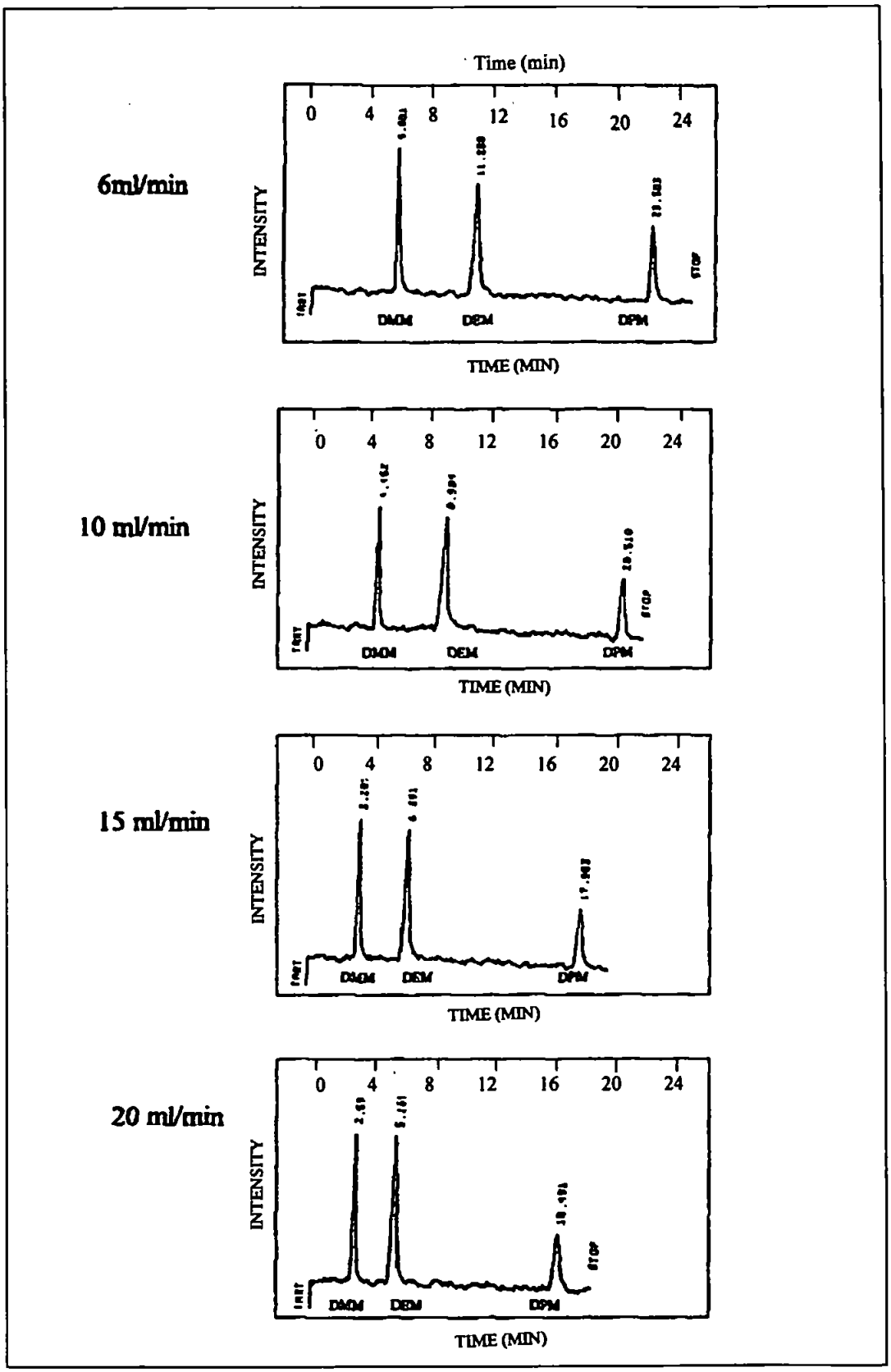
The importance of using argon gas as 'carrier' should be discussed. While many GC systems use helium, it is of note that when AFS is employed as the detection system, some suppression of mercury signal is experienced from the presence of helium. To reduce this effect, argon gas is used to 'dilute' the helium at the post column make-up and detector stages. To negate the effect of helium and to simplify the system, an all argon gas supply was used and studied.



Note :

Injector Temp	:	125 °C - 220 °C
Make-up gas	:	300 ml min^{-1}
Shield gas	:	600 ml min^{-1}
Oven temp	:	Initial 40 °C (10 min)
		Program rate 4 ° C/ min
		Final temperature : set at 300 °C
Column	:	RTx - 1 (30 metres, i.d.0.53mm, di methyl silicone 100%,)

Figure 4. 5 : Chromatograms for effect of injector temperature



Note :

Injector Temp	: 125 °C
Make-up gas	: 300 ml min^{-1}
Shield gas	: 600 ml min^{-1}
Oven temp	: Initial 40 °C (10 min), Program rate 4 ° C/ min, Final temperature : 300 °C
Column	: RTx - 1 (30 metres, i.d.0.53mm, di methyl silicone 100%),

Figure 4.6 : Chromatograms for the effect of carrier (column) gas flow-rate

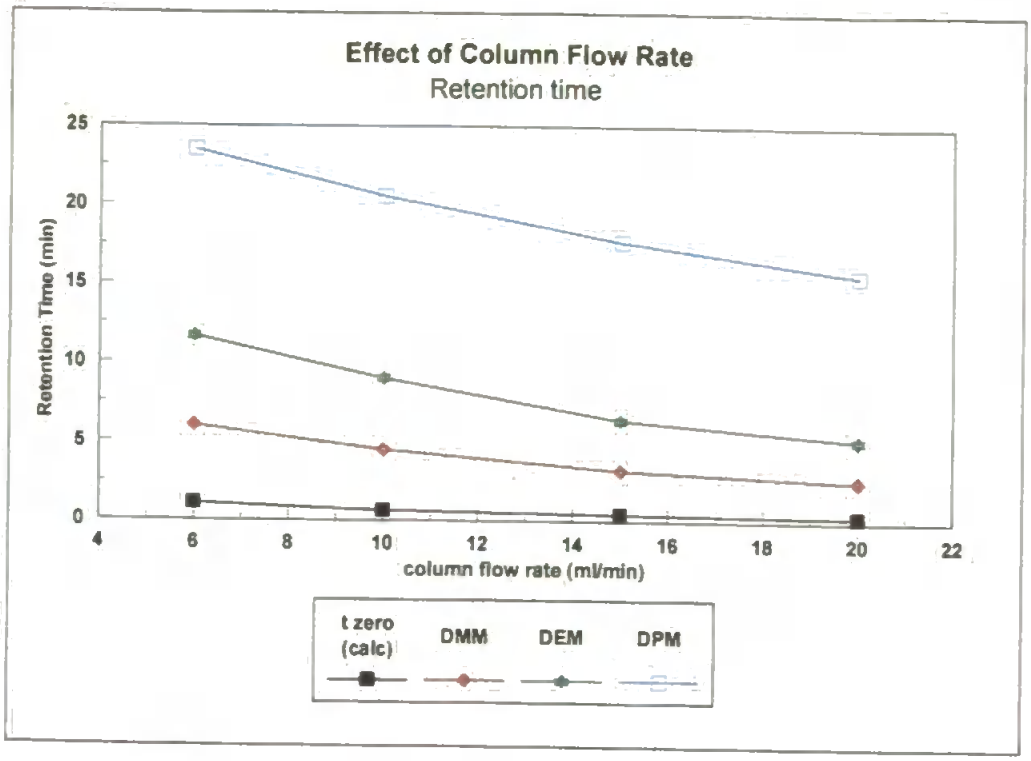


Figure 4.7: Effect of column gas flow rate

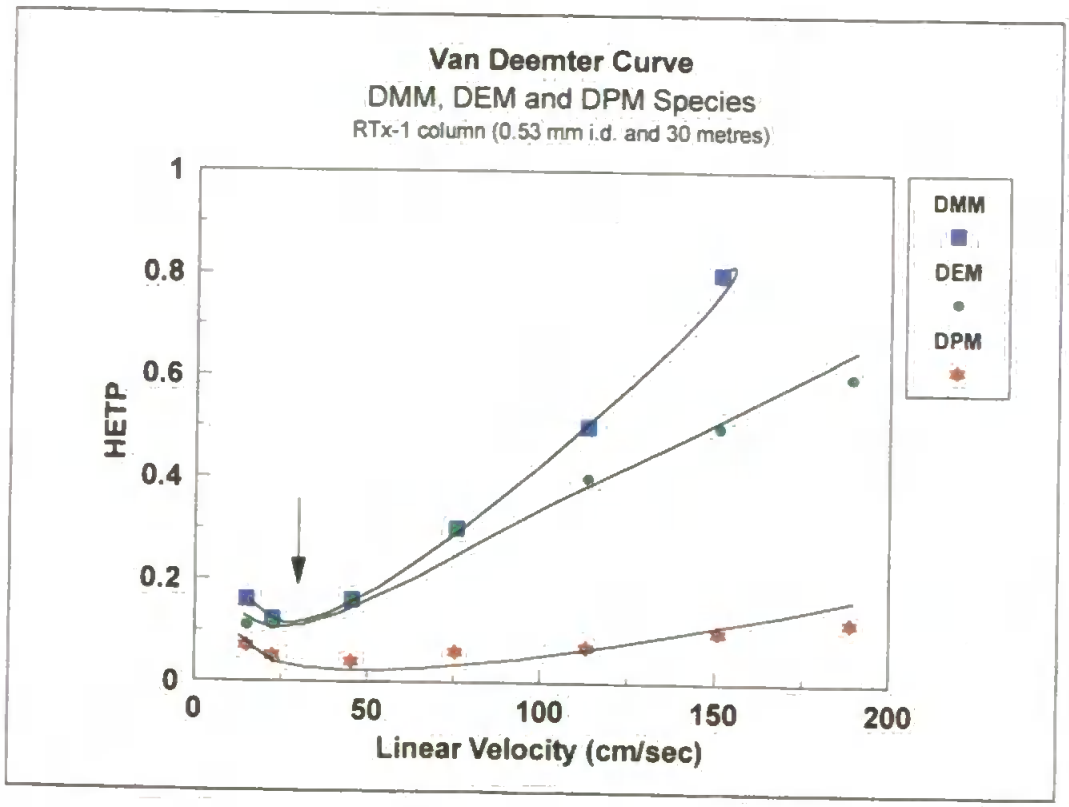


Figure 4.8 : Van Deemter plot for RTx-1 column for DMM, DEM and DPM

4.3.3 Effect of make-up gas

Due to the low gas flow through the column, it is necessary to incorporate the flow from an additional gas, called the make-up gas, to assist in carrying an eluted species from the column to the detector. The effects of different flow rates of make-up gas were monitored by varying the flow rate from 100 ml min^{-1} to 400 ml min^{-1}. The results showed this flow rate did not effect the response of the detector significantly. However a flow-rate of 300 ml min^{-1} was found to give the highest detector signal for all the species. These results are presented in Figure 4.9.

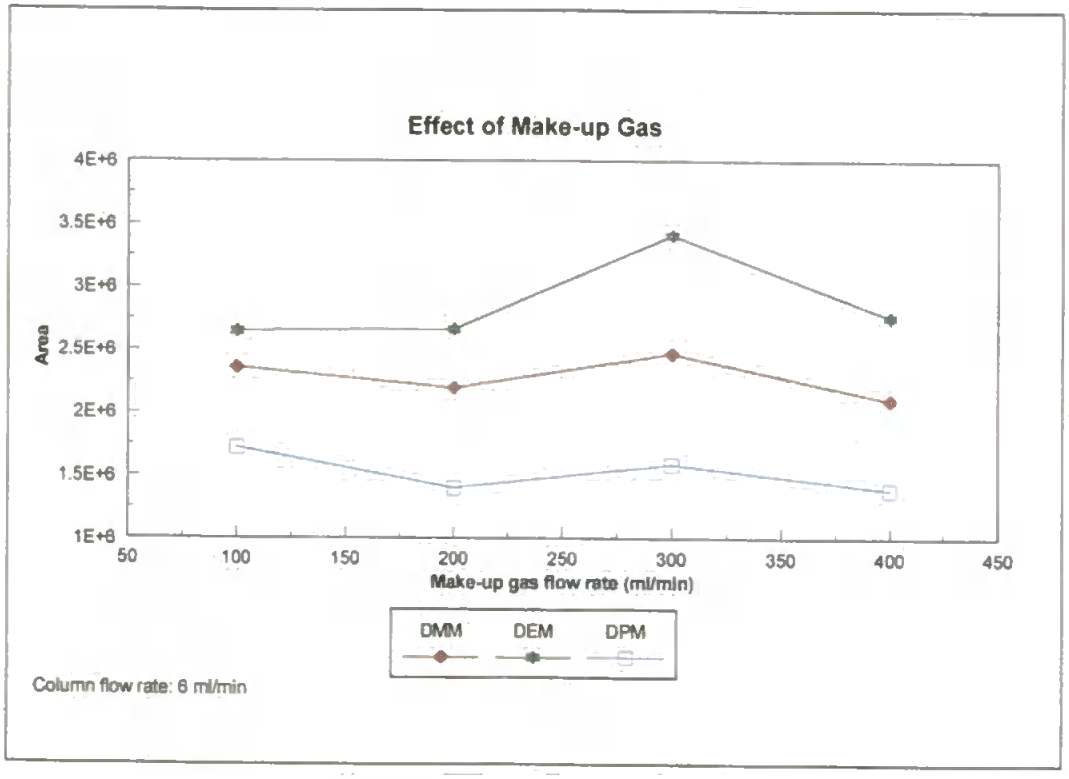


Figure 4.9 : The effect of argon make-up gas upon mercury signal

4.3.4 Resolution of organomercury halides by non-polar column

The Resolution of di-alkyl mercury species such as DMM, DEM and DPM was achieved satisfactorily by using the non-polar RTx-1 megabore column as shown earlier in the optimisation study. A mixture of organomercury halides 10 pg μl^{-1} each, of MMC, EMC

and PMC together with the mixture of dialkyl mercury species and admixtures of both were studied. Of the three organomercury halide species, only MMC was eluted and was resolved at the same retention time as DEM. The other two species (EMC and PMC) were found not to be eluted from this column. This was confirmed using individual species injections. The comparison of the three sets of mercury species mixtures injected are shown as chromatograms a to c in Figure 4.10. It is noted that, in the event of organomercury halides being present in the gas condensate, the RTx-1 column would be unable to (i) resolve MMC and DEM and (ii) elute EMC and PMC and hence an alternative column would be required.

Parameters	Values
Injector temperature	125 °C
Column carrier gas - Argon	6 ml min^{-1}
Make-up gas - Argon	300 ml min^{-1}
Column Programme :	
Initial temperature	40 °C
Ramp temperature	4°C min^{-1}
Final temperature	300 °C
Pyrolysis temperature	800 °C
Mercury wavelength	253.7 nm

Table 4.1 : GC-pyrolysis-AFS operating conditions for RTx-1 column

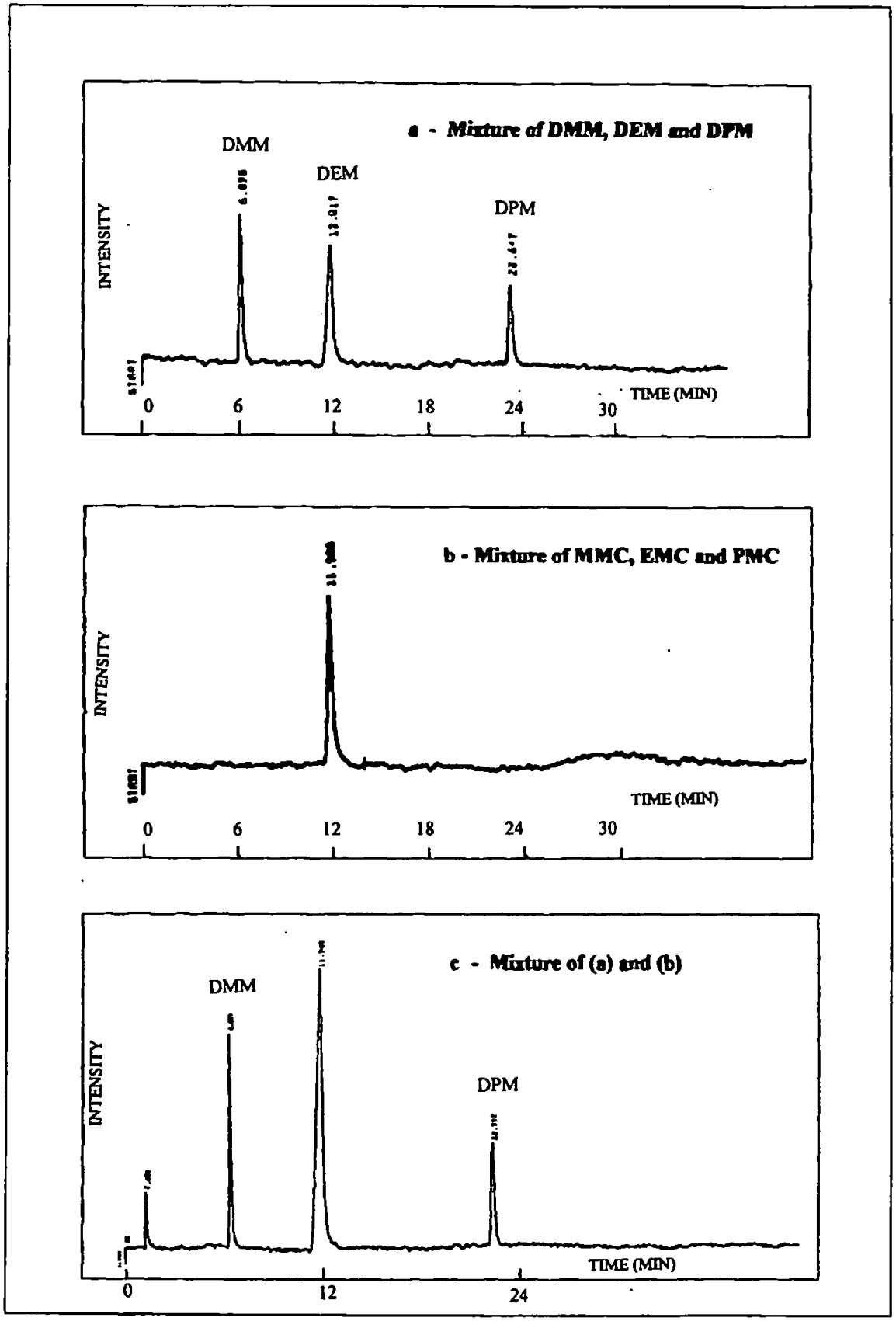


Figure 4.10 : Chromatograms for (a) di alkyl mercury, (b) organomercury halide and (c) mixture of a + b.

4.3.5 Retention times for mercury species on RTx-1 column

Using the standard calibrations previously acquired from the performance experiments, Table 4.1, the retention times for the mercury species that could be eluted were determined using RTx-1 column. These are shown in Table 4.2.

Species	Retention time (min)
Hg°	2.022 ± 0.051
DMM	6.049 ± 0.198
DEM/MMC	11.944 ± 0.221
DBM	19.766 ± 0.152
DPM	23.789 ± 0.251
EMC/PMC	not eluted

Table 4.2 : Retention times for mercury species using RTx-1 column and conditions shown in Table 4.1

4.3.6 Chromatographic performance using a polar column

The column used was a Cp-Wax megabore capillary column with an internal diameter of 0.53 mm and 25 metres length. The performance of the column was tested by injecting known amounts of various di alkyl mercury and organomercury halide species spiked into hexane. The results obtained from the analyses showed that the polar column was able to elute the seven mercury species injected and to separate the mercury species including the organomercury halides with the exception of MMC which was co-eluted with diethyl mercury. As this is a polar column, the non-polar species i.e. DMM, DEM, DBM were eluted according to their boiling point but with a reduced retention time compared with their retention time on the non-polar RTx-1 column. In comparison, the polar column exhibits improved performance by being able to resolve not only the dialkyl mercury

species quicker but also by elution and resolution of the organomercury halide species. Example of the chromatograms for the set mixtures of organomercury species spiked into the liquid hydrocarbon and injected onto the polar Cp-wax column are shown in Figure 4.11.

4.3.7 Retention time for mercury species on the Cp-wax column

Using the standard calibrations previously acquired from the performance experiments Table 4.1, the retention times for the mercury species that could be eluted were determined using Cp-wax column. These are shown in Table 4.3.

Species	Retention time (min)
Hg°	0.902 ± 0.031
DMM	1.607 ± 0.085
DEM/MMC	3.345 ± 0.221
DBM	6.798 ± 0.561
DPM	16.314 ± 0.197
EMC	34.650 ± 0.308
PMC	39.597 ± 0.463

Table 4.3 : Retention time for mercury species using the Cp-wax column and conditions shown in Table 4.1

4.3.8 Calibrations of mercury species

A series of concentrations of individual organomercury species i.e. DMM, DEM and DBM, together with Hg°, were analysed to obtain the relationship between the detector response (area counts) and concentration of species injected, using the polar column Cp-wax. The results indicated that the slopes obtained for all the species were almost identical to the calibration slope of Hg°. As the AF technique detects only elemental mercury, this

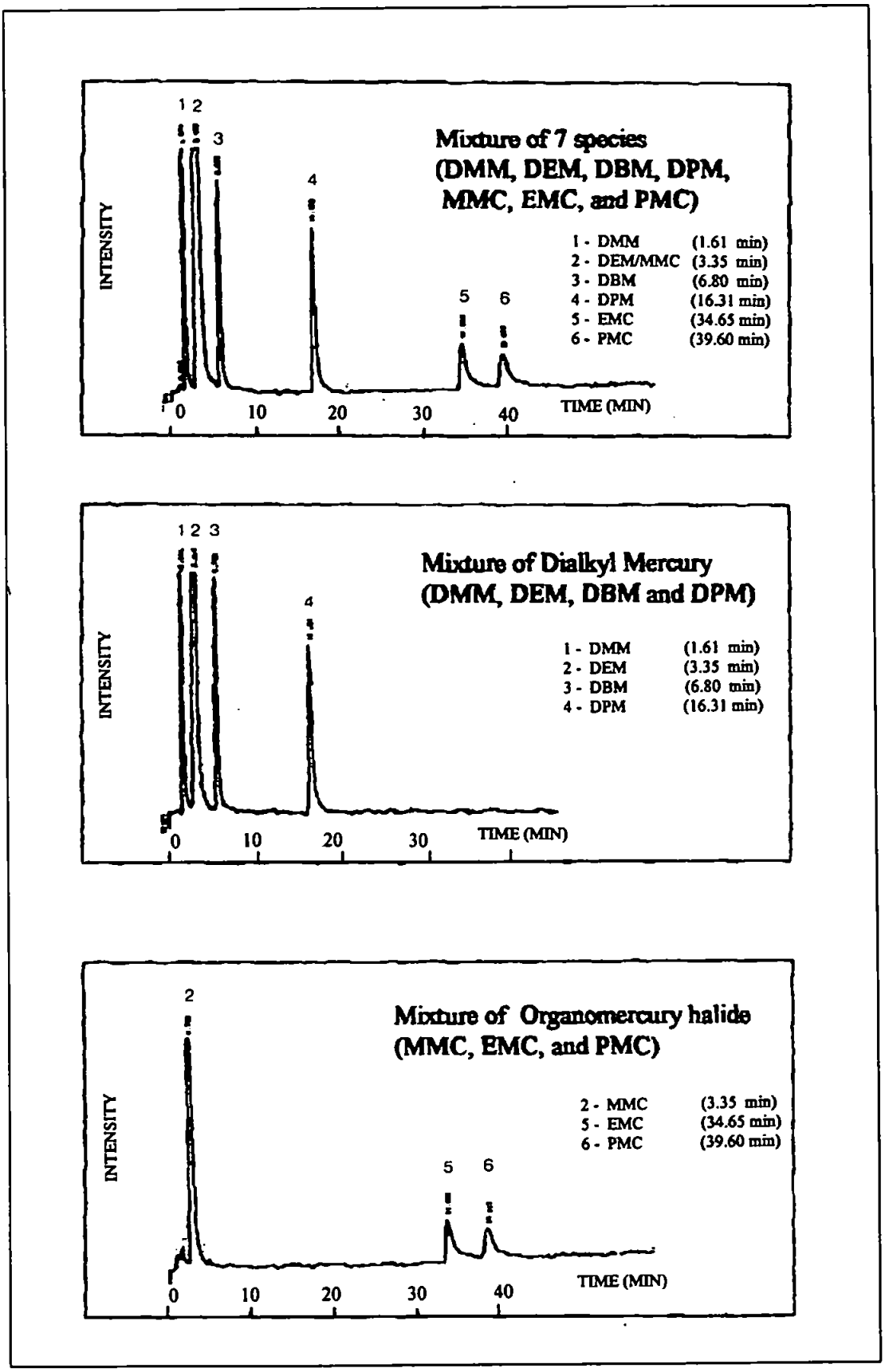


Figure 4.11 Chromatograms for organo alkyl mercury, organo halide mercury and a mixture of them separated using Cp-wax column

indicated that the organomercury species were completely recovered (i.e. not retained by the column) and afterwards were completely converted into elemental mercury by the pyrolysis unit at a temperature of 800 °C before detection. The calibration results for the di alkyl mercury species and for elemental mercury are presented in Figure 4.12.

Since the calibrations of the individual organomercury species exhibit an almost identical slope to the calibration using elemental mercury, this indicates that the species are almost completely eluted from the column and display the same high recovery values. Based on this, the response of the organomercury species relative to elemental mercury can be considered as 1 and therefore elemental mercury may be used for the calibration and quantitative determination of unknown species in samples..

To compare both the non-polar and polar column performances, a series of concentrations of dialkyl mercury (DEM) and elemental mercury were injected using both types of columns. The operating conditions of the GC system were identical for both sets of runs. The results shown in Figure 4.13 indicate that both columns produced linear calibrations with near identical slopes. The regression data are summarised in Table 4.4.

The precision of the experimental set-up was carried out by injecting 6 times for each mercury species (DMM, DEM and DBM) in hexane individually (30 pgμl $^{-1}$ as mercury) and a mixture of the three species with same concentration (*30* pgμl $^{-1}$ each). The area counts were measured. The column used was the Cp-wax megabore column. The results indicated that the RSD for n = 6 was in the range of 2.8 to 7.7 %. The area counts for the experiment are summarised in Table 4.5 and the comparison for DMM species individually and from a mixture as an example shown in Figure 4.14.

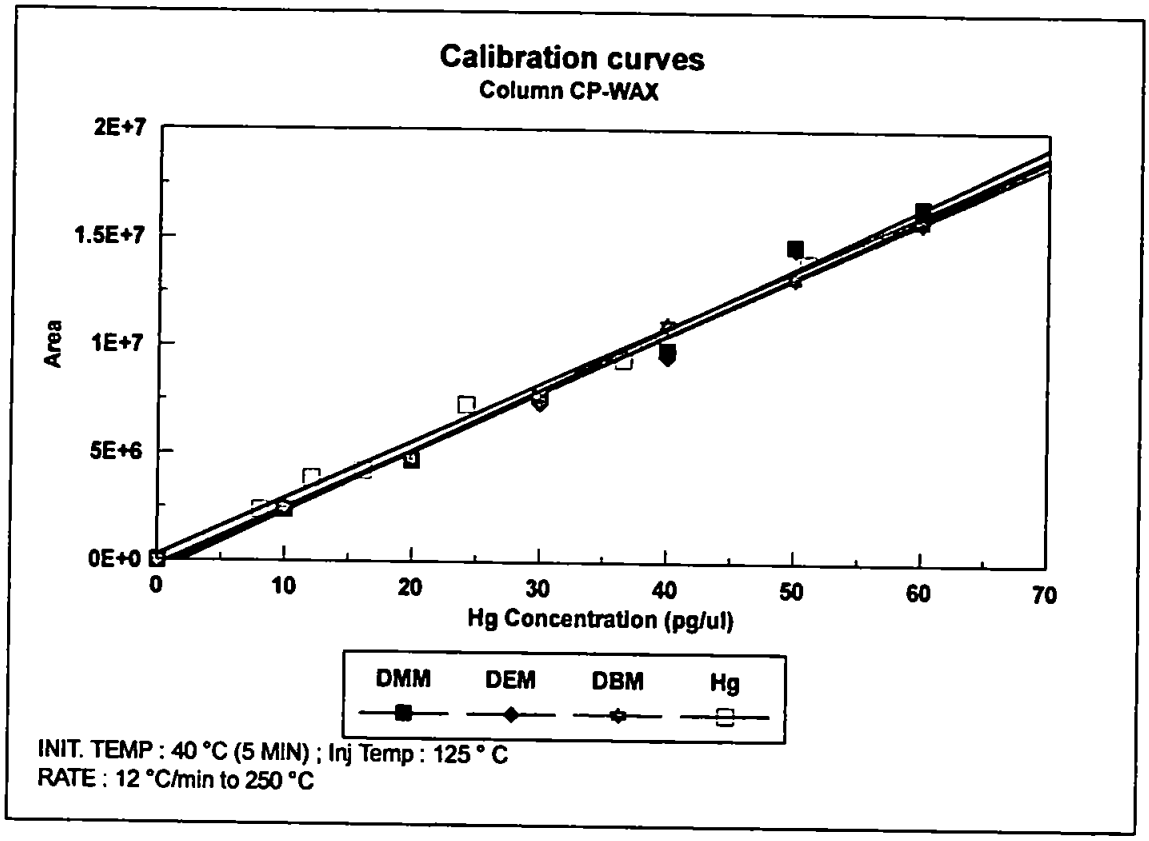


Figure 4.12 : Calibration graphs for Hg°, DMM, DEM and DBM using Cp-Wax column

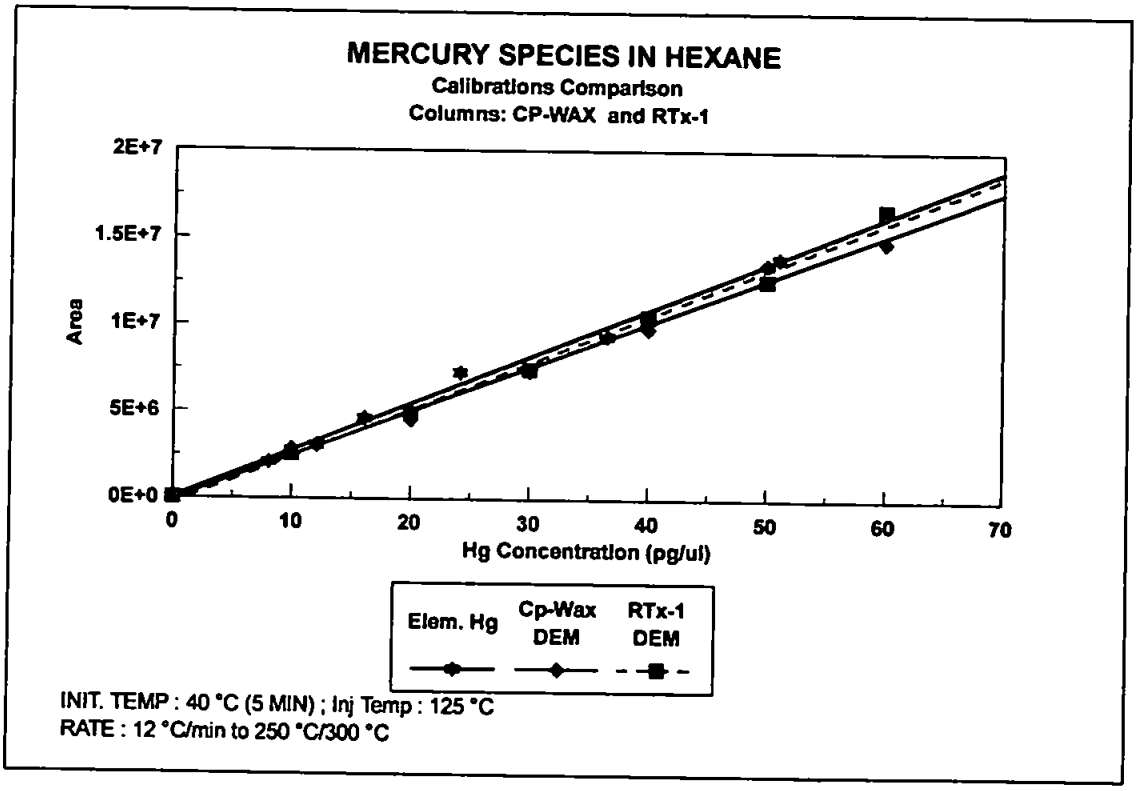


Figure 4.13 : Calibration comparison of DEM using Cp-Wax and RTx-1 column

	Regression Data		
	Hg°	DEM(Cp-wax)	DEM(RTx-1)
slope	270,159	254,356	270,372
intercept	41,765	- 73823	- 316182
r^2	0.99	0.99	0.99

Table 4.4 : Regression data

Species	Area counts ± s.d. (' x 10^6)		
	DMM	DEM	DBM
Individual	7.6 ± 0.4 (RSD = 5.3 %)	7.3 ± 0.4 (RSD = 5.5 %)	7.5 ± 0.5 (RSD = 6.7 %)
Mixture	7.8 ± 0.4 (RSD = 5.1 %)	7.2 ± 0.2 (RSD = 2.8 %)	7.8 ± 0.6 (RSD = 7.7 %)
Note : n = 6 ; column Cp-wax			

Table 4.5 : Area counts for mercury species injected as individual and as mixture.

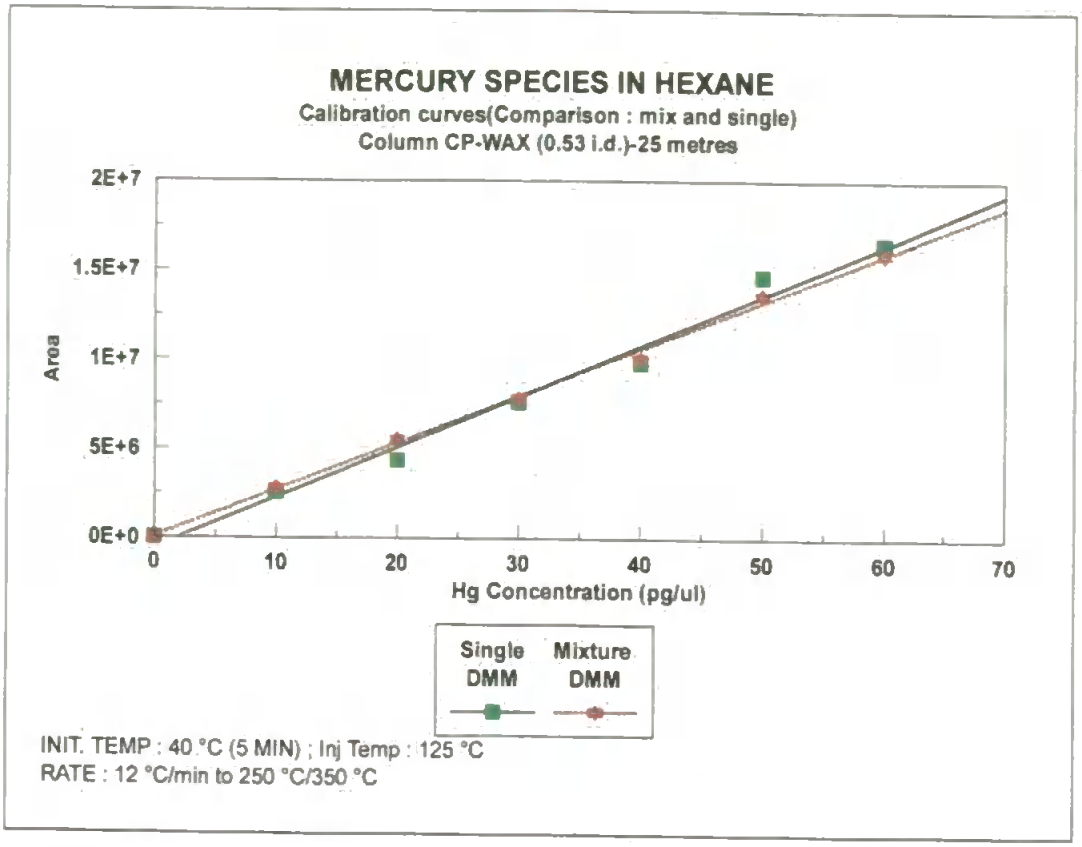


Figure 4.14: Area counts comparison for DMM injected individually and from mixture

4.3.9 Limits of detection

Limits of detection of the mercury species were determined from the calibration experiment using both types of column and several species of mercury injected individually with their series of concentrations ranging from 10 to 60 pgμl^{-1} as mercury. Each concentration was injected 6 times. The limit of detection was based on the intercept plus three times the standard deviation of random error of the intercept and the slope (Y = Yb+ 3 Sy/x)**(160)**. The absolute detection limits of the Hg°, DMM, DEM and DPM using the RTx-1 column are 5 pg, 8 pg, 3 pg and 6 pg respectively, whilst the detection limits of Hg°, DMM, DEM and DBM using the Cp-Wax column are 5 pg, 4 pg, 6 pg and 6 pg respectively. When based on individual species and concentrations injected six times, their absolute limits of detection are similar, laying in the range 2.5 to 7 pg.

4.3.10 Speciation analysis of actual condensates

Analyses of actual natural gas condensate samples were carried out using both types of column. Different condensate samples gave different ratios of mercury species. These ranged from elemental mercury, through the dialkyl mercury series, up to diphenyl mercury. Some species such as DMM, DEM, DBM and DPM were identified positively by matching their retention times with pure species mixtures injected or by spiking experiments. The other peaks could be attributed to other members of the homologous series of organomercury compounds because they eluted in proportion to their boiling point.

Quantification of the mercury species in the gas condensate samples was based on calibration curves (peak area against concentration of either organomercury species or elemental mercury). The calibration using elemental mercury was based upon the knowledge that at a fixed temperature, the saturated vapour pressure of mercury is known and a fixed volume of vapour will contain a known quantity of mercury **(168)** . A gas tight syringe was used for the introduction of the elemental vapour to the GC injector. The elemental mercury calibration was chosen because it yielded the same response as that for the other organomercury species during the calibration procedures under identical conditions.

4.3.10.1 The RTx-1 non-polar column

Five real gas condensates injected into the non-polar Rtx-1 column produced the range of mercury species shown in Table 4.6. Each condensate was injected at least four times. While a number of species were found to be close to their limit of detection, tentative values were assigned in order to estimate the total mercury content from species for later

comparison in the mass balance. Only those peaks that were reproducibly present over the four or more runs were considered valid.

The presence of a peak between the retention time of DEM and DBM standards was observed. Based upon the retention characteristic of the dialkyl mercury homologous series, this peak may be attributed to dipropyl mercury (DPrM). This following of the retention times versus the homologous series can be seen in the literature **(187)**.

With the exception of condensate TX1, the major species observed were DMM, DEM and DPrM. Few workers have attempted full mercury speciation of gas condensate and most have targeted specific species only (e.g. DMM, MMC, etc., **(9,78)**). However, the presence of DMM and DEM is noted by other workers **(78, 187)**. Sample TX1 is unusual, compared with the other condensate, in that the major component is identified as DPM and has a high elemental mercury (30 % m/m). This condensate however, is from a totally different source and may reflect the origins and unprocessed nature (raw sample) of this condensate.

Indeed, the presence and proportions of mercury species in gas condensate is highly dependent upon source, stage of production, sampling, storage of sample and age of sample. While it is stated that these column systems are unable to resolve DEM and MMC, a recent study has shown that the latter species is only a very minor component in gas condensate **(187)**.

Chromatograms of the condensate samples are shown in Figure 4.15. Figure 4.16 shows a condensate sample, BS 3/4, with and without spiking with selected mercury species. The recovery data from this experiment are shown in Table 4.7.

Species	Mercury Species Concentration (pg μl^{-1})				
	TC 123	TC 102	BS 1/2	TX 1	BS 3/4
Hg°	-	-	-	5.6	(0.5)
DMM	(0.8)	5.0	7.7	(2.4)	8.0
DEM	6.3	12.6	11.4	(1.0)	14.2
DPrM	(0.4)	14.4	(1.3)	(0.1)	10.3
DBM	-	(0.4)	-	(0.9)	7.3
DPM	-	-	-	8.1	(0.8)
Organo Hg (unknown) R_t = 26.3 mins	-	4.0	-	-	(1.1)
Total mercury species: (pg μl^{-1})	7.5 ± 0.6	36.4 ± 1.4	20.4 ± 2.5	18.3 ± 2.3 183.0 *	42.2 ± 2.2
No. of species detected	3	5	3	7	7

Note : * Corrected value for TX1 (10X dilution).

Response factors are based on calibration of elemental mercury

( ) = estimated value due to L.O.D.

ng ml^{-1} = pg μl^{-1}

Table 4.6 : Mercury species content and total mercury content for gas condensate samples - column RTx-1

Species	DMM	DEM	DPM
Recovery (%)	98.9 ± 5.1	89.6 ± 3.0	94.6 ± 4.3

Table 4.7 : Recovery data for mercury species spiked into condensate - column RTx-1

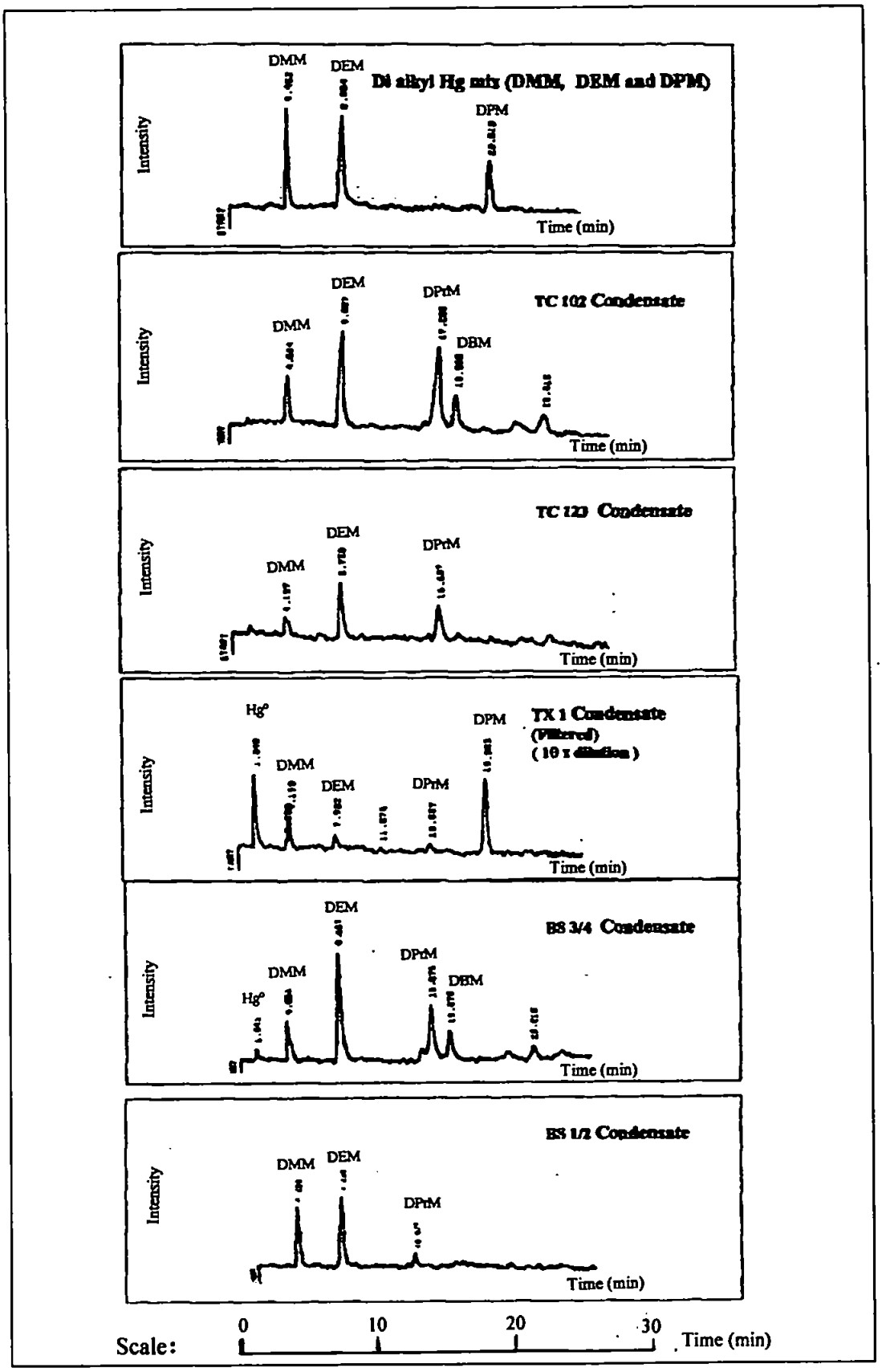


Figure 4.15 : Chromatograms for speciation of mercury in condensate samples

- Column RTx -1 (column flow rate 10 ml min $^{-1}$)

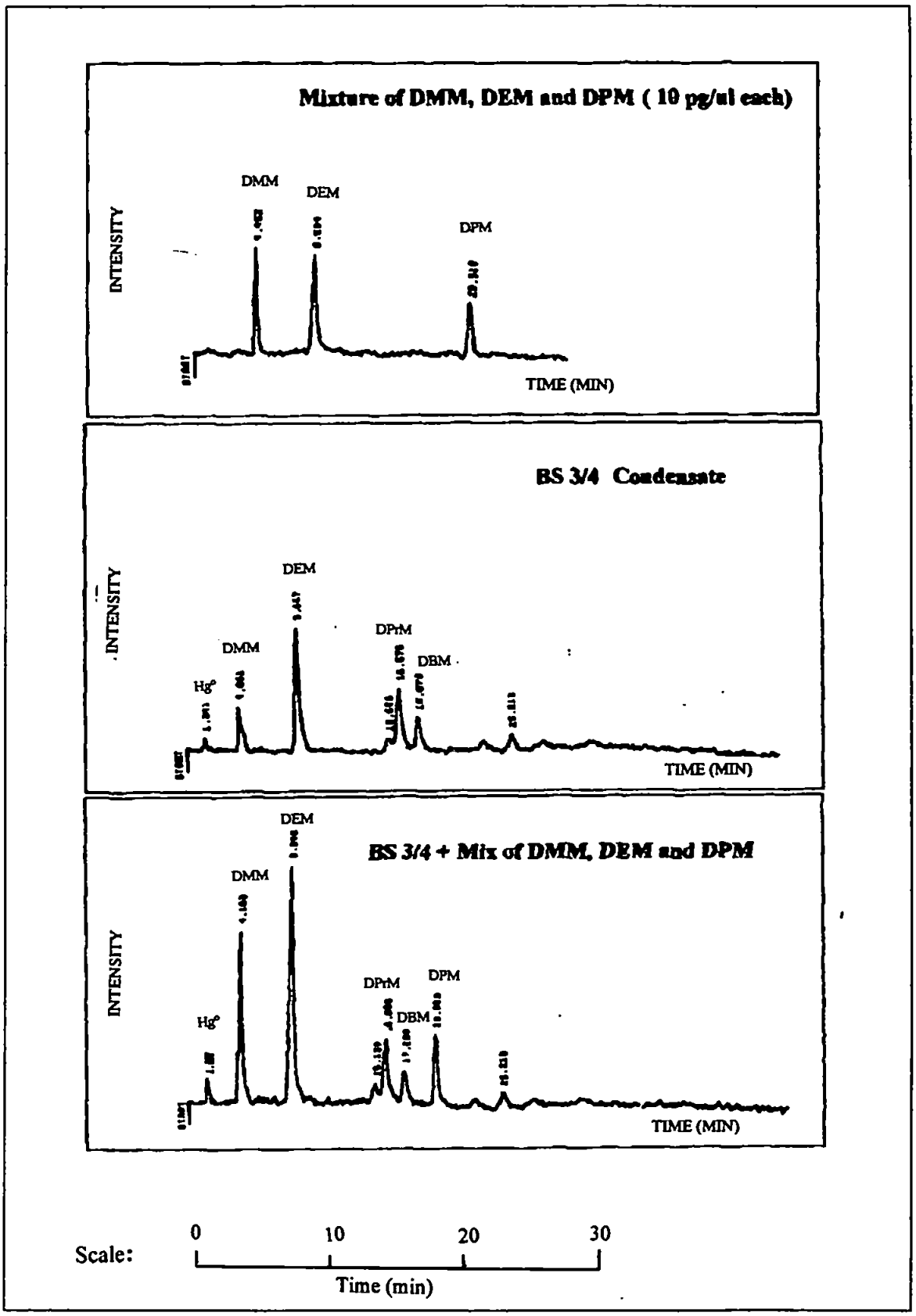


Figure 4.16 : Chromatograms of mixture of (DMM, DEM and DPM), BS 3/4 condensate and mixture of both - Column RTx-1 (column flow rate 10 ml min $^{-1}$)

4.3.10.2 The Cp-wax polar column

The results from running a similar set of gas condensate samples using Cp-wax column for mercury speciation are shown in Table 4.8. Again the major components shown to be DMM, DEM and DPrM. One sample TBHN1, is a condensate not from natural gas origin but from crude oil and is identified as naphtha condensate. As a result this sample shows a higher proportion of heavier dialkyl mercury species and include DBM.

The sample designated BS 3/4 is also noted to be heavier fraction of gas condensate. The presence of a higher boiling point fractions is again reflected in the distributions of mercury species i.e. the higher proportions of DBM and DPM.

Chromatograms of the condensate sample are as shown in Figure 4.17. Figure 4.18 shows a condensate sample, BS 3/4, with and without spiking with selected mercury species. The recovery data from this experiment are shown in Table 4.9.

Species	Mercury Species Concentration (*pg* μl $^{-1}$)				
	TC 123	TC 102	BS 1/2	TBHN 1	BS 3/4
Hg°	(1.2)	4.4	(1.1)	(0.6)	(2.3)
DMM	3.5	2.9	4.9	8.3	8.5
DEM	6.5	14.4	10.9	22.8	19.3
DPrM	(2.4)	11.1	3.9	33.7	13.9
DBM	-	(2.2)	-	13.1	5.9
Organo Hg (unknown) R_t = 14.7 mins	-	(1.0)	-	-	(1.7)
DPM	-	-	-	-	-
Total mercury species: (*pg* μl $^{-1}$)	13.6±1.1	36.1 ± 1.8	20.8 ± 3.4	78.5 ± 5.1	51.6 ± 3.2
No. of species detected	4	6	4	5	6

Note : Response factors are based on calibration of elemental mercury
( ) = estimated value due to L.O.D.
ng ml $^{-1}$ = pg μl $^{-1}$

Table 4.8 : Mercury species content and total mercury content for gas condensate samples - column Cp-wax

Species	DMM	DEM	DBM
Recovery (%)	90.1 ± 5.5	98.0 ± 4.5	91.6 ± 3.2

Table 4.9 : Recovery data for mercury species spiked into condensate -column Cp-wax

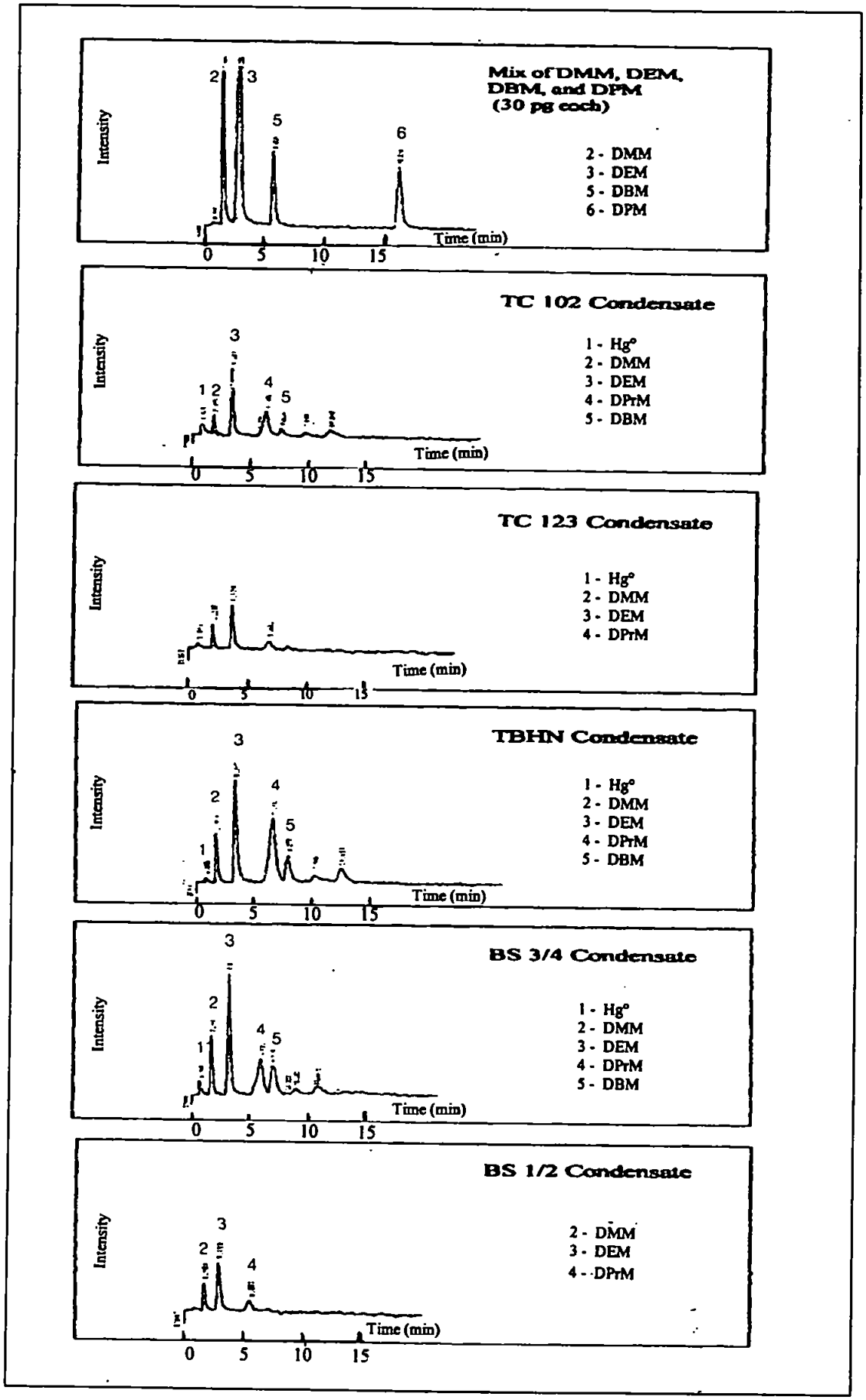


Figure 4.17 : Chromatograms of speciation of mercury in condensate samples

- Column Cp-Wax (column flow rate 10 ml min $^{-1}$)

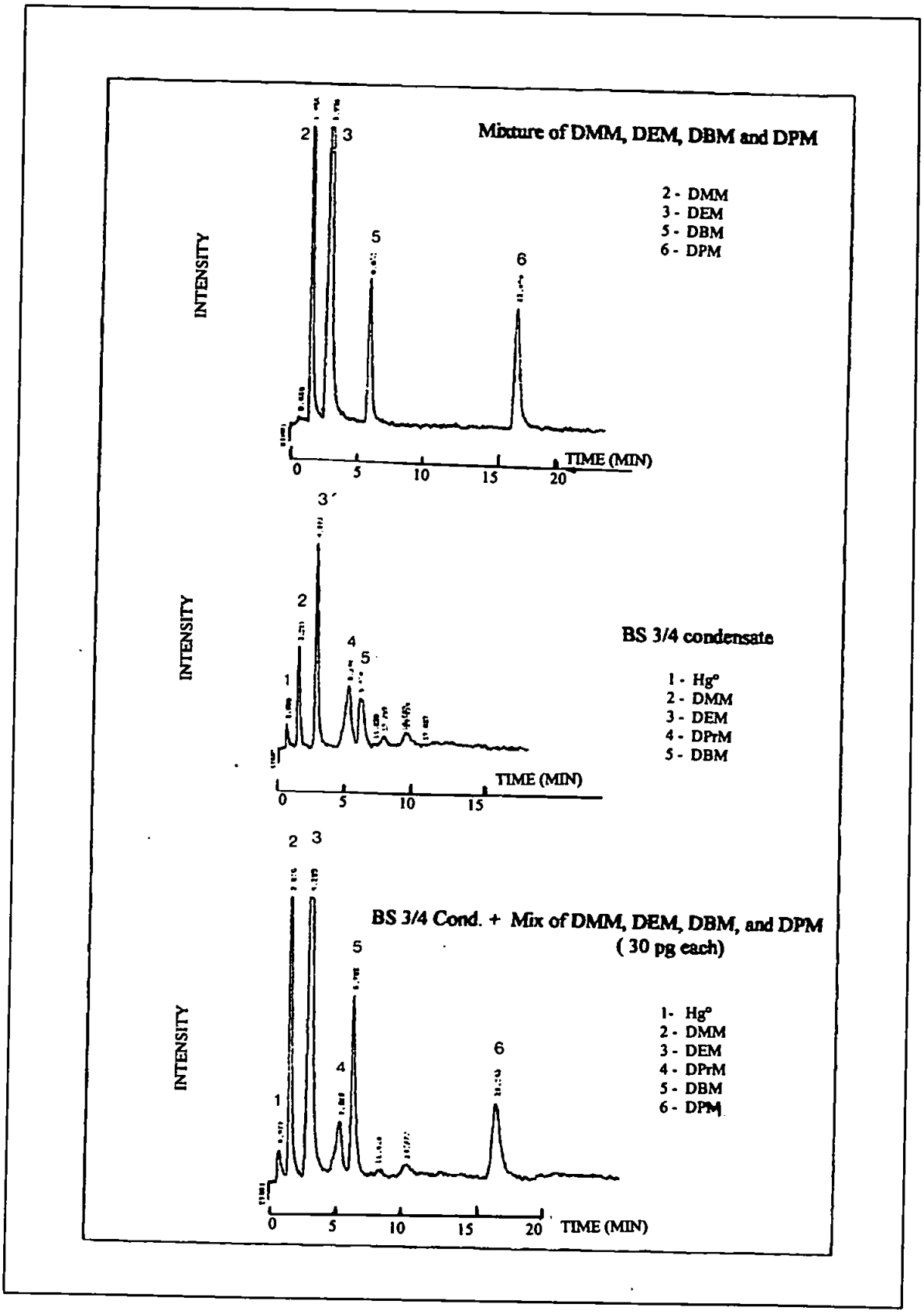


Figure 4.18: Chromatograms for mixtures DMM, DEM, DBM and DPM, BS 3/4 condensate and mixtures of both-Column Cp-Wax.
(column flow rate 10 ml min^{-1})

4.3.11 Mass balance calculations

The total mercury, calculated from the sum of individual species for each condensate was compared with its 'total' mercury content determined by the new vaporisation-trap-AFS technique reported in Chapter 3 **(188)**. This latter technique is based on a simple and reliable procedure for the determination of total mercury in natural gas condensate which eliminates the use of chemical/additives and complicated digestion procedures. The determinations were carried out by the direct vaporisation of samples at 400 °C with subsequent adsorption of mercury species by a gold-coated silica trap maintained at 200°C. To release metallic mercury, the trap was heated to 900 °C and the analyte determined by atomic fluorescence spectrometry. Taking into consideration the complexity of the sample together with, high volatility of both the matrix and mercury species , the total mercury results obtained from both techniques are reasonable agreement. These results, for both column systems, are shown in Table 4.10. One anomaly is seen. This is sample TC 123 using the CP-wax column with gave an abnormally high total mercury content from summation of the individual species. However, the major species seen in the sample, DEM is the same using both column systems, and both are in quantitative agreement (6.3 and 6.5 pg μl^{-1}, Table 4.6 and 4.8 respectively).

Species	Mercury Species Concentration (pg μl^{-1} = ng ml^{-1})					
	TC 123	TC 102	BS 1/2	TX 1	BS 3/4	TBHN 1
RTx-1	7.5 ± 2.3	36.4 ± 7.1	20.4 ± 4.8	183.0 ± 32	42.2 ± 8.9	-
Cp-wax	13.6 ± 3.4	36.1 ± 6.5	20.8 ± 5.2	-	51.6 ± 8.4	78.5 ± 10.2
Vaporisation technique	7.5 ± 0.3	43.3 ± 1.7	22.3 ± 1.4	187.2 ±16.1	49.7 ± 2.6	82.2 ± 4.5

Table 4.10 : Total mercury mass balance for condensate samples using colum systems RTx-1 and Cp-wax compared with vaporisation technique

4.4 CONCLUSIONS

The direct determination of mercury species in hydrocarbon liquids and gas condensate samples was carried out successfully by using both polar or non-polar megabore capillary columns. Of the two, the polar column exhibited slightly superior performance in terms of the elution of organomercury halide species. The use of megabore capillary columns permitted larger volumes of hydrocarbon samples to be injected and therefore improved sample loading. The injector port, which was maintained at 125 °C consisted of a deactivated silica liner for direct sample injections. This temperature was the highest that could be used safely without degradation or conversion of mercury species taking place.

Gas chromatography when coupled, *via* a pyrolysis unit with an AF detector, was able to determine mercury species directly in natural gas condensate at the picogram level. The instrumentation is relatively simple and easy to operate. No pre-treatment of the samples was required prior to mercury determination. The results obtained were reliable for a given column system and gave positive identification of organomercury species with the exception of DEM and MMC that co-elute.

The quantification of the species concentration can be made by using both calibration against elemental mercury and individual mercury species since the response of all species are nearly identical.

Mass balance calculations show a strong correlation between the total mercury content of a sample obtained from the vaporisation technique and the summation of all species eluted by GC-Pyrolysis-AFS.

The major species observed in condensate samples were DMM, DEM and the assumed DPrM. The presence and proportions of mercury species in gas condensate is highly

dependent upon the source, the stage of production, the sampling technique used, storage of the sample and age of the sample.

CHAPTER 5

THE PRELIMINARY EVALUATION OF AN ADSORBENT-BASED MERCURY REMOVAL SYSTEM FOR GAS CONDENSATE

CHAPTER 5

THE PRELIMINARY EVALUATION OF AN ADSORBENT-BASED MERCURY REMOVAL SYSTEM FOR GAS CONDENSATE

5.1 INTRODUCTION

Mercury removal systems for both gas and liquid hydrocarbon streams are commercially available. However, removal systems for natural gas condensates have not been thoroughly tested under real plant conditions. Only a few units have been installed in real plants and most of these were on a trial basis. One plant which possessed a mercury removal facility still experienced mercury contamination in their process steams i.e. only mercury metal vapour was targeted. This was due to little or no information **(103)** of the mercury species present in the streams. This lack of information leads to difficulties in deciding the most suitable removal system on both technical and economic grounds. In general, this limited knowledge on mercury in condensate arises because:

- The amount of mercury and the types of mercury species present are not easily determined. This is due to the nature of the samples. Natural gas condensates are very volatile complex mixtures. In addition, the mercury species are volatile and can be transformed into different forms of mercury, brought about by changes in their environment such as temperature, pressure and the presence of active particles or impurities.
- The techniques employed for the determination of mercury content in different process streams are not standardised, validated or well documented.

It is also noted that the problem arise at the process plant and laboratory level because:

- The removal system selected may not perform to expectation when installed in an actual, real plant environment due to unexpected interferences and the more challenging nature of the real plant environment.
- Among the plant's operators and laboratory staff, some may not be aware of the finer technical details required in mercury removal and determination, while others may not confide their expertise

5.1.1 Characteristics of the mercury-removal system

The characteristics required of any mercury removal system are as follows: **(10, 11, 13)**

- The removal agent must be highly active towards all forms of mercury, preferably bonding irreversibly to the agent (not to be re-released to the treated stream).
- The removal agent must remain active, i.e. the active surface must be resistant to blinding (or masking) by components in the stream being treated.
- The removal agent must not be harmful to the end use of the products, or potentially harmful to down-stream components, i.e. by leaching of chemicals or particulates.
- The system should ideally be flexible to the demanding and uncertain nature of conditions of feed and process streams.
- The removal agent should be inexpensive, readily available.
- The removal agent should hold the mercury in either a solid form, or in a liquid form from which it could be precipitated by a readily available agent and then filtratered and disposed.

5.1.2 Mercury-removal from natural gas condensate.

The removal of mercury from natural gas condensate is very different to that from natural gas because it is in the liquid phase during the operation and the main types of mercury present in the condensate are organometallic (> 80 % - refer to Chapter 4). At present, three 'technologies' are said to be effective for the removal of total mercury from feeds, destined for steam cracking or aromatisation (reforming). There are several manufacturers, but most of the products are still under development i.e. at the pilot plant stages. The removal systems can be divided into several types:

5.1.2.1 Sulphide-containing ion exchange resin material (23).

This system first developed by DSM of Holland claimed to be effective for the removal of elemental and organomercury halide. However, when considering the ion exchange characteristics, the effectiveness of the system in removing dialkyl mercury species, which are known to be non-ionic compounds, is not known.

The other examples of these system are, TP214 (Bayer), S-929 (Purolite International) and GT73 (Rohm and Haas)

5.1.2.2 Sulphide-containing alumina

One example of this system is that developed by Procatalyse, France. This system is only capable of adsorbing elemental mercury. In order for the removal system to include other species, e.g. organomercury species, a primary or pre-processing stage is required. This should convert all forms of mercury into the metallic species. Hence, this process is in two stages (7,105). The first stage of the process comprises a reactor loaded with a 'hydrogenolysis' catalyst, MEP841 (Procatalyse), operating under suitable conditions, in the presence of hydrogen, to convert both ionic and organomercury species present in the condensate into metallic mercury. This is subsequently trapped on the sulphide-containing

alumina in the second stage. However the efficiency of the first reactor to ultra convert trace concentrations of ionic and organomercury compounds into elemental mercury is in doubt because of the lack of speciation information post-processing. This is particularly important when the condensate contains alkyl mercury as the major species.

Another example of the two stage commercial removal system is that manufactured by the Japanese Gasoline Corporation, known as the JGC process **(106)**.

5.1.2.3 Other systems.

There are several manufacturers who also produce mercury-removal systems for gas condensate. However, these are still in the development stage. Two examples are:

i. Sulphur-containing molecular sieve by Katalco (5156, 5157).

ii. Sulphur-containing activated carbon by Calgon (HGR).

5.1.3 Aims of the study

The aim of this study was to assess the efficiency of three commercially available mercury removal systems in removing several mercury species particularly the alkyl mercury forms i.e. DMM, DEM and DBM from liquid hydrocarbon and gas condensate. This chapter presents the pilot plant performance of several commercially available adsorbents. Due to confidentiality, the commercial name of the removal system cannot be revealed. The adsorbents were designated adsorbent A, B, and C. In order to critically assess the efficiency of the B and C removal systems, the experiments were sample controlled using n-hexane with various species of organoalkyl mercury. Due to the specific two stage process of the AA removal system, the feed sample required had to be a real condensate.

5.2 EXPERIMENTAL

5.2.1 Chemicals

DMM, DEM and DBM (Strem Chemical, Massachusetts, USA) were used in the experiments either for calibration or for spiking into 'real' condensate samples or AnalaR n-hexane as a replacement for the condensate sample.

5.2.2 Identification of mercury removal adsorbents/catalyst

Two classes of mercury-removal system were identified. The classification was based on the number of stages that the process required. The adsorbent system designated A required a 2 stage process, i.e. hydrogenation prior to mercury removal. The adsorbent systems B and C only required a single stage i.e. direct adsorption.

For the A system, a hydrogenolysis catalyst was used to convert organo and inorganic mercury to elemental mercury and a sulphide-containing alumina was used for the removal of elemental mercury.

The B mercury-removal system, was a carbon based adsorbent which contained sulphur as the active material. The C mercury-removal system was a molecular sieve based adsorbent with undisclosed active material.

5.2.3 Testing Procedure.

5.2.3.1 Two stages process (Adsorbent AA)

A schematic diagram for the pilot plant is shown in Figure 5.1. The pilot unit contains three reactors. The hydrogenolysis reactor R1 is fed with an upward flow of condensate and loaded with hydrogenolysis catalyst (32 ml, four beds of catalyst) in order to transform the various mercury species to metallic mercury. The two other reactors, R2 and R3

contain the trapping media (32 ml) and are used in separate liquid and gas lines for removing elemental mercury.

Activation of the hydrogenolysis catalyst is required prior to processing and this is achieved by reducing the catalyst with hydrogen. The effect of this reduction is to remove the chloride precursor. The operating conditions for the activation process are as follows:

Pressure	30 bar
Temperature	300 ° C
Hydrogen flow	3 litres hour $^{-1}$
Liquid condensate flow	128 ml hour $^{-1}$
Duration	12 hours

At the end of the activation procedure, the reactor temperature is reduced to 150 °C under the same hydrogen flow rate and the condensate feed is injected when the temperature is stabilised. The hydrogenolysis reactor is maintained at 200 °C and the flow rate for the actual samples was set to 128 ml hr $^{-1}$ (Liquid Space Hourly Velocity (LSHV) 4 hour $^{-1}$). For mercury removal, reactors R2 and R3 are at the same flow rate as the R1 reactor, but maintained ambient temperatures.

The system was conditioned for 48 hours before the collection of condensate feed samples, samples after the R1 reactor and products from the R3 reactor.

5.2.3.2 Single stage process

Two types of adsorbent were tested using the single stage pilot plant. These were adsorbents B and C. The schematic diagram for the pilot plant is shown in Figure 5.2. The pilot plant consists of a single reactor R1 (diameter 4 cm, length 40 cm) and variable flow

liquid pump. The processes were operated at ambient temperature. The amount of adsorbent loaded in the reactor was 100 ml. The adsorbent was packed between two plugs of carborundum packing material. Prior to the actual run, the system was conditioned for six hours by introduction of mercury free n-hexane. The feed flow rate was set at 400 ml hr^{-1} (LSHV about 4 hr^{-1}). After completion of the conditioning stage, n-hexane spiked with organomercury species was introduced as feed. The system was stabilised for another two hours before collection of samples from both feed and product stages were taken (every two hours for mercury species determination).

The mercury removal process was carried out for a total of 8 hours. After this process, a mercury-free n-hexane feed was introduced and the reactor tube was reversed. Samples taken after the reactor were monitored for mercury species content. The experiments were only performed to assess the capability of the adsorbents at removing particular mercury species, i.e. the organomercury compounds. The adsorbing capacity or break through curve was not determined due to time constraints and specification limitations.

5.2.4 The determination of total and mercury species in samples

The determination of mercury species in the samples was carried out using gas chromatography coupled with pyrolysis-AFS. The details of this technique were discussed in Chapter 4.

For the adsorbent A system, the GC column used for speciation analysis of samples was an RTx-1 non-polar capillary column (i.d. 0.53 mm, 30 metre length and 1.0 μm film thickness). The operating conditions used were those given in Chapter 4, Table 4.1. For adsorbents B and C, the column used was a WCOT Ultimetal, with Cp-SimDist stationary phase,1.2 μm thickness, i.d. 0.53 mm, 10 metre length (Chrompac, Middleburg, The

Netherland). The operating conditions used for this column are shown in Table 5.5. The determination of the total mercury content in samples fed to the adsorbent A system was carried out using the vaporisation and trapping technique discussed in Chapter 3

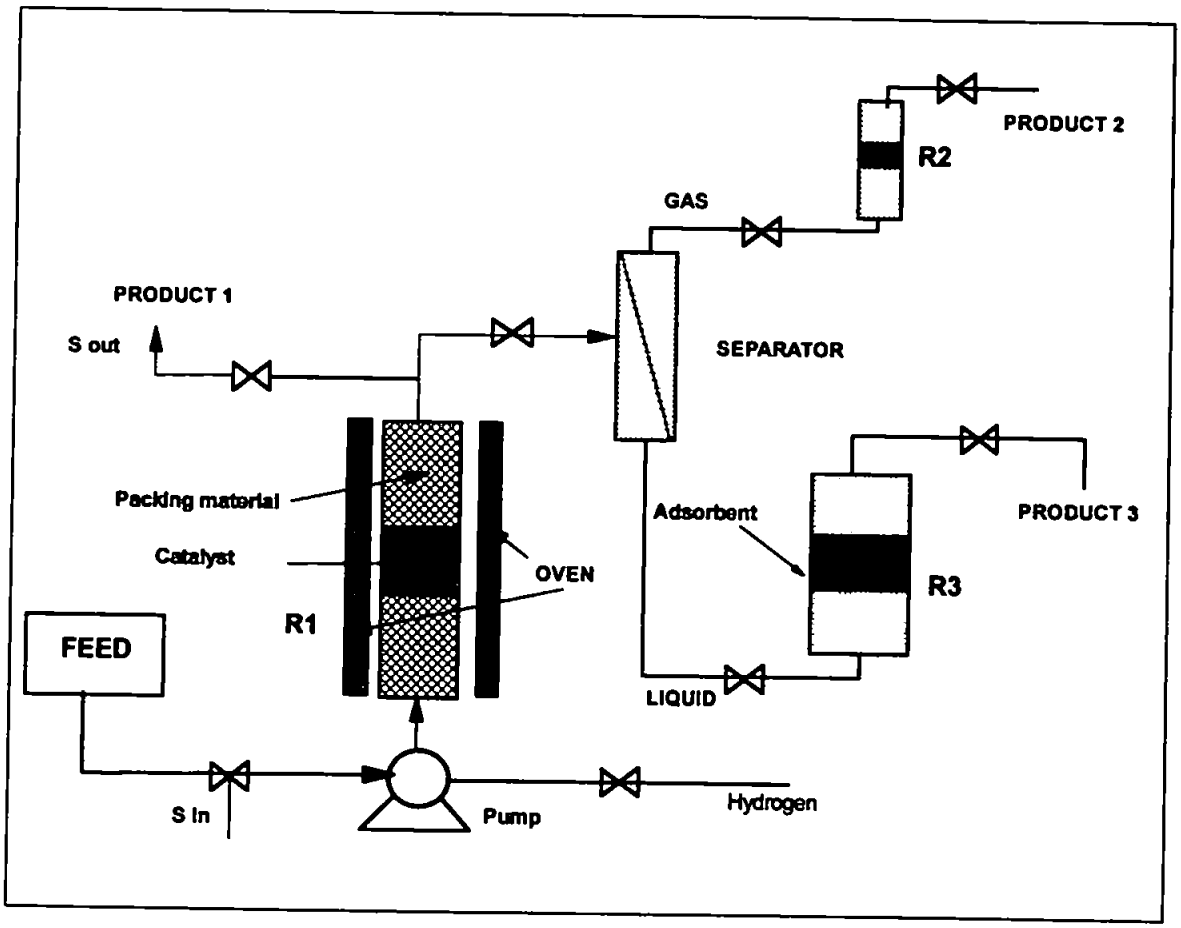


Figure 5.1 : A schematic diagram of the two stage mercury-removal pilot plant (lab scale)

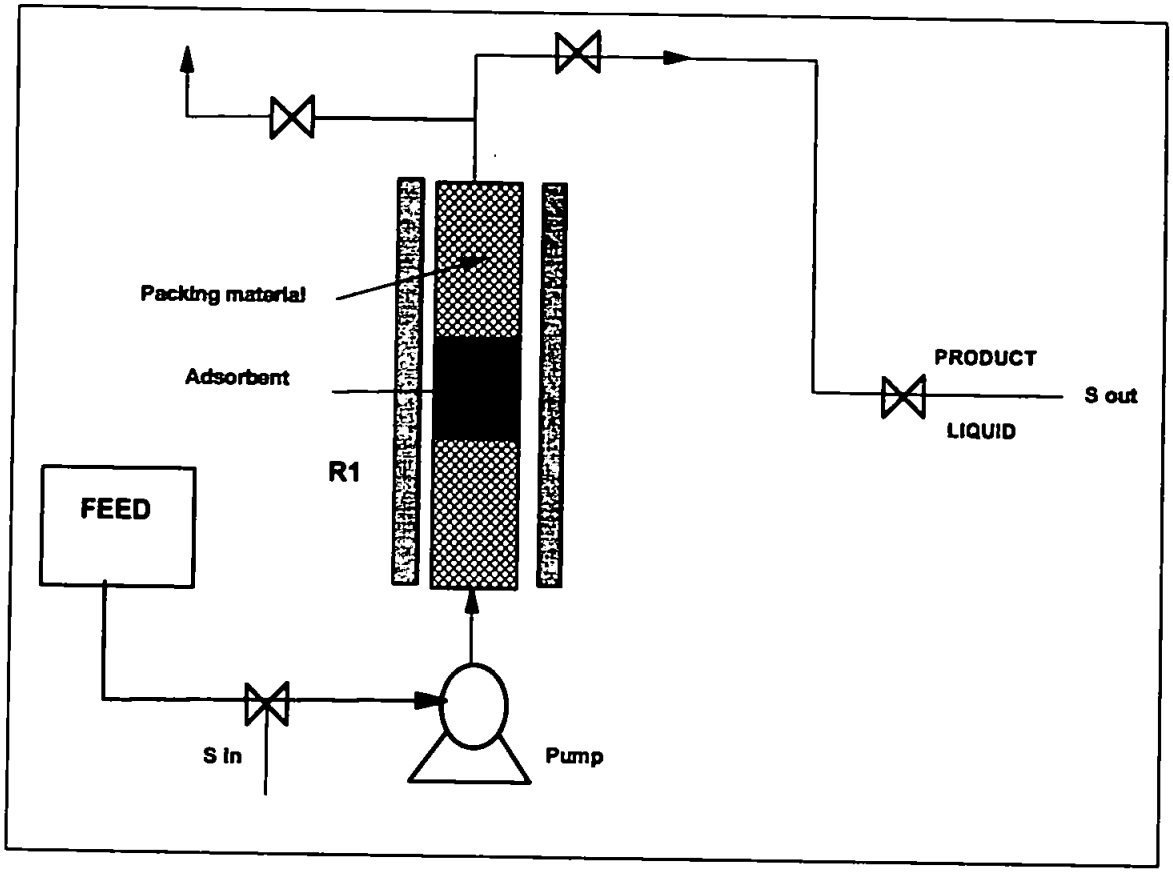


Figure 5.2 : A schematic diagram of the single stage mercury-removal pilot plant (labscale)

5.3 RESULTS AND DISCUSSION

5.3.1 Adsorbent A system

5.3.1.1 Total Mercury By Vaporisation-Trap-AFS

The total mercury contents for the 'condensate' feed sample, the sample after the hydrogenolysis reaction R1 and the sample after the mercury trapping reactor R3 are shown in Table 5.1. The results show that the system was unable to remove all mercury species in the condensate stream. The higher value for the sample from the reactor R1 may be, in part, due to a pre-concentration effect by this reactor and hence contributed to carry over effects.

Feed Average ± S.D. (ng ml $^{-1}$)	After hydrogenolysis reactor Average ± S.D. (ng ml $^{-1}$)	After mercury trapping reactor Average ± S.D. (ng ml $^{-1}$)
26.2 ± 1.3	**70.9 ± 8.1 ***	**17.8 ± 1.4**
*Based on 6 and 10 * replicates*		

Table 5.1 : Total Mercury Content in samples by the vaporisation technique-system A

5.3.1.2 Determination of mercury species content

The feed sample was found to contain 4 different mercury species as shown in Table 5.2. Two of these were identified as DMM and DEM. From the retention times the other two organomercury species were attributed to alkyl mercury species between DMM and DEM (possibly Methyl Ethyl Mercury (MEM) and Methyl Propyl Mercury (MPM))**(187)**. These species was not determined due to the absence of suitable standards and do not correspond to other species determined using this column system i.e. Hg°, DPrM, DBM, MMC, EMC, DPM and PMC. The presence of MEM in gas condensate has recently been identified **(187)**.

The samples after the hydrogenolysis reactor also nominally contain four species, Table 5.3, three of these were identified as elemental mercury, DMM and DEM. The fourth species was also attributed to a dialkyl mercury species (possibly MEM). These results show that the elemental mercury present was a conversion product from an organomercury species. However, the conversion was found to be only about 30 % of the total mercury in the sample. One other reason for the low elemental mercury could be that elemental mercury was carried over to the gas stream (via R2) instead of remaining in the liquid stream.

As stated previously, condensate can contain about 20 % wt of unsaturated hydrocarbons in the form of aromatic and olefin compounds. One possibility is that the hydrogenation process in reactor1, targets the unsaturated compounds rather than the organomercury itself. Hence the efficiency of conversion of the organomercury species to the elemental form is reduced by these components. One important drawback to this two stage process is that the feed condensate has to be hydrogenated. This changes the grade of condensate, in particular the aromatic content, which defines its quality. A downgraded product is therefore created in order for partial mercury removal to be achieved.

The mercury species found in the sample after the mercury trapping reactor, Table 5.4, were DMM, DEM and the two other previously attributed alkyl mercury species. No elemental mercury was detected. This indicated that the elemental mercury from the first reaction had been adsorbed by the second trapping reactor. Examples of the chromatograms for the three sample stages including the standard mercury species are shown in Figure 5.3.

Peak No	RT (min) ± 0.5 min	FEED CONDENSATE		Species
		Area %	Mercury Content calculated based on Total mercury analysis (ng ml $^{-1}$)	
1	1.7	0	0	Hg°
2	5.5	10.3 ± 0.5	2.7	DMM
3	9.5	43.4 ± 5.1	11.3	Dialkyl Hg Species
4	12.5	29.2 ± 5.1	7.7	DEM
5	13.5	17.1 ± 1.8	4.5	Dialkyl Hg Species
Total			26.2	
S.D. base on 4 replicate analyses				

Table 5.2 : Speciation data for feed condensate- system A

Peak No	RT (min) ± 0.5 min	CONDENSATE AFTER HYDROGENOLYSIS REACTOR (R1)		Species
		Area %	Mercury Content calculated based on Total mercury analysis (ng ml $^{-1}$)	
1	1.7	33.4 ± 3.2	23.7	Hg°
2	5.5	8.1 ± 1.1	5.8	DMM
3	9.5	39.0 ± 2.9	27.6	Dialkyl Hg Species
4	12.5	19.5 ± 1.4	13.8	DEM
5	13.5	0	0	Dialkyl Hg Species
Total			70.9	
S.D. base on 4 replicate analyses				

Table 5.3 : Speciation data for samples after the hydrogenolysis reactor R1 (system A)

Peak No	RT (min) ± 0.5 min	CONDENSATE AFTER TRAPPING MERCURY REACTOR (R3)		Species
		Area %	Mercury Content calculated based on Total mercury analysis (ng ml $^{-1}$)	
1	1.7	0	0	Hg°
2	5.5	11.3 ± 0.1	2	DMM
3	9.5	50.3 ± 0.7	9.0	Dialkyl Hg Species
4	12.5	38.4 ± 1.7	6.8	DEM
5	13.5	0	0	Dialkyl Hg Species
Total			17.8	
S.D. base on 4 replicate analyses				

Table 5.4 : Speciation data for sample after the mercury trapping reactor R3 (system A)

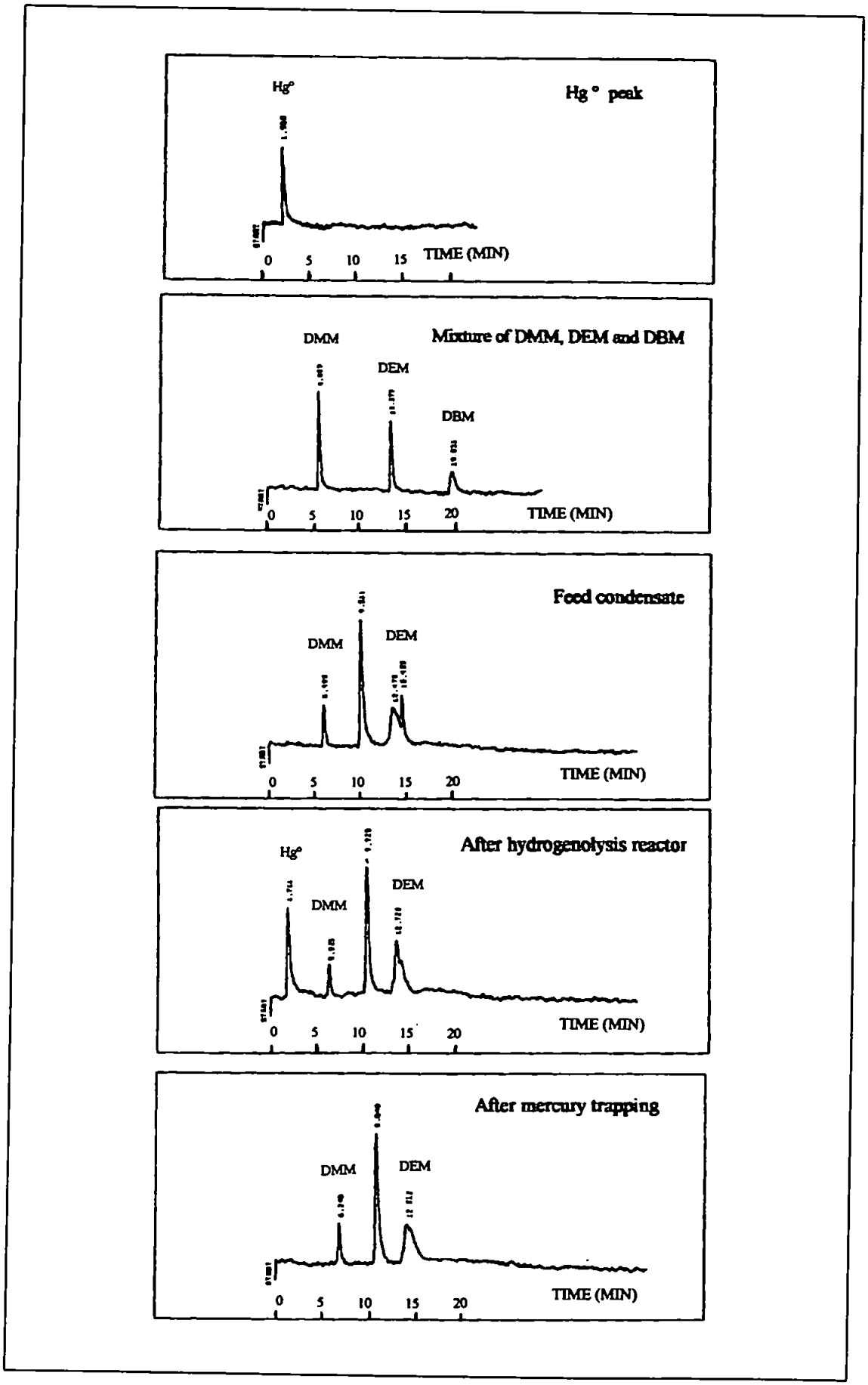


Figure 5.3: Mercury chromatograms from feed, hydrogenolysis reactor and trapping reactor samples.

5.3.2 Adsorbent B

Adsorbent B was a carbon based product impregnated with a sulphur compound. The species identification in the feed samples and product (after trapping) samples are shown in Table 5.5. Three species of organomercury (DMM, DEM and DBM) were spiked into the n-hexane (20, 30 and 20 ng ml^{-1} respectively as Hg). There were no peaks detected in the product samples after the reactor i.e. the removal of mercury species spiked into the feed stream was 100 % efficient. Examples of the chromatograms before and after the reactor are shown in Figure 5.4.

ADSORBENT : B (Carbon Based)						
Sampling No	Feed			Product		
	Area (x 10^6)			Area (x 10^6)		
	Peak 1 (DMM)	Peak 2 (DEM)	Peak 3 (DBM)	Peak 1 (DMM)	Peak 2 (DEM)	Peak 3 (DBM)
Sample 1 11.00 hrs	9.1	16.4	9.7	0	0	0
Sample 2 13.00 hrs	8.9	15.9	8.1	0	0	0
Sample 3 15.00 hrs	7.9	15.4	9.1	0	0	0
Sample 4 17.00 hrs	6. 8	14.9	9.4	0	0	0
Overall	8.2 ± 1.1	15.7 ± 0.7	8.9 ± 0.7	0	0	0

Column used : WCOT Ultimetal, with Cp-SimDist stationary phase (1.2 μm thickness, i.d. 0.53mm, 10 metre length)
Column flow rate : 5 ml min^{-1} Argon
Oven temperature : 35 °C (5 min) to 300 °C (5 °C min^{-1})

Table 5.5 : Mercury species before and after removal system for adsorbent B

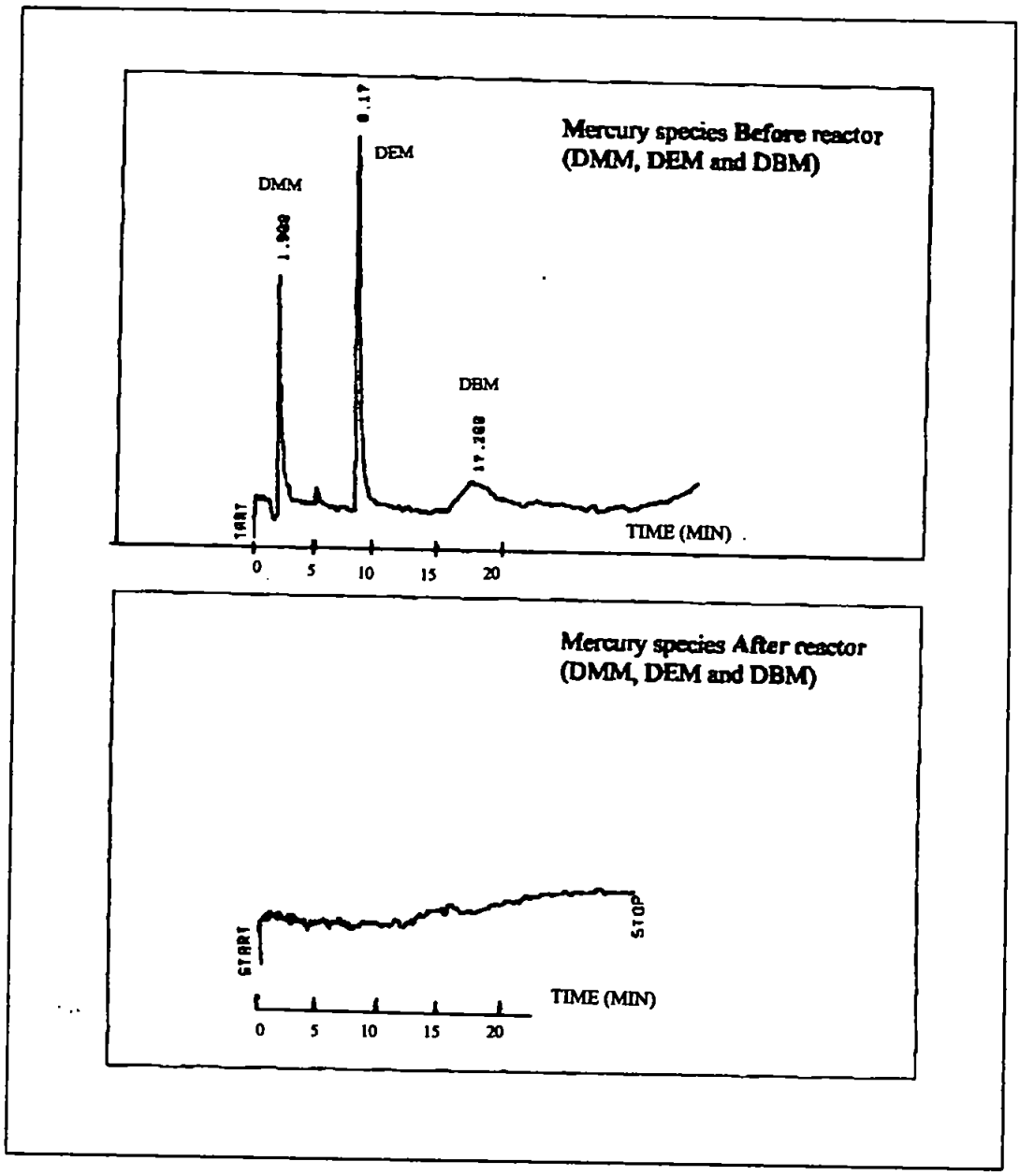


Figure 5.4: Chromatogram for mercury species before and after removal system (B)

5.3.3 Adsorbent C

The performance of this mercury species- removing adsorbent is shown in Table 5.6. The concentration of species in n-hexane was 20 ng ml $^{-1}$ DMM, DEM and DBM each as Hg. From the results after the reactor, there was some reduction of the DMM peak (from 20 ng ml $^{-1}$ in feed to 9 ng ml $^{-1}$ in sample after the reactor). The DEM species was detected in some of the collected samples with the concentration in the range 4 to 8 ng ml $^{-1}$. However the peak area of DBM while showing a reduction during the initial stages i.e. after two

hours the DBM content had reduced by 83 %, then began to increase with reaction time showing a dramatic increase after four hours. One possibility is that the DBM species was temporarily contained in the reactor (chromatographic effect) then re-released to the stream in a similar 'manner'to an eluent exiting a column. An alternative to this is an effect due to competition for active sites. The overall performance of the adsorbent in removing DMM, DEM and DBM species was 55, 80 and 22 % respectively. Examples of the chromatograms are shown in Figure 5.5.

ADSORBENT : C (Molecular sieve Based)						
Sampling No	Feed			Product		
	Area(x 10^6)			Area (x 10^6)		
	Peak 1 (DMM)	Peak 2 (DEM)	Peak 3 (DBM)	Peak 1 (DMM)	Peak 2 (DEM)	Peak 3 (DBM)
Sample 1 11.00 hrs	8.5	7.9	16.4	3.8	2.9	2.8
Sample 2 13.00 hrs	8.1	7.7	16.10	3.9	0	4.5
Sample 3 15.00 hrs	8.8	8.2	15.8	3.9	0	13.4
Sample 4 17.00 hrs	8.1	7.2	16.2	3.8	1.4	29.4
Overall	8.4 ± 0.4	7.8 ± 0.4	16.1 ± 0.2	3.8 ± 0.1	1.1 ± 1.3	12.5 ± 12.1

Column used : WCOT Ultimetal, with Cp-SimDist stationary phase (1.2 μm thickness , i.d. 0.53 mm, 10 metre length)
Column flow rate : 5 ml min^{-1} Argon
Oven temperature : 35 °C (5 min) to 300 °C (5 °C min^{-1})

Table 5.6: Mercury species before and after removal unit for adsorbent C.

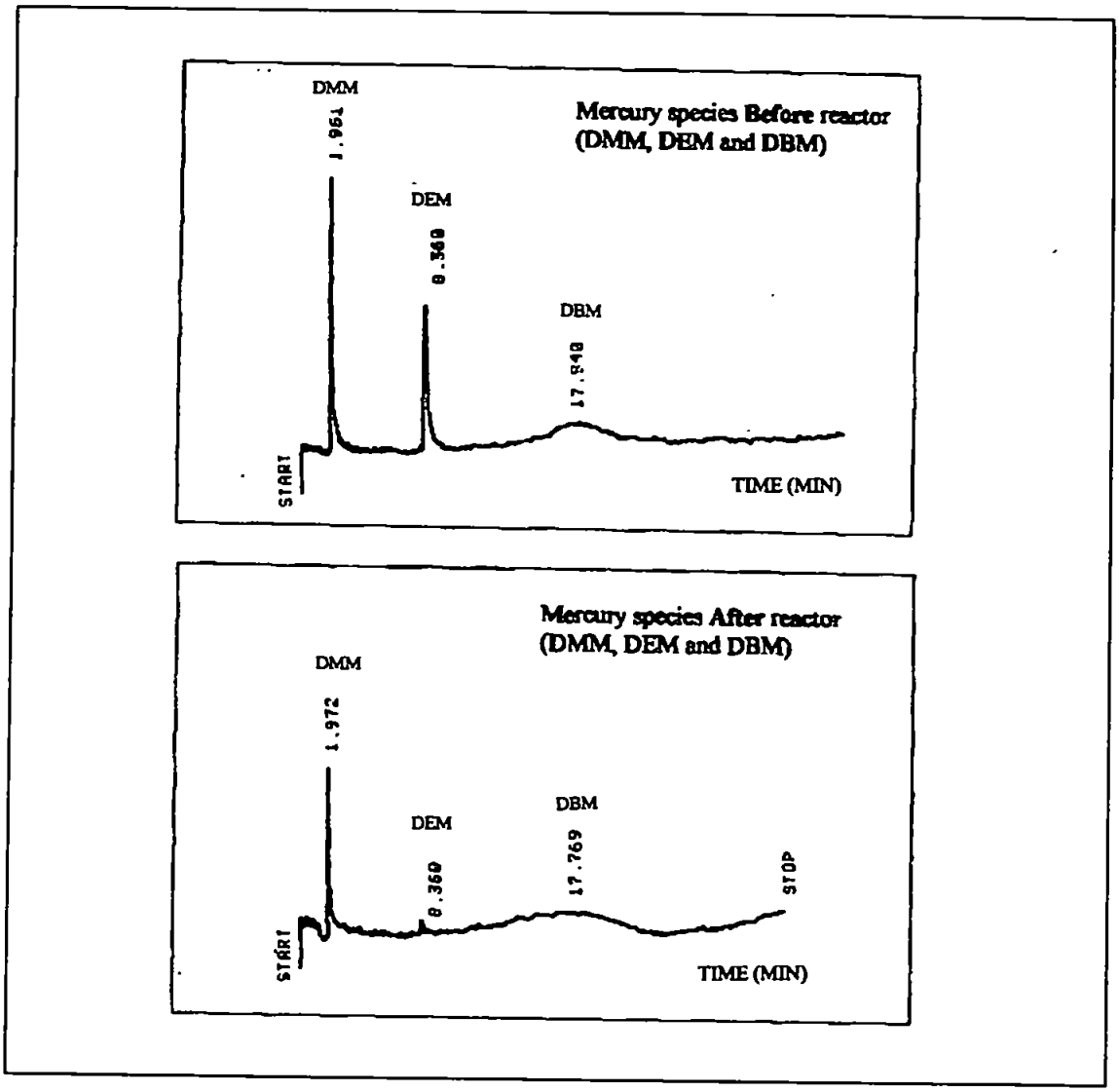


Figure 5.5 : Example of mercury chromatograms before and after removal unit for adsorbent C

5.4 CONCLUSION

All three pilot plant-tested mercury-removal systems A, B and C showed a reduction in the mercury content of the final products. For the adsorbent system A, the hydrogenolysis reactor was able to convert some of the organomercury present in the gas condensate feed to its elemental form. However the amount of elemental mercury measured was only about 30 % of the total mercury content. Incomplete conversion of the organomercury species to mercury metal may be due to competition between the organomercury species and the

unsaturated compounds in the matrix during the hydrogenation reaction. One other reason could be that elemental mercury was carried over to the gas stream instead of remaining in the liquid stream. The result from the first reactor (hydrogenation) also showed a higher total mercury content compared with the feed condensate. This could be due to a pre-concentration effect resulting in mercury carry- over by the liquid condensate stream to the adsorber. The second reactor (mercury trapping) was able to adsorb elemental mercury present in the stream (the product from the first reactor) but was unable to remove the organomercury content from the condensate stream.

For the single stage adsorbent system B, the efficiency in removing spikes of DMM, DEM and DBM from the n-hexane hydrocarbon sample was very high. Removal of the species was 100 % with no indication of mercury present in the product. For adsorbent system C, efficiency of removal for the different mercury species spiked into the n-hexane was variable. Over 50 % of DMM was removed using the adsorbent, while the DEM showed a range of 60 to 80 % removal. The DBM was initially adsorbed efficiently (>80% at two hours) but was rapidly released back into the product stream after four hours.

The above results indicated that speciation of the mercury content is vital in the evaluation of an adsorbent systems efficiency. The performance of an adsorbent was dependent upon the type of adsorbent and, for the A and C systems, the mercury species present in the feed stream. The determination of total mercury only in feed and product samples in the system will not give all the necessary information for an unbiased evaluation to be made of the performance of an adsorbent.

The results obtained, while indicative of the adsorbents performance are no guarantee of their efficiency using a real sample and should only be used as a guide. Those adsorbents

which show a suitable potential for removing mercury species, will require longer pilot plant studies using real gas condensate as the feed over a longer monitoring plant period.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

The study which investigated the recovery of various organic and inorganic mercury species, spiked into synthetic and real condensate samples using different digestion and/or extraction techniques, showed that recovery was dependent upon the speciation.

Using a persulphate digestion technique, the recovery of an organomercury standard was less than 30 %. Further experiments indicated that the persulphate added for the digestion step had been consumed by the sample matrix rather than targeting the mercury species.

When using the iodide/iodate digestion technique, only one mercury species, DPM, gave full recoveries. Other mercury species, EMC, PMC and DMM gave recovery values of less than 50 %.

The extraction procedures involving complexation with dithizone and/or thiosulphate were found to be unsuitable for 'real' condensate samples. Very low recoveries, less than 18%, of various mercury species were obtained.

The combined extraction and digestion technique involving L-cysteine and potassium persulphate gave encouraging results with recoveries of over 90 % for the species DPM, EMC, MC and PMC. However, one species of considerable interest in gas condensate is DMM and using this procedure a recovery value of 15 % was observed. Further studies of the critical extraction and digestion parameters failed to improve the recovery value for DMM.

It was concluded that the favoured procedures previously used for digestion and/or extraction of mercury species from water and sediment samples together with some modified and new procedures were of limited application to gas condensates. This was in-part, if not entirely, due to the complex and volatile nature of the non-polar organic liquid sample which contained only ultra-trace levels of different mercury species.

A relatively simple, rapid, accurate and precise technique for the determination of total mercury in gas condensate and other liquid hydrocarbon samples has been developed. A glass chamber, maintained at 400 °C was used to vaporise samples which were carried in argon, *via* a heated transfer line, to a gold-coated silica trap held at 200 °C. At this temperature the mercury species were adsorbed efficiently and retained on the trap while the complex volatile matrix was swept to waste. Elemental mercury was released rapidly when the trap temperature was raised to 900 °C and swept with argon gas to an atomic fluorescence detector for measurement.

Experiments which investigated the optimum operating conditions, sample volumes and certain design characteristics of the technique showed that the double-sized trap was required to retain mercury species efficiently for sample volumes up to 1.0 ml. An argon carrier flow rate of 300 ml min^{-1} was used to transport the matrix and the mercury vapour in the system. The sample vaporisation time was dependent upon the sample volume and sample type (usually 5 to 10 minutes for 0.25 to 0.5 ml of condensate).

The recoveries for eight different mercury species spiked in toluene and in 'real' gas condensate (10 to 50 ng ml^{-1}) were generally over 90 %. The types of species studied were dialkyl and diaryl mercury, alkyl mercury chloride, aryl mercury chloride, mercury chloride and organo-thio mercury. The absolute limit of detection for a mercury species spiked into

gas condensate, for example DEM, was found to be 270 pg. This corresponded to, approximately 1 ng ml $^{-1}$ for a 0.25 ml sample injection. When injection errors were removed, the limit of detection corresponded to 11 pg (absolute).

Five 'real' gas condensate samples gave total mercury values between 7.5 and 50 ng ml $^{-1}$. When the technique was extended to look at the mercury content of light fraction 'gasolines' at ultra-trace level (< 1 ng ml $^{-1}$ mercury) sample volumes of 1.0 ml were required. Total mercury values ranged from 42 to 87 pg ml^{-1} for different 'gasolines'. In order to measure the mercury content of 'higher fraction' oils, samples were required to be mixed with a suitable solvent e.g. toluene. This was to increase their vaporisation rate and to remove the trap-based interference effect from the very high boiling point components of the matrix. It was also evident that the mercury content of the 'heavy' oil sample was much higher than gas condensates (ranging from 2 to 22 μg ml $^{-1}$) and a dilution step was necessary for this sample type. Sample dilutions in the range 20 to 100 times were found to be effective.

Gas chromatography when coupled, *via* a pyrolysis unit, with an AF detector was able to determine mercury species directly in natural gas condensate at the picogram level. The instrumentation is relatively simple and easy to operate. No pre-treatment of the samples was required prior to mercury determination. The results obtained were reliable for a given column system and gave positive identification of the organomercury species, DMM, DEM, DBM, DPM, MMC, EMC, and PMC. It was noted that the species DEM and MMC co-eluted when both were present in a synthetic mixture.

Direct sample injection were performed into a deactivated silica liner maintained at 125 °C in the injector port. This temperature was the highest that could safely be used without degradation or conversion of mercury species taking place.

The direct determination of mercury species in hydrocarbon liquids and gas condensate samples was carried out successfully by using both polar or non-polar megabore capillary columns. The use of megabore capillary columns permitted larger volumes of hydrocarbon samples to be injected and therefore improved sample loading and the limits of detection for mercury species (2.5 to 7 pg, absolute, for 1.0 μl injections of a range of species).

The slopes of the calibration graphs from different organomercury species were found to be nearly identical to that of elemental mercury. This response effect allowed unidentified species to be quantified in terms of their mercury contribution.

The major species observed in condensate samples were DMM, DEM and the assumed DPrM. Mass balance calculations show a strong correlation between the total mercury content of a sample obtained from the vaporisation technique and the summation of all species determined by GC-Pyrolysis-AFS.

The presence and proportions of certain mercury species in gas condensate are highly dependent upon the source, the stage of production, the sampling technique used, storage of the sample and age of the sample.

All three pilot plant-tested mercury-removal systems A, B and C showed a reduction in the mercury content of the final products. In the two stage system, A, the hydrogenolysis reactor converted some of the organomercury present in the gas condensate feed to its

elemental form. However the elemental mercury measured in the liquid product from this first reactor was only about 30 % of the total mercury content. Incomplete conversion of the organomercury species to mercury metal by this reactor may be due to competition between the organomercury species and the unsaturated compounds in the matrix during the hydrogenation reaction. The second reactor, for mercury trapping, was able to adsorb elemental mercury present in the liquid stream (the product from the first reactor) but was unable to remove the organomercury content from the condensate stream.

For the single stage adsorbent system B, the efficiency in removing the species DMM, DEM and DBM from n-hexane hydrocarbon samples was 100 % with no indication of mercury present in the product stream over an eight hours continuous run.

For the adsorbent system C, the efficiency of removal for different mercury species in n-hexane was variable. While DMM and DEM showed a consistent removal range of 50 to 80 %, the DBM was efficiently adsorbed, but only for a short period (> 80 % at two hours) and it was rapidly released back into the product stream after four hours.

Speciation of the mercury content of gas condensates is vital in the evaluation of an adsorbent systems efficiency. The determination of total mercury only in feed and product samples in the system will not give all the necessary information.

6.2 FUTURE WORK

The vaporisation and trapping technique at elevated temperatures, discussed in Chapter 3, was very successful for the determination of total mercury in natural gas condensate samples and other liquid hydrocarbons. This technique could be extended to include other samples types that are related to the petroleum industry as well as to general environmental samples. For the former this could include heavy crude and fuel oils, waste waters and sludges; all of which are produced in very large volumes during the processing of gas and oil. Many of these sample types are discharged to the environment after only limited treatment and the monitoring of toxic elements, especially mercury, in these samples is very important. For its determination, some modifications of the technique will be required, especially with regard to the sample introduction system.

The high 'total mercury' content of the heavier oils may be due to the presence of sulphur-bonded species. One possible route to the speciation of its mercury content could be from the use of suitably high ratio mixing with solvent (1:500) prior to direct injection into the GC-pyro-AFS system.

Although not tried to date with the vaporisation technique, an extension should be made to include (i) organic liquid extractions of solid samples, and (ii) aqueous samples directly, in order to determine their total mercury content. The ability to determine the mercury species in these organic extractants is also possible given the results from the column speciation studies in Chapter 4.

The performance of two types of megabore column, polar and non-polar were evaluated in Chapter 4 in terms of their ability to separate and identify mercury species in natural gas condensate. Both columns were able to separate several dialkyl mercury species that were

likely to be present in natural gas condensate while only the polar column could be used for separation of several organomercury halide species. However, it was found that the MMC species was eluted at the same retention time as DEM for both column. Although the presence of MMC in gas condensate is still in debate (and if present, is it only a very minor constituent) a study of other column types should be made to bring about their separation. The use of columns with different stationary phases/different polarity, pre-treatment or chemical modification may be introduced. One important modification to the operating conditions should, however, be tried first with the current polar column. That is the use of a cryogenic oven to extend the programme facility and take greater advantage of the physical properties of the species.

The distribution and concentration of total mercury and its species in a condensate line from a processing plant has not been performed to date because of the analytical problem discussed in this thesis. a comprehensive i.e. mass balance, study can now be carried out using the technique developed and discussed in Chapter 3 and 4. This information is very important, not only for processing purposes, but also for monitoring the safety implications for the food chain and the environment.

The efficiencies of different commercially available adsorbents in removing mercury from condensates, on a laboratory/pilot scale are varied and are dependent upon the type of adsorbent, the mercury species present and the type of feed. Of the three mercury removal systems tested to date, only 'adsorbent B' showed the required removal efficiencies (100%) for the major mercury species expected in condensates. However, this trial was performed using a substitute, liquid hydrocarbon. Pilot tests using real gas condensate should be performed, prior to any larger scale studies together with break-through capacities and life time efficiencies. Other commercial adsorbents can be evaluated and all can be ranked in

terms of their efficiency for mercury removal from condensates under real plant conditions together with their cost implications. Such an undertaking could not be considered feasible prior to the research and development contained in this thesis.

It was found, from the studies shown in Chapter 2, that the digestion and/or extraction techniques, used for the determination of total mercury in hydrocarbon samples were species dependent. These reactions were based upon both known and new liquid-liquid phase systems. However, the results from Chapter 5 indicate that an adsorber, such as the type 'BB' (sulphur on carbon), could have some promise as a solid-phase extractor for total mercury measurement. A study of this material. and similar types should be made to evaluate their use as a solid-phase 'total mercury remover' from hydrocarbon, condensate and aqueous samples. Both batch and column systems could be employed, with separation if necessary, prior to a suitable aqueous digestion or stripping technique being used to release the mercury for its total determination.

CHAPTER 7

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PUBLICATIONS

1. Shafawi, A., Foulkes, M.E., Ebdon, L., Stockwell, P.B., and Corns, W.T., 'The Determination of Total Mercury in Natural Gas Condensate by Atomic Fluorescence Spectrometry', *Analyst*, (in press)

2. Shafawi, A., Foulkes, M.E., Ebdon, L., Stockwell, P.B., and Corns, W.T., 'Mercury Speciation in Natural Gas Condensate by Gas Chromatography Coupled with Atomic Fluorescence Spectrometry', submitted to *J. Anal. At. Spectrom.*

3 Shafawi, A., Foulkes, M.E., Ebdon, L., Stockwell, P.B., and Corns, W.T., 'The Preliminary Evaluation of Adsorbent-Based Mercury Removal system for Gas, submitted to *Anal. Chim. Acta.*

PRESENTATIONS

1. *A study of The Total Mercury and mercury Species Content of natural Gas an Gas Condensate*, presented at Eighth Biennial National Atomic Spectroscopy Symposium, University of East Anglia, 17-19 July, 1996

2. *A Simplistic and Reliable Method for The Determination of Mercury in Condensate*, presented at The Pittsburgh Conference (PITTCON '98), New Orleans, USA, 1-5 March, 1998.

3. *Determination of Mercury Levels in Petrochemicals by Atomic Fluorescence Spectrometry*, presented at Ninth Biennial National Atomic Spectroscopy Symposium, University of Bath, 8-10 July, 1998.

4. *The Determination of Total Mercury and Mercury Species in Natural Gas Condensate: Yesterday, Today and Tommorrow*, presented at 'Malaysian Gas Processor and Oil Refiner Workshop', Petroleum Research Institute, Petronas, Kuala Lumpur, Malaysia, 26 August 1998.