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Emission of toxic organic microcontaminants from ship's engines:
First measurements on three cruising ships

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CONTENTS

SUMMARY

On three cruising ships the engine emissions have been measured for:
- hexachlorobenzene and polychlorinated biphenyls,
- polychlorinated dibenzodioxins and furans,
- polycyclic aromatic hydrocarbons,
- nitro-polycyclic aromatic hydrocarbons.

The levels found are given below:

Compounds	Units	S1	S3	S5
HCB + PCB	ng/m^3	20 - 60	90 - 240	< 60
Σ 17 PCDD/F	ng/m^3	0.09 - 0.2	0.01 - 0.04	0.002 - 0.2
PAH	μg/m^3	64 - 92	29 - 52	13 - 29
mono-NO$_2$-PAH	μg/m^3	1.7 - 10	0.20 - 0.36	0.74 - 3.6

Concerning the results for the NO$_2$-PAH of S1, one has to be aware that due to the extreme sampling conditions, the NO$_2$-PAH levels are probably lower than found here. Next, due to the measured breakthrough, the PAH levels emitted by S1 are probably higher than reported here. Overall, the PCDD/F and PCB emissions are rather low. The PAH emissions are considered representative for all ship's emissions on the North Sea, shipping contributes relatively little to the atmospheric deposition of these substances on the North Sea.

A few recommendations are made for future studies.

LIST OF ABBREVIATIONS

GC-ECD	GasChromatography with Electron Capture Detection
GC-MSD	GasChromatography with Mass Selective Detection
HCB	HexaChloro Benzene
HPLC	High Performance Liquid Chromtography
HRGC	High Resolution Gas Chromatography
HRMS	High Resolution Mass Spectrometry
IMW	dutch abbrev. for "Institute for Environmental Sciences"
ng	nanogram (10 exp.-9 gram)
nm	nanometer
pg	picogram (10 exp.-12 gram)
PAH	Polycyclic Aromatic Hydrocarbon(s)
Nitro-PAH	Nitro-PolyCyclic Aromatic Hydrocarbon(s)
NO_2-PAH	ibid.
PCB	PolyChlorinated Biphenyl(s)
PCDD/F	PolyChlorinated DibenzoDioxin(s) and -Furans
PUF	PolyUrethane Foam
TNO	dutch abbrev. for (the Netherlands Organisation for) Applied Scientific Research
TOCl	Total Organic Chlorine
TOX	Total Organic Halogen (= Cl + Br + I ; F excluded !)

1.   INTRODUCTION

This work was undertaken within the framework of Lloyd's Register's Marine Exhaust Emissions Research Programme. Phase II of this research programme [1] evaluated exhaust emissions from ships in service under steady state and transient modes of operation and incorporated measurements of CO, CO_2, O_2, SO_2, NO_x and hydrocarbons on board eight ships. Additional measurements of heavy metal and organic micropollutant emissions were undertaken on three of these vessels. The organic micropollutant measurement exercise is reported herein.

The purpose of the investigations reported here is to get a **first impression** of the emissions of organic microcontaminants from ship engines under "real world" conditions, at sea as well as on inland waterways. The work was also meant to find out whether more elaborate investigations are needed or should not have priority.

We will describe here in short the reasons for the investigation and for the choice of the substances measured. For each topic only one reference will be given, selected from the voluminous scientific literature.

During the past decennium different attempts have been made to make a pollution inventory of the North Sea. Among other things, it turned out that insufficient information is available on pollution by toxic organic microcontaminants. Recently the North Sea Directorate of the Dutch Ministry of Transport and Public Works published a list of pollutant inputs into the North Sea [2]. Only two categories of organic micropollutants were mentioned in this list: PCB and PAH (many PAH are known to be carcinogenic, also to humans). For PAH the total input in 1990 into the Dutch part of the North Sea was estimated to be in the order of 110 tons, of which about 90 tons are coming from wet and dry atmospheric deposition. For the total North Sea area the atmospheric input of PAH was estimated to be between 80 and 1500 tons/year [7]. These are very rough estimates and probably indicate the order of magnitude only. In those estimates the emissions from shipping were *not* taken into account. However it is also estimated that between 2 and 5 million tons of marine oil fuel is combusted on the North Sea every year [3]. Diesel engines are well known sources of PAH and, perhaps more important, nitro-PAH [4,5], among which are the most genotoxic substances presently known.

Although no hard data are available, it is suspected that sometimes waste oil is used for combustion in ship's engines. In that case PCB are the organic contaminants most likely to be found in the fuel oil as well as in the exhaust.

PCB present in the fuel oil and/or in the combustion air passing the engine room, as well as chlorine present in marine air may cause the presence of polychlorinated dioxins and

-furans (PCDD and PCDF) in the exhaust. These substances are the most toxic synthetic chemical substances presently known. They are a major cause of concern with respect to the emissions from municipal waste incinerating plants but have been detected also in the exhaust of motor car engines, in particular those running on leaded gasoline. Very small amounts of PCDD/F also have been detected in diesel engine exhaust [6].

From the marine environmental point of view we would like to make the following remarks. All substances of the four groups mentioned above are known to be **very toxic** and **persistent** and to **accumulate** in sediments, marine organisms and the sea surface microlayer [7,8].

The group of PAH has many carcinogenic members and is in the ecotoxicological literature repeatedly suspected of having to do something with the high incidence of liver carcinomas in flat-fish, also in the North Sea [9].
The nitro-PAH are the most genotoxic substances presently known, but there are no data on their significance in marine or river ecosystems. They have been detected in river bottom sediments [10].
The PCB are well known marine pollutants and have been proven to hamper reproduction in seals and to cause a decline in the population of fish eating birds [7].
The chlorinated dioxins and -furans are known to be extremely toxic for fish larvae [11], but their significance in marine pollution is not known yet.
Hexachlorobenzene (HCB) has been analysed in the exhaust because it is an indicator substance for incomplete combustion of organo-chlorine compounds [19].

The exhaust plumes from the funnels of sea going ships will not be able to penetrate the inversion layer existing at a height of about 200 to 300 meter above the North Sea. It is therefore to be expected that the emissions from ships will precipitate on the sea surface within a distance from the ships of, say, 50 km. Much research on this subject has been carried out in Germany [14].

From the shipping point of view it has been pointed out that a complete insight in the environmental problems caused by shipping does not yet exist [12].

The only reference on the subject of this study we were able to find in the literature concerned the emission of PAH, PCB, PCDD and PCDF from ship Diesel engines in a test situation, probably on land [13].

2.   ENGINE EXHAUST GASES

2.1   Comments on the method of sampling

The sampling of (motor car) Diesel engine exhaust for the analysis of organic microcontaminants is usually carried out by leading the exhaust into a so-called "dilution tunnel" after which samples are taken from the diluted (with clean air) exhaust in the tunnel [14]. This technique is difficult to handle on a ship. Based on the fact that we have more experience with this type of sampling we therefore chose the sampling method commonly used for incinerator stack sampling.

Diesel exhaust usually contains soot. The compounds to be analysed here, are known to be adsorbed strongly on soot. At first sight therefore it seems important to ascertain that gases and particles are both sampled representatively from the exhaust. In order to achieve representative sampling of gases and particles, the sampling should be carried out "isokinetically" at 5 different points in the cross section of a stack with an inner diameter between 50 and 100 cm, or at one point in the centre of a stack with a diameter smaller than 50 cm.

"Isokinetically" means that the gas entering the sampling probe has the same velocity as the gas in the stack immediately around the probe. When this is not the case the particles in the stack gas are not being sampled in a representative (proportional) way. Isokinetic sampling can only be achieved at a point in the stack where the gas flow is laminar. This situation is assumed to exist (by definition!) at a distance from the last bend or obstacle in the stack of at least 16 times the stack diameter. Such a point is probably not present on the ships used in this investigation.

Furthermore, we were not completely free in the selection of a sampling point, because of the constructional geometry of the exhaust systems and because of the wish to avoid drilling holes in these systems.

When the stack gas flow is varying during the sampling, a flow sensor should be placed near the sampling point and the signal of this sensor should be used for a computer controlled continuous adjustment of the sampling flow. Samplers of this type are on the market and available in our institute, but they are very expensive and not easy to install on the ships on which our measurements were made.

Given the limited budget available and the exploratory nature of the project, we decided against isokinetic sampling.

The temperatures at the sampling points turned out to be between 300° and 350°C. We probably can assume safely that at these high temperatures most organic contaminants are present completely in the gas phase, although it may not be the case for the least volatile congeners of the different groups studied here. We therefore assume that the fact that we

did not sample isokinetically, in the worst case caused only discrepancies for the least volatile compounds to be analysed. Errors of up to 30% are possible for these compounds [16,17].

Sample volumes of at least 10 m^3 and therefore sampling times of at least 8 hours are needed because of:

- the low levels of the substances to be analysed,
- the fact that the flow through the sampling trains is limited by constructional details per se and by the need for absorption equilibrium in the train,
- the sensitivity of the existing analytical methods.

The analytical results will give time-averaged data.

It will be difficult to produce a time-resolved picture of the emissions during ship movements in port.

Engine room air was analysed for PCB's on both ships in order to be sure that substances found in the exhaust gases could not originate from polluted combustion air.

The fuel oil was analysed for the presence of organochlorine compounds for the same purpose.

2.2   Sampling

The principle of the sampling method is the following. A small part of the exhaust is pumped off through a glass tube and cooled as quickly as possible by using an unheated probe and four ice-cooled impingers in series. The first impinger is empty and serves to collect condense. The impingers 2 and 3 contain pure water and serve mainly for cooling the exhaust gas and collecting acids. The last impinger is empty again and serves for the collection of spray from the water containing impingers 2 and 3. After the last impinger the gas is passing a non-heated glass fiber filter for the collection of particles and after that the gas is led through an organic vapour adsorption train consisting of polyurethane foam (PUF), XAD-4 resin (50 ml) and PUF again, in that order.

Before sampling, the first (empty) impinger is spiked (enriched) with exactly known amounts of 6-methylchrysene, PCB-88 and ^{13}C6-1,2,3,4-T4CDD. In this way the complete sequence from sampling to analysis can be checked for losses of the substances to be analysed.

The whole sampling train from the entrance of the glass sampling probe to and including the last PUF plug contains the sample and has to be extracted with organic solvents. So-called "nano-grade" solvents for residue analysis have to be used.

This type of sampler is used by many researchers and has been validated for PAH analysis at our laboratory [18].

Sampling has taken place on three different ships, S1, S3 and S5. A summary of particulars of the ships participating in this survey is given in the table below.

Ship	Ship type	Engine type	MCR (kW)	Drive line	Fuel grade
S1	Ferry	Medium speed	4895	Gearbox/CPP	Fuel oil
S3	Rhine barge	Medium speed	772	Gearbox/FPP	Gas oil
S5	Container	Slow speed	19720	Direct/FPP	Fuel oil

The sampling equipment used on the ships is shown in Fig.1. The glass sampling probes had to be adapted to the circumstances on the three different ships. They are shown in the color photographs 1 - 6.

On S3 no ice was available and the sampling impingers were cooled with a continuous flow of river water with a temperature of about 15°C.

On S1 the samples were taken from the exhaust duct of the largest port side engine, at a point about 10 meters below the top of the duct. At the sampling point the lid of an existing manhole was replaced by one especially adapted for the passage of two sampling probes. The inner diameter of the exhaust canal at this height is about 70 cm.

On S3 the samples were taken through the top of the exhaust pipe at a point about 80 cm below the top. The inner diameter of the exhaust pipe at the top is about 30 cm.

Due to the many windings of the exhaust pipe in the engine room, it was not possible to perform a good sampling in the 'inside' engine room. A second reason is that sampling must take place as far as possible from the engine itself, because of formation of chemical substances in the exhaust gasses from the pipe line.

The best alternative was to sample through the top of the exhaust pipe at a point about 80 cm below the top.

On S5 the samples were taken from the exhaust duct of the starboard engine, at a point about 23 meters below the top of the duct. At the sampling point, a flange with a diameter of 60 cm was available. The inner diameter of the exhaust canal at that point is about 230 cm. To support the sampling probes, two stainless steal pipes with a length of

approximately 3/4 of the length of the sampling probes were welded on the inside of the flange. A second flange was made in order to close the hole after sampling.

The first sampling attempts, when S1 was leaving the Dutch port, showed that large amounts of soot were present in the exhaust, amounts we have not encountered before. The soot very soon blocked the glass fiber filters and the sampling flow decreased accordingly. Therefore the largest samples we were able to take during one North Sea crossing, had a volume of about 11 m^3. The same problems occurred during the sampling on the container ship. In this case samples with a volume of about 10 m^3 could be taken. We had somewhat less soot problems on the S3 and could take samples of about 17 m^3.

The temperature at the sampling point on the S1 varied between 300°C and 320°C. On the S3 and the S5 this temperature was about 350°C and 250°C respectively.
Because of the high temperatures of the exhaust gas at the sampling points the ice around the sampling impingers melted too fast. During future sampling trips, a probe cooling system should be added to the sampling system.

The sample volume was determined with a dry gas meter in the sample pumping system.
All sampling data (date, time, volume, etc.) are given in the Tables 1, 7 and 13 (see Chapters 2.4.1.1, 2.4.2.1 and 2.4.3.1).

2.3 Analysis

An overall scheme of the analytical procedures is given in Figure 2.

2.3.1 Extraction of the samples

Before extraction, the filter-XAD-PUF unit is spiked with exactly known amounts of benzo(b)chrysene, 1,2,3,4-tetrachloronaphtalene and 1,2,3,4-TCDD $^{13}C12$. The impinger unit is spiked only with 2-methylchrysene prior to the extraction. These spikes are added in order to have a check on losses during the extraction.
Except for the measurements on the S1, the impinger contents are extracted with n-hexane. For the S1 the impinger contents are extracted with toluene. The extracts are combined per sampling train and used to extract the filter-XAD-PUF unit. The final extract is evaporated to a volume of 5 ml. Because of problems with the soot, the extracts of the samples taken

on the S3 are evaporated and dissolved in 10 ml of acetone. 1 ml of this extract is used for the determination of PCDD/F; 1 ml is used for the determination of PCB + HCB and NO_2-PAH; 1 ml is used for the determination of PAH. The remaining 2 ml respectively 7 ml are stored in the freezer at -20°C.

2.3.2 Clean-up and analysis of the extracts

The analysis of PCDD/F is carried out as described in the standard operating procedure IMW-TNO MTA/SG/020 [27]. The final analysis is done with HRGC-HRMS.

For the analysis of NO_2-PAH and PCB + HCB, a first cleanup is performed with a "Seppak" C18 cartridge followed by a second cleanup with semipreparative HPLC. Different fractions are collected. The first fraction is used for the analysis of PCB + HCB. The second fraction is used for the analysis of NO_2-PAH. The analysis of PCB + HCB is carried out as described in the standard operating procedure IMW-TNO MTA/SG/016 [28]. The analysis is carried out with GC-ECD. Due to problems with the matrix, the samples from the S5 are analysed on their content of PCB + HCB with GC-MSD.

The NO_2-PAH are reduced on-line in a precolumn to their corresponding amino-PAH and analysed with HPLC followed by fluorescence detection.

For the determination of PAH, a cleanup with a "Seppak" Silica cartridge is performed. The analysis of PAH is carried out as described in the standard operating procedure IMW-TNO MTA/SV/014 [29]. Analysis takes place with HPLC and fluorescence detection.

On the next page an overview is given concerning the internal and external standards used and whether the results for the PCB + HCB, PAH, NO_2-PAH and PCDD/F analysis are corrected for the %recovery internal and/or external standards.

	Spikes used*		Quantification	Correction results
	before sampling	before extraction		
PAH	6Mchr	B(b)chr 2Mchr	external standards	no
NO$_2$PAH	-	-	external standards	no
PCDD/F	13C6-TCDD/ TCDD-13C12**	TCDD13C12	Internal+external standards	yes
PCB+HCB	PCB-88	TCN	external standards	yes

* 6mChr = 6-methylchrysene, 2Mchr = 2-methylchrysene, B(b)chr = benzo(b)-chrysene, 13C6-TCDD = 13C6 1,2,3,4-T4CDD, TCDD13C12 = 1,2,3,4-T4CDD 13C12, TCN = 1,2,3,4-tetrachloronaphtalene

** For the measurements on the S5, only TCDD-13C12 is used. TCDD-13C12 is added before sampling.

2.4 Results

2.4.1 Results for the S1

2.4.1.1 The samples

Table 1 shows the samples taken, the amount of m^3 sampled and the analyses carried out. Sample 'Micro 1' and 'Micro 2' are the samples taken before S1 left the port. The other samples ('Macro 1, 2, 3 and 4') were taken during the crossing of the North Sea.

We decided to combine the samples 'Micro 1' and 'Micro 2' because of their small volume sampled.

In order to check for the breaking through of samples through the sampling train, the last PUF-plug of the sampling train of sample 'Macro 4' was extracted and analysed separately. The background levels were determined by extracting and analysing a blank sampling train.

Table 1   *The S1 samples (26-28 June '91)*

Sample	m^3 sampled*	Analysis for	Time code
Micro 1	2.807	PAH, NOH$_2$-PAH, PCB, HCB	18.16-19.45
Micro 2	1.754	PAH, NO$_2$-PAH, PCB, HCB	18.16-19.45
Macro 1	11.589	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	20.56-06.50
Macro 2	11.038	PAH, NO$_2$-PAH, PCB+HCB	23.32-06.50
Macro 3	15.221	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	21.45-07.40
Macro 4	11.323	PAH, NO$_2$-PAH, PCB+HCB	21.45-07.40
Blank	-	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	

(*) the sample volume has been measured at about 35°C

2.4.1.2 The analytical results (see also the summary in Table 6)

All values given in μg/m^3 or ng/m^3 are given for cubic meters exhaust gas with a temperature of 35°C and saturated with water vapour.

PCDD/F

The well known "dirty 17" congeners have been determined and the final results have been expressed in Toxicity Equivalent Toxicities [20]. This is common practice at the moment in most countries and these values are also used in legislation.

The results of the analysis for PCDD/F are given in Table 2. The content of PCDD/F is given in ng per congener in the sampling train and in ng/m^3. The results are corrected for the %recovery of internal and external standards only for the available ^{13}C-labelled standards.

Table 2 *Results of the PCDD/F analysis of the S1 exhaust (TEF = toxicity equivalence factor, TEQ = toxicity equivalent quantity: quantity x TEF).*

Sample : Blank

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.06	1.000	< 0.06	65
12378 P5CDD	< 0.06	0.500	< 0.03	81
123478 H6CDD	< 0.13	0.100	< 0.01	
123678 H6CDD	< 0.13	0.100	< 0.01	
123789 H6CDD	< 0.13	0.100	< 0.01	100
1234678 H7CDD	0.34	0.010	0.00	114
12346789 O8CDD	5.82	0.001	0.01	98
2378 T4CDF	< 0.10	0.100	< 0.01	60
12378 P5CDF	0.28	0.050	0.01	
23478 P5CDF	0.40	0.500	0.20	78
123478 H6CDF	< 0.11	0.100	< 0.01	
123678 H6CDF	< 0.11	0.100	< 0.01	
123789 H6CDF	< 0.10	0.100	< 0.01	
234678 H6CDF	< 0.13	0.100	< 0.01	98
1234678 H7CDF	0.85	0.010	0.01	105
1234789 H7CDF	< 0.16	0.010	0.00	
12346789 O8CDF	< 4.37	0.001	0.00	77

Total TEQ (ng)　　　0.25 < X < 0.42

Recovery 13C6 1234-T4CDD: 61% ; 13C12 1234-T4CDD: 59%

Sample : Macro 1

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.10	1.000	< 0.10	73
12378 P5CDD	< 0.17	0.500	< 0.09	67
123478 H6CDD	< 0.26	0.100	< 0.03	
123678 H6CDD	< 0.24	0.100	< 0.02	
123789 H6CDD	1.11	0.100	0.11	63
1234678 H7CDD	18.03	0.010	0.18	57
12346789 O8CDD	169.93	0.001	0.17	50
2378 T4CDF	0.19	0.100	0.02	67
12378 P5CDF	< 0.15	0.050	< 0.01	
23478 P5CDF	0.33	0.500	0.16	60
123478 H6CD	< 0.32	0.100	< 0.03	
123678 H6CDF	< 0.31	0.100	< 0.03	
123789 H6CDF	3.45	0.100	0.35	
234678 H6CDF	5.93	0.100	0.59	60
1234678 H7CDF	41.00	0.010	0.41	58
1234789 H7CDF	1.11	0.010	0.01	
12346789 O8CDF	35.02	0.001	0.04	39

Total TEQ (ng)　　　2.04 < X < 2.35

Total TEQ (ng/m^3)　0.18 < X < 0.2

Recovery 13C6 1234-T4CDD: 38% ; 13C12 1234-T4CDD: 37%

Sample : Macro 3

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.27	1.000	< 0.27	80
12378 P5CDD	< 0.43	0.500	< 0.21	72
123478 H6CDD	< 0.32	0.100	< 0.03	
123678 H6CDD	< 0.31	0.100	< 0.03	
123789 H6CDD	< 0.34	0.100	< 0.03	75
1234678 H7CDD	2.28	0.010	0.02	68
12346789 O8CDD	91.68	0.001	0.09	64
2378 T4CDF	0.13	0.100	0.01	75
12378 P5CDF	0.67	0.050	0.03	
23478 P5CDF	1.58	0.500	0.79	76
123478 H6CDF	0.16	0.100	0.02	
123678 H6CDF	0.18	0.100	0.02	
123789 H6CDF	0.99	0.100	0.10	
234678 H6CDF	0.83	0.100	0.08	74
1234678 H7CDF	12.82	0.010	0.13	73
1234789 H7CDF	< 1.20	0.010	< 0.01	
12346789 O8CDF	26.66	0.001	0.03	56

Total TEQ (ng) $1.32 < X < 1.89$

Total TEQ (ng/m^3) $0.087 < X < 0.12$

Recovery 13C6 1234-T4CDD: 54% ; 13C12 1234-T4CDD: 52%

PCB and HCB.

HCB and PCB were analysed in the first fraction of the cleanup with semipreparative HPLC. The results are given in Table 3. The results are corrected for the %recovery of 1,2,3,4-tetrachloronapthalene.

Table 3   *PCB- and HCB-content in ng/m^3 for the S1 samples.*

Sample	Blank	Micro1+2	Macro1	Macro2	Macro3	Macro4(*)	PUF
HCB	0.5	0.3	0.9	0.4	2.3	0.5	0.15
PCB15/18	19	3	3	3	5	4	0.9
PCB28	13	1.4	9	1.7	7	2.1	0.6
PCB52	12	1	6	1	5.6	1.5	0.3
PCB49	38	1.3	3.7	1.8	3.1	2.3	0.8
PCB44	8	1	13	1.5	13	2.3	0.3
PCB66	16	1.1	3.5	1.5	4.3	1.8	0.5
PCB101	23	1.2	1.4	1.6	2.5	3	0.6
PCB77	75	2.7	1.3	1.2	3.3	2.9	0.8
PCB118	54	2	2.4	3.6	3.6	4.1	1
PCB153	61	2	1.2	3.2	3.8	6.1	1
PCB138	66	2	1	3.2	3.6	4.7	0.75
PCB128	21	0.6	0.7	0.9	1	2.1	0.2
PCB187	12	0.3	0.3	0.5	0.4	1.2	1
PCB180	24	0.6	0.6	1.1	1.4	2	0.2
Total		20.5	48	26.2	59.9	40.6	
% recov. PCB88	116	79	86	63	89	12	45

(*) the results for the second PUF-plug are included.

Polycyclic Aromatic Hydrocarbons

The results of the analysis of PAH are given in Table 4. The results are not corrected for % recovery of internal standards. Sample 'Macro 4', the last PUF plug of sample 'Macro 4' and the 'Blank' were analysed after cleanup with semipreparative HPLC. Because the pump of the semipreparative HPLC broke down several times due to problems with the matrix of the samples (soot), the other samples were cleaned up only with a "Seppak" Silica cartridge.

Table 4   *Results of the PAH analysis in μg/m³ for the S1 (*).*

Sample	Micro1+2	Macro1	Macro2	Macro3	Macro4(**)	PUF4	Blank
Ph	28	41	50	50	34	20	0.6
Ant	0.44	0.16	0.22	0.3	0.16	0.03	0.01
Flua	5.5	6.6	8.3	8.5	7.1	3.5	0.37
Pyr	9.6	9.5	12	12	8.9	4.9	0.16
Dmph	3.3	2.1	3.3	3.4	2.2	1	<0.04
Tphe	6.8	5.5	7.9	7.9	6.3	2.2	<0.1
B(b)f	3.3	2.7	4.0	3.9	3.6	1.3	0.05
B(a)a	1.4	1.0	1.5	1.6	1.2	0.44	0.006
Chr	4.2	1.8	3.1	3.3	2.5	0.21	0.05
B(e)p	<0.1	<0.1	<0.1	<0.1	<0.01	<0.01	<0.1
B(j)fa	<0.2	<0.2	<0.2	<0.2	<0.02	<0.02	<0.2
Per	0.22	0.06	<0.008	0.07	0.06	<0.0009	<0.009
B(b)fa	0.48	0.37	0.42	0.43	0.37	<0.002	<0.02
B(k)fa	0.11	0.05	0.06	0.08	0.07	<0.0006	<0.006
B(a)p	0.24	0.03	0.034	0.02	0.04	<0.0007	<0.008
D(aj)a	0.24	0.05	0.08	0.06	<0.002	<0.002	<0.03
D(al)p	0.31	0.21	0.25	0.18	0.17	<0.002	<0.02
B(ghi)p	<0.03	0.14	0.16	<0.03	0.11	<0.003	<0.04
D(ah)a	<0.1	<0.1	<0.1	<0.1	0.082	<0.01	<0.1
I(cd)p	<0.03	0.17	<0.03	<0.03	<0.003	<0.003	<0.03
Mchol	<0.006	0.01	0.02	<0.006	<0.0007	<0.0007	<0.008
Anth	<0.008	<0.008	<0.008	<0.008	<0.0008	<0.0008	<0.008
Total	64.14	71.45	91.344	91.74	66.862		
%recovery internal standards							
6Mchr	200	238	334	467	255	-	105
2Mchr	250	278	320	410	310	-	79
B(b)chr	104	92	89	86	63	-	95

(*)   Ph = phenanthrene, Ant = anthracene, Flua = fluoranthene, Pyr = pyrene,

Dmph = 3,6-dimethylphenanthrene, Tphe =triphenylene, B(b)f=benzo(b)fluorene,

B(a)a = benzo(a)anthracene, Chr = chrysene, B(e)p =benzo(e)pyrene, B(j)fa=benzo(j)fluoranthene,

Per = perylene, B(b)fa = benzo(b)fluoranthene, B(k)fa = benzo(k)fluoranthene,

B(a)p = benzo(a)pyrene, D(aj)a = dibenzo(a,j)anthracene, D(al)p = dibenzo(a,l)pyrene,

B(ghi)p = benzo(g,h,i)perylene, D(ah)a = dibenzo(a,h)anthracene, I(cd)p = indeno(1,2,3-c,d)pyrene,

Mchol = 3-methyl-cholanthrene, Anth = anthanthrene, 6Mchr = 6-methylchrysene,

2Mchr = 2-methylchrysene, B(b)chr = benzo(b)chrysene.

(**)   The results for the second PUF-plug are included.

Nitro substituted Polycyclic Aromatic Hydrocarbons

The results of the analysis for NO2-PAH are given in Table 5. The samples 'Blanco', 'Macro4' and 'PUF Macro4' were cleaned up directly with semipreparative HPLC, while the other samples were cleaned up with a "Seppak" C18 cartridge prior to the semi-preparative cleanup.

Because the knowledge about the existence and/or formation of NO2-PAH is still limited and only a few standard reference materials are available, it was not possible to use an internal standard in order to determine the recovery. For the determination of NO2-PAH, in addition to external retention standards, a further confirmation of the peak identity is possible by analysing the extract with and without the reduction column. The peaks which disappear when the reduction column is not used are identified as nitro-substituted PAH.

Table 5   *Results of the NO2-PAH analysis in µg/m³ for the S1.*

Sample	Blank	Micro1+2	Macro1	Macro2	Macro3	Macro4(*)	PUF
1,6/1,8-dinitropyrene	<0.3	<0.1	<0.04	12 (?)	80 (?)	2.7	2.5
2-nitrofluorene	<25	250	80	112	164	62	-
9-nitroanthracene	<0.1	<0.04	<0.02	<0.02	<0.01	0.5	0.1
3-nitrofluoranthene	<0.14	3.4	1.6	<0.02	0.4	1.2	0.2
1-nitropyrene	<0.13	2.7	1.6	1.4	0.8	4	-
6-nitrochrysene	<1	<0.3	2.2	<0.13	1.2	2.9	0.5
7-nitrobenzo(a)antrac.	<0.09	0.4	0.4	0.3	<0.2	1	-
6-nitrobenzo(a)pyr.	<0.09	<0.03	<0.01	<0.01	<0.01	0.4	-
Total mono-NO2-PAH (2-nitrofluorene excluded)		6.5	5.8	1.7	2.4	10	

(*)   The results for the PUF-plug are included.

Remark: The analysis of 1,6/1,8-dinitropyrene for Macro2 and Macro3 is probably disturbed by another unknown compound. Due to the low sensitivity for 2-nitrofluorene, relatively high concentrations compared to the other NO2-PAH were found.

Summary of the analytical results for the S1 exhaust.

Table 6   *The total amount of PCDD/F, HCB + PCB, PAH and NO$_2$-PAH found in the S1 exhaust samples*

	Micro1&2	Macro1	Macro2	Macro3	Macro4
PCDD/F as total TEQ(ng/m^3)	-	0.18-0.2	-	0.087-0.12	-
HCB+PCB (ng/m^3)	20	48	26	60	41
PAH (µg/m^3)	64	71	91	92	67
mono-NO$_2$-PAH µg/m^3 (2-NO$_2$-Flu excl.)	6.5	5.8	1.7	2.4	10

The results for the PCDD/F analysis are corrected for the %recovery of internal and external standards. The results for the PCB+HCB analysis are corrected for the %recovery of 1,2,3,4-tetrachloronaphtalene. The results for the PAH- as well as the NO$_2$-PAH analysis are not corrected for the %recovery of internal standard. None of the results are corrected for the blank.

2.4.2   Results for the S3

2.4.2.1 The samples from S3

Table 7 shows the samples taken, the exhaust sample volumes in m^3 and the analyses carried out. Because of problems during the sampling, sample Macro 1 is cancelled. Instead, it was decided to determine the content of PAH, NO$_2$-PAH, PCB + HCB and PCDD/F in sample Macro 6. The background levels were determined by extracting and analysing a blank sampling train.

Table 7 *The samples from the S3 (10-10-1991)*

Sample code*	m³ sampled**	Analysis for	time
Macro 1(1a)	-	cancelled	
Macro 2(1b)	10.434	PAH, NO$_2$-PAH, PCB+HCB	07.25-12.38
Macro 3(2a)	10.638	PAH, NO$_2$-PAH, PCB+HCB	11.47-14.18
Macro 4(2b)	9.874	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	12.57-15.33
Macro 5(3a)	15.465	PAH, NO$_2$-PAH, PCB+HCB	14.43-19.32
Macro 6(3b)	17.026	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	15.45-19.32
Blank	-	PAH, NO$_2$-PAH, PCB+HCB, PCDD/F	

(*)   Samples codes between the brackets are the codes used in preliminary reports.
(**) m³ sampled is measured at 27°C.

2.4.2.2 The analytical results (see also the summary in Table 12)

PCDD/F

The results of the analysis for PCDD/F are given in Table 8. The content of PCDD/F is given in ng per congener in the sampling train and in ng/m³.

The results are corrected for the %recovery of internal and external standards (only for the available ^{13}C-labelled standards).

Table 8   *Results of the PCDD/F analysis of S3 exhaust (TEF = toxicity equivalence factor, TEQ = toxicity equivalent quantity: quantity x TEF).*

Sample : Blank

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.05	1.000	< 0.05	122
12378 P5CDD	< 0.03	0.500	< 0.02	124
123478 H6CDD	< 0.21	0.100	< 0.02	
123678 H6CDD	< 0.19	0.100	< 0.02	
123789 H6CDD	< 0.20	0.100	< 0.02	118
1234678 H7CDD	5.83	0.010	0.06	119
12346789 O8CDD	23.80	0.001	0.02	118
2378 T4CDF	< 0.03	0.100	< 0.00	117
12378 P5CDF	0.38	0.050	0.02	
23478 P5CDF	0.26	0.500	0.13	108
123478 H6CDF	2.18	0.100	0.22	
123678 H6CDF	1.75	0.100	0.18	
123789 H6CDF	< 0.22	0.100	< 0.02	
234678 H6CDF	3.53	0.100	0.35	97
1234678 H7CDF	24.06	0.010	0.24	110
1234789 H7CDF	< 0.07	0.010	0.00	
12346789 O8CDF	<14.87	0.001	< 0.01	

Total TEQ (ng) $1.22 < X < 1.39$

Recovery 13C6 1234-T4CDD: 44% ; 13C12 1234 T4CDD: 43%

Sample : Macro 4

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.02	1.000	< 0.02	94
12378 P5CDD	< 0.06	0.500	< 0.03	87
123478 H6CDD	< 0.25	0.100	< 0.02	
123678 H6CDD	< 0.22	0.100	< 0.02	
123789 H6CDD	< 0.23	0.100	< 0.02	83
1234678 H7CDD	5.06	0.010	0.05	83
12346789 O8CDD	16.81	0.001	0.02	88
2378 T4CDF	< 0.03	0.100	0.00	94
12378 P5CDF	< 0.02	0.050	0.00	
23478 P5CDF	< 0.02	0.500	< 0.01	84
123478 H6CDF	< 0.18	0.100	< 0.02	
123678 H6CDF	< 0.16	0.100	< 0.02	
123789 H6CDF	< 0.31	0.100	< 0.03	
234678 H6CDF	0.45	0.100	0.05	70
1234678 H7CDF	7.77	0.010	0.08	77
1234789 H7CDF	< 0.07	0.010	0.00	
12346789 O8CDF	<10.37	0.001	< 0.01	

Total TEQ (ng) $0.20 < X < 0.40$

Total TEQ (ng/m^3) $0.02 < X < 0.04$

Recovery 13C6   1234 T4CDD : 65%

Recovery 13C12   1234 T4CDD : 64%

Sample : Macro 6

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	< 0.02	1.000	< 0.02	98
12378 P5CDD	< 0.05	0.500	< 0.02	143
123478 H6CDD	< 0.15	0.100	< 0.01	
123678 H6CDD	< 0.13	0.100	< 0.01	
123789 H6CDD	< 0.14	0.100	< 0.01	95
1234678 H7CDD	2.59	0.010	0.03	91
12346789 O8CDD	21.82	0.001	0.02	81
2378 T4CDF	< 0.02	0.100	0.00	95
12378 P5CDF	0.02	0.050	0.00	
23478 P5CDF	< 0.05	0.500	< 0.03	91
123478 H6CDF	< 0.11	0.100	< 0.01	
123678 H6CDF	0.15	0.100	0.02	
123789 H6CDF	< 0.19	0.100	< 0.02	
234678 H6CDF	0.94	0.100	0.09	78
1234678 H7CDF	4.91	0.010	0.05	83
1234789 H7CDF	< 0.03	0.010	0.00	
12346789 O8CDF	< 9.54	0.001	< 0.01	

Total TEQ (ng) $0.21 < X < 0.36$

Total TEQ (ng/m^3) $0.012 < X < 0.021$

Recovery 13C6   1234 T4CDD : not added

Recovery 13C12   1234 T4CDD : 65%

PCB and HCB.

HCB and PCB were analysed in the first fraction of the cleanup with semipreparative HPLC. The results are given in Table 9. The results are corrected for the %recovery of PCB-88.

Table 9   *PCB- and HCB-content in ng/m^3 for the S3 exhaust samples.*

Sample	Blank	Macro2	Macro3	Macro4	Macro5	Macro6
HCB	2.2	3.7	2.3	-	0.3	0.6
PCB52	13	12	30	24	12	10
PCB49	7.8	9.6	29	17	7.2	7.7
PCB44	-	-	-	-	-	-
PCB101	28	11	31	7.4	8.7	4.3
PCB118	35	17	39	19	11	19
PCB153	35	18	44	6.5	0.7	2.1
PCB138	130	14	41	116	77	54
PCB180	940(*)	22000(*)	200(*)	75	9	3.5
Total		85.3	216.3	243.3	125.9	101.2
%recovery PCB-88	170	14	16	23	37	69

(*) Peak is disturbed by another unknown compound.

Polycyclic Aromatic Hydrocarbons

The results of the analysis for PAH are given in Table 10. The results are not corrected for % recovery of internal standards.

Table 10   *Results of the PAH analysis in $\mu g/m^3$ for S3 samples (**,***).*

Sample	Macro2	Macro3	Macro4	Macro5	Macro6	Blank
Ph	13	19	20	16	16	<0.2
Ant	0.4	0.7	0.7	0.7	0.8	<0.01
Flua	3.7	5.2	5.2	4.6	4.5	<0.1
Pyr	3.8	5.4	5.4	5	4.9	<0.1
Dmph	1.3	1.9	1.8	1.7	1.6	<0.1
Tphe	3.7(*)	5.1(*)	6(*)	4.7(*)	5.1(*)	<0.3
B(b)f	5.6	8.4	8.5	7.4	7.2	<0.3
B(a)a	<0.009	<0.009	<0.009	<0.009	<0.009	<0.009
Chr	0.96	1.3	1.6	1.4	1.1	<0.2
B(e)p	2.1(*)	1.9(*)	2.8(*)	1.9(*)	1.8(*)	<0.4
B(j)fa	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Per	0.04	0.1	0.1	0.08	0.08	<0.03
B(b)fa	0.1	0.14	0.13	0.13	0.14	<0.04
B(k)fa	0.03	0.03	0.03	0.04	0.04	<0.02
B(a)p	0.01	0.02	0.03	0.02	0.01	<0.02
D(aj)a	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
D(al)p	<0.007	<0.007	<0.007	<0.007	<0.007	<0.07
B(ghi)p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.1
D(ah)a	<0.03	<0.03	<0.03	<0.03	<0.03	<0.3
I(cd)p	<0.01	<0.01	<0.01	<0.01	<0.01	<0.1
Mchol	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Anth	<0.003	<0.003	<0.003	<0.003	<0.003	<0.03
Total	28.94- 34.74	42.19- 49.19	43.49- 52.29	37.07- 43.67	36.37- 43.27	

%recovery internal standards						Blank
6Mchr	227	291	311	374	347	90
2Mchr	117	113	142	152	113	90
B(b)chr	22	57	84	32	30	88

*   The peak is disturbed by another, unknown, compound. The given concentration is the maximum possible concentration. The total PAH content is therefore given without and with these values.

**   Ph = phenanthrene, Ant = anthracene, Flua = fluoranthene, Pyr = pyrene,
Dmph = 3,6-dimethylphenanthrene, Tphe = triphenylene, B(b)f = benzo(b)fluorene,
B(a)a = benzo(a)anthracene, Chr = chrysene, B(e)p = benzo(e)pyrene,
B(j)fa = benzo(j)fluoranthene, Per = perylene, B(b)fa = benzo(b)fluoranthene,
B(k)fa = benzo(k)fluoranthene, B(a)p = benzo(a)pyrene, D(aj)a = dibenzo(a,j)anthra-cene,
D(al)p = dibenzo(a,l)pyrene, B(ghi)p = benzo(g,h,i)perylene,
D(ah)a = dibenzo(a,h)anthracene, I(cd)p = indeno(1,2,3-c,d)pyrene,
Mchol = 3-methyl-cholanthrene, Anth = anthanthrene, 6Mchr = 6-methylchrysene,
2Mchr = 2-methylchrysene, B(b)chr = benzo(b)chrysene.

***   For the determination of the detection limits in $\mu g/m^3$, an average sample volume of 10 m^3 NTP has been taken.

Nitro substituted Polycyclic Aromatic Hydrocarbons

The results for the analysis of NO$_2$-PAH are given in Table 11. Because the knowledge about the existence and/or formation of NO$_2$-PAH is still limited and only a few standard reference materials are available, it was not possible to use an internal standard in order to determine the recovery. For the determination of NO$_2$-PAH, in addition to external retention standards, a further confirmation of the peak identity is possible by analysing the extract with and without the reduction column. The peaks which disappear when the reduction column is not used are identified as nitro-substituted PAH.

Table 11   Results of the NO$_2$-PAH analysis in µg/m^3 for S3 exhaust samples.

Sample	Macro2	Macro3	Macro4	Macro 5	Macro6
1,6/1,8dinitropyrene	0.1	0.1	0.2	0.1	0.1
2-nitrofluorene	<0.5	<0.5	<0.6	<0.4	<0.3
9-nitroanthracene	<0.01	<0.01	<0.01	<0.01	<0.01
3-nitrofluoranthene	<0.01	<0.01	<0.01	<0.01	<0.004
1-nitropyrene	0.25	0.14	0.16	0.10	0.10
6-nitrochrysene	<0.07	<0.07	<0.08	<0.05	<0.04
7-nitrobenzo(a)antracene	<0.01	<0.01	<0.01	<0.01	<0.01
6-nitrobenzo(a)pyrene	<0.01	<0.01	<0.01	<0.01	<0.01
Total	0.35	0.24	0.36	0.2	0.2

Summary of the analytical results for the S3 exhaust.

Tabel 12   The total amounts of PCCD/F, HCB + PCB, PAH and NO$_2$-PAH found in the S3 exhaust.

Sample	Macro2	Macro3	Macro4	Macro5	Macro6
PCCD/F as total TEQ(ng/m^3)	-	-	0.02-0.04	-	0.012-0.021
HCB+PCB (ng/m^3)	85	216	243	126	101
PAH (µg/m^3)	29-35	42-49	44-52	37-44	36-43
NO$_2$-PAH (µg/m^3)	0.35	0.24	0.36	0.20	0.20

The results for the PCDD/F analysis are corrected for the %recovery of internal and external standards. The results for the PCB+HCB analysis are corrected for the %recovery of

PCB-88. Because the peak is disturbed by another unknown compound, the results for PCB180 of Macro 2 and 3 is not included in the totals.

The results for the PAH- as well as the NO_2-PAH analysis are not corrected for the %recovery of internal standard. For the results of the PAH, the first and second figure demonstrates the total of PAH without and with the components which are disturbed by other, unknown compounds.

None of the results are corrected for the blank.

2.4.3   Results for the S5

2.4.3.1 The samples from the S5

Table 13 describes the samples taken, the exhaust sample volumes in m^3 and the analysis carried out. The background levels were determined by extracting and analysing a blank sampling train.

Table 13   *The samples from the S5 (april 1992)*

Sample code (*)	m^3 sampled (**)	Analysis for	Time code
Macro1(1x)	9.403	PAH	23.38-10.40
Macro2(1y)	10.678	PAH	23.38-10.40
Macro3(2x)	10.893	PAH, NO_2-PAH, PCB+HCB, PCDD/F	21.25-10.03
Macro4(2y)	11.771	PAH, NO_2-PAH, PCB+HCB, PCDD/F	21.25-9.45
Macro5(3x)	10.085	PAH, NO_2-PAH	10.15-6.24
Macro6(3y)	9.817	PAH, NO_2-PAH	10.15-6.24
Blank1	-	PAH, NO_2-PAH, PCB+HCB, PCDD/F	

(*)   Samples codes between the brackets are the codes used in preliminary reports.
(**) m^3 samples is measured at 27°C

2.4.3.2 The analytical results (see also the summary in Table 18)

PCDD/F

The results of the analysis of PCDD/F are given in Table 14. The content of PCDD/F is given in ng per congener in the sampling train in ng/m^3. The results are corrected for the %recovery of internal and external standards (only for the available ^{13}C-labelled standards).

Table 14   *Results of the PCDD/F analysis of the S5 exhaust (TEF = toxicity equivalence factor, TEQ =*
toxicity equivalent quantity: quantity x TEF).

Sample : Blank

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	<0.032	1.000	<0.032	110
12378 P5CDD	<0.093	0.500	<0.046	96
123478 H6CDD	<0.272	0.100	<0.027	81
123678 H6CDD	<0.391	0.100	<0.039	
123789 H6CDD	<0.338	0.100	<0.034	80
1234678 H7CDD	<0.268	0.010	<0.003	67
12346789 O8CDD	2.444	0.001	0.002	57
2378 T4CDF	0.055	0.100	0.006	120
12378 P5CDF	<0.034	0.050	<0.002	
23478 P5CDF	<0.027	0.500	<0.014	99
123478 H6CDF	<0.054	0.100	<0.005	
123678 H6CDF	<0.050	0.100	<0.005	84
123789 H6CDF	<0.263	0.100	<0.026	77
234678 H6CDF	<0.242	0.100	<0.024	
1234678 H7CDF	<0.294	0.010	<0.003	75
1234789 H7CDF	<2.893	0.010	<0.010	63
12346789 O8CDF	n.d.	0.001	n.d.	

Total TEQ (ng)   :   0.008 < TEQ < 0.297
Recovery 13C12   1234 T4CDD : 19%

Sample : Macro 3

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	<0.030	1.000	<0.030	121
12378 P5CDD	<0.092	0.500	<0.046	109
123478 H6CDD	<0.222	0.100	<0.022	102
123678 H6CDD	<0.323	0.100	<0.032	
123789 H6CDD	<0.262	0.100	<0.026	104
1234678 H7CDD	<0.209	0.010	<0.002	99
12346789 O8CDD	1.337	0.001	0.001	97
2378 T4CDF	0.080	0.100	0.008	121
12378 P5CDF	<0.014	0.050	<0.001	
23478 P5CDF	0.031	0.500	0.016	112
123478 H6CDF	<0.043	0.100	<0.004	
123678 H6CDF	<0.040	0.100	<0.004	107
123789 H6CDF	<0.097	0.100	<0.010	102
234678 H6CDF	<0.067	0.100	<0.007	
1234678 H7CDF	<0.136	0.010	<0.001	107
1234789 H7CDF	<1.010	0.010	<0.010	93
12346789 O8CDF	n.d.	0.001	n.d.	

Total TEQ (ng)   : 0.025 < TEQ < 0.221
Total TEQ (ng/m^3) : 0.002 < TEQ < 0.020
Recovery 13C12   1234 T4CDD : 22%

Sample : Macro 4

Congener	ng	TEF	TEQ	recovery(%)
2378 T4CDD	<0.042	1.000	<0.042	118
12378 P5CDD	<0.091	0.500	<0.045	105
123478 H6CDD	<0.222	0.100	<0.022	96
123678 H6CDD	<0.323	0.100	<0.032	
123789 H6CDD	0.622	0.100	0.062	100
1234678 H7CDD	3.600	0.010	0.036	96
12346789 O8CDD	192.941	0.001	0.193	90
2378 T4CDF	0.081	0.100	0.008	120
12378 P5CDF	0.138	0.050	0.007	
23478 P5CDF	0.147	0.500	0.074	108
123478 H6CDF	0.310	0.100	0.031	
123678 H6CDF	0.451	0.100	0.045	100
123789 H6CDF	2.636	0.100	0.264	95
234678 H6CDF	4.798	0.100	0.480	
1234678 H7CDF	122.259	0.010	1.223	105
1234789 H7CDF	2.204	0.010	0.022	80
12346789 O8CDF	n.d.	0.001	n.d.	

Total TEQ (ng)   : 2.444 < TEQ < 2.586

Total TEQ (ng/m^3) : 0.208 < TEQ < 0.220

Recovery 13C12   1234 T4CDD : 22%

PCB and HCB

HCB and PCB were analysed in the first fraction of the cleanup with semipreparative HPLC. The results are given in Table 15. Because no PCB/HCB could be detected in the samples, the results are reported as their detection limits per PCB/HCB-congener. For the samples, the results are not corrected for the %recovery of PCB-88. The %recovery of PCB-88 in blank 1 is corrected for the %recovery 1,2,3,4-tetrachloronaphtalene (TCN).

Table 15   *PCB- and HCB-content in ng (for the Blank) and ng/m^3 for the S5 samples.*

Sample	Recovery (%)		(ng/m^3) PCB/HCB
	PCB-88	TCN	
Macro3	*	*	< 60
Macro4	*	*	< 60
blank 1	83.9	24.9	< 700

*) Due to problems with the matrix, the samples had to be diluted prior to analysis. This explains the fact that
    the percentage recovery for PCB-88 as well as TNC could not be determined.

Polycyclic Aromatic Hydrocarbons

The results of the analysis of PAH are given in Table 16. The results are not corrected for % recovery of internal standards.

Table 16   *Results of the PAH analysis in ug/m³ for the S5 samples (**,***).*

Sample	Macro1	Macro2	Macro3	Macro4	Macro5	Macro6	Blank
Ph	5.410	6.445	7.967	7.640	8.767	7.063	0.10
Ant	0.049	0.0576	0.130	0.333	0.197	0.158	0.001
Flua	1.972	2.904	3.018	3.520	3.891	3.278	0.044
Pyr	2.547	3.361	3.662	3.935	4.666	3.949	0.026
Dmph	0.608	1.027	0.753	1.226	1.186	1.314	<0.009
Tphe	2.944(*)	3.807(*)	4.068(*)	5.819(*)	5.856(*)	5.596(*)	<0.02
B(b)f	0.285	0.254	1.290	1.490	1.644	1.108	<0.02
B(a)a	0.249	0.933	<0.007	<0.007	<0.007	<0.007	0.006
Chr	0.855	0.804	1.433	2.455	2.572	2.247	0.027
B(e)p	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026	<0.026
B(j)fa	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030	<0.030
Per	<0.0326	0.0435	<0.003	0.0856	0.0896	0.150	<0.003
B(b)fa	<0.004	<0.004	0.260	0.347	0.444	0.347	<0.004
B(k)fa	0.0192	0.0388	0.0507	0.035	0.0568	0.0769	0.005
B(a)p	<0.002	<0.002	<0.002	<0.002	0.0581	0.0836	<0.002
D(aj)a	0.072	0.220	0.153	0.138	1.921(*)	0.0529	<0.009
D(al)p	0.054	0.103	0.152	0.137	0.106	0.200	<0.006
B(ghi)p	0.106	0.211	0.456	0.353	0.678	0.364	<0.009
D(ah)a	0.219	0.151	0.892	1.080	1.569	0.822	<0.014
I(cd)p	0.182	0.375	0.266	0.237	0.183	0.327	<0.008
Mchol	0.0124	0.0231	0.0183	0.0932	0.106	0.0485	<0.002
Anth	0.0047	0.030	0.0192	0.107	0.116	0.109	<0.002
Total	12.7- 15.6	17.0- 20.7	20.5- 24.6	23.2- 29.0	26.3- 34.1	21.7- 27.2	
%recovery internal standards							**Blank**
6Mchr	66	153	66	156	159	175	58
2Mchr	55	83	273	291	50	305	54
B(b)chr	25	40	23	17	30	27	10

*   The peak is disturbed by another, unknown, compound. The presented concentration is the maximum possible concentration. The total PAH content is therefore given without and with these values.

**   Ph = phenanthrene, Ant = anthracene, Flua = fluoranthene, Pyr = pyrene,
Dmph = 3,6-dimethylphenanthrene, Tphe = triphenylene, B(b)f = benzo(b)-fluorene,
B(a)a = benzo(a)anthracene, Chr = chrysene, B(e)p = benzo(e)-pyrene, B(j)fa = benzo(j)fluoranthene,
Per = perylene, B(b)fa = benzo(b)-fluoranthene, B(k)fa = benzo(k)fluoranthene,
B(a)p = benzo(a)pyrene, D(aj)a = dibenzo(a,j)anthra-cene, D(al)p = dibenzo(a,l)pyrene,
B(ghi)p = benzo-(g,h,i)perylene, D(ah)a = dibenzo(a,h)anthracene, I(cd)p = indeno(1,2,3-c,d)pyrene,
Mchol = 3-methyl-cholanthrene, Anth = anthanthrene, 6Mchr = 6-methylchrysene,
2Mchr = 2-methylchrysene, B(b)chr = benzo(b)chrysene.

***   For the determination of the detection limits in ng/m³, an average amount of 10 m³ is taken.

Nitro substituted Polycyclic Aromatic Hydrocarbons

The results of the analysis of NO_2-PAH are presented in Table 17. Because the knowledge about the existence and/or formation of NO_2-PAH is still limited and just a few standard reference materials are available, it was not possible to use an internal standard in order to determine the recovery. For the determination of NO_2-PAH, next to external standards, an extra identification is possible by analysing the extract with and without the reduction column. The peaks which disappear when not using the reduction column are identified as nitro-substituted PAH.

Table 17   *Results of the NO_2-PAH analysis in ug/m^3 for the S5 samples.*

Sample	Macro3	Macro4	Macro5	Macro6
1,6/1,8-dinitropyrene	<0.002	1.3	0.63	0.58
2-nitrofluorene	<0.2	<0.2	<0.2	<0.2
9-nitroanthracene	<0.003	<0.002	<0.003	<0.003
3-nitrofluoranthene	<0.001	<0.001	<0.002	<0.002
1-nitropyrene	0.74	0.77	0.61	0.78
6-nitrochrysene	1.5(*)	1.3	1.2	2.2
7-nitrobenzo(a)antracene	<0.003	<0.003	<0.003	<0.003
6-nitrobenzo(a)pyrene	<0.001	<0.001	<0.002	<0.002
Total	0.74-2.24	3.37	2.44	3.56

(*) The peak is disturbed by another, unknown, compound. The presented concentration is the maximum possible concentration.

Summary of the analytical results for the S5 exhaust

Table 18   *The total amount of PCDD/F, PCB + HCB, PAH and NO_2-PAH found in the S5 exhaust.*

Sample	PCDD/F total TEQ (ng/m^3)	PCB+HCB (ng/m^3)	PAH (μg/m^3)	NO$_2$-PAH (μg/m^3)
Macro1	-	-	12.7-15.6	-
Macro2	-	-	17.0-20.7	-
Macro3	0.002-0.02	<60	20.5-24.6	0.74-2.24
Macro4	0.208-0.22	<60	23.2-29.0	3.37
Macro5	-	-	26.3-34.1	2.44
Macro6	-	-	21.7-27.2	3.56

The results for the PCDD/F analysis are corrected for the %recovery of internal and external standards. Due to problems with the matrix, it was not possible to determine the

%recovery of the internal standards. Therefore, the results for the PCB+HCB analysis are not corrected for the %recovery of the internal standard.

The results for the PAH- as well as the NO_2-PAH analysis are not corrected for the %recovery of internal standard. For the results of the PAH and NO_2-PAH (Macro 3), the first and second figure demonstrates the total of PAH without and with the components which are disturbed by other, unknown compounds. None of the results are corrected for the blank.

Discussion

After the **sampling** on the S1, we found that the sampling materials PUF and XAD were destructed partly, probably by the acids which broke through the impingers. This was *not* the case with the S3 and the S5 samplers. In future experiments the impingers should contain alkali for a better acid absorption.

During the **analysis** of the PCDD/F no difficulties were observed. However, the % recovery of the internal standard 1,2,3,4-T4CDD 13C12 after sampling and extraction of the samples of the S5 were significantly lower compared to the other results.

Problems occurred during the analysis of PCB and HCB. Due to problems with the matrix it was not possible to analyse the content of PCB and HCB in the first fraction collected during the cleanup for the analysis of the PCDD/F. Because of problems with the matrix and probably a low content of PCB and HCB in the extracts, it was decided to use GC-MSD instead of GC-ECD for the analysis. However, even with GC-MSD identification of the peaks with GC-MSD was difficult.

Cleanup with semipreparative HPLC, however, gave more satisfactory results.

Prior to analysis, the cleanup with the semipreparative HPLC was calibrated with a mixture of PCB + HCB, PAH and NO_2-PAH. In the first fraction the PCB and HCB could be quantitatively recovered. Although most of the PAH eluted in the second fraction, some PAH eluted also in the fraction where the NO_2-PAH eluted. Approximately 20% of benzo(b)fluoranthene, 70% of dibenzo(a,j)-anthracene, 50% of dibenzo(a,l)pyrene and 30% of indeno(1,2,3-c,d)pyrene were found in that fraction. The NO_2-PAH were found quantitatively in the third fraction. The following fractions were also collected. These fractions probably contain the more polar substituted PAH, like hydroxy-, hydroxy-nitro- and acetoxy-PAH.

Because the sample matrix gave severe problems with the pump of the semipreparative HPLC, a pre-cleanup had to be developed. Experiments with a standard mixture of PAH showed that approximately 100% of the PAH were recovered after a cleanup with a 'Seppak' Silica cartridge. NO_2-PAH, however, were recovered for only 60%. Therefore, another cleanup procedure had to be developed. The application of a 'Seppak' C18 cartridge gave satisfactory results for the NO_2-PAH as well as for the HCB + PCB.

So, for the analysis on PAH, it was decided to use a cleanup with a 'Seppak' Silica cartridge, while for the analysis on NO_2-PAH, PCB and HCB a cleanup with a 'Seppak' C18 cartridge followed by semipreparative HPLC was used.

Concerning the results for the PCB and HCB, it has to be remarked that the % recoveries for the internal standards vary significantly and some of them are relatively low. For the measurements on the S5, both internal standards are not recovered at all. This is probably due to the fact that because of severe problems with the matrix, the samples of the S5 had to be diluted prior to analysis. This also probably explains the relatively low % recovery of 1,2,3,4-T4CDD 13C12 (internal standard PCDD/F analysis) and benzo(b)chrysene (internal standard PAH analysis).

Furthermore, although the analysis for PAH after cleanup with a 'Seppak' silica cartridge was possible, the extract had to be diluted in order to be able to analyse the PAH. Due to this dilution, the concentrations of the internal standards (6- and 2-methylchrysene) were probably too low for an accurate determination of the %recovery. However good % recoveries of 2-and 6-methylchrysene were found for the blank. This means that the extremely high recoveries of internal standards are also due to the fact that both internal standards probably co-elute with other, unknown, compounds.

Because the knowledge about the existence and/or formation of NO_2-PAH is still limited and just a few reference materials are available, it was not possible to use an internal standard for the determination of NO_2-PAH. However, next to external standards, an extra identification is possible by analysing the extract with and without the reduction column. The peaks which disappear when not using the reduction column are identified as nitro-substituted PAH. Concerning the analysis of the NO_2-PAH, strange results were obtained for the S1. Especially for 1,6/1,8-diNO_2-pyrene, extremely high contents were observed. Although we probably dealing with a NO_2-PAH (because the peak disappeared in the chromatogram when using no reduction column), it is very unlikely that the content of 1,6/1,8-diNO_2-PAH is in the same range as the PAH content. Also for 2-NO_2-fluorene, high concentrations were observed in some samples of the S1. This is probably due to the fact that this compound can be measured less sensitive under these conditions of the

fluorescence detector. This means that small peaks already yield high concentrations. Secondly, the fault in the analysis nearby the detection limits is mostly higher. However, one has to be aware that especially during the sampling on the S1, high concentrations of soot and acids were observed, and that in the end the sampling materials PUF and XAD were partly destructed. It is a well-known fact that NO_2-PAH can be formed during sampling [30]. Due to the extreme conditions during the measurements on the S1, it is not unlikely that significant amounts of NO_2-PAH are formed in the sampling train. This means that the content of NO_2-PAH analysed in the samples, gives no good information considering the real emitted amount of NO_2-PAH by the S1. So, therefore, we decided to report for the measurements on the S1 only the results of the mono-NO_2-PAH.

3.   ENGINE ROOM AIR

3.1   Sampling

Engine room air samples were taken by pumping 0.3 - 0.4 m^3 of air at room temperature through two adsorption tubes in series. The tubes contained 200 mg of XAD-2 resin each. Before sampling the first tube of every pair was spiked with an exactly known amount of PCB-88. The second adsorption tube served as a check on sample break through.
The sample volumes were determined with a dry gas meter. The engine room air analysis were taken, near by the air 'inlet' canals of the engine room on the S1, S3 and S5.
Two samples were taken on each ship.

3.2   Analysis

The XAD resin was extracted with n-hexane. The extracts were analysed without further treatment for the presence of PCB, with GC-ECD or in case of the measurements on the S5 with GC-MSD.

3.3   Results and comments

On all ships no PCB could be detected above the analytical blank levels in the engine room air. This means that the PCB concentrations in the air were below 1-2 ng/m^3 for each congener. They do not give reason for concern because they approach the normal values for outside air.

4.   FUEL OIL

4.1   Sampling

On the S1 a fuel oil sample was taken by a member of the ship's crew when the ship had returned to the Dutch port.

On the S3 a fuel sample was also taken by a member of the crew during the day of the sampling.

On the S5 a fuel oil sample was taken by a member of the ship's crew during the fourth day of the sampling.

4.2   Analysis

The analysis for the S1 and the S3 was carried out by the Analytical Laboratory "Monitor" in Amersfoort, The Netherlands. The analysis for the S5 was carried out by the Analytical Laboratory "Caleb Brett Nederland BV" in Rotterdam. Both laboratories are specialised in the determination of Total Organic Halogen etc.. The method used is combustion at 950°C in oxygen and automatic coulometric argentometric titration.

4.3   Results and comments

The samples were analysed in duplicate.

In the fuel of the S3 no TOCl could be found; in both analyses the levels were below the limit of detection: < 2mg/kg.

In the sample from the S5 1.2 mg TOCl/kg was found.

In the sample from the S1 12.7 and 8.8 mg TOCl/kg was found respectively. The mean value given here is 11 mg/kg.

The nature of the organochlorine compounds in the fuel samples (probably 15 - 20 mg/kg) is not known. When they would not be destroyed in the engine, they would cause an organochlorine compound concentration of about 0.04 till 0.4 mg/m^3 in the exhaust gases, under the assumption that 1 kg of fuel gives rise to about 40 m^3 of exhaust gas.

It is not clear whether they contribute to the PCDD/F content of the exhausts. (The fuel with the highest organochlorine content gave the highest PCDD/F emissions, but a lower PCB emission compared to the S3! In reference 13 the relatively high PCDD/F emissions go together with the relatively high PCB emissions. In reference 26 the opposite has been found.)

5.   DISCUSSION

In Table 19 the results of the exhaust analyses have been summarised and brought together with a few data from the literature.

Table 19   Summary of exhaust data found in this study and a few literature data for comparison.

compounds	units	S1	S3	S5	literature data on	
					motor cars	ship's engine
references:		this work			[5,6,22-26]	[13]
HCB + PCB	ng/m^3	20 - 60	90 - 240	n.d.		1300
PCDD/F	ng/m^3	0.09-0.2	0.01-0.04	0.002-0.2	1 - 18	1.34
PAH	µg/m^3	64 - 92	29 - 52	13 - 29	20 - 160	20
NO$_2$-PAH	µg/m^3	1.7-10	0.20-0.36	0.74-3.6	1 - 10	-

During sampling on the S1, the sampling materials PUF and XAD were partly destructed, probably by the acid which broke through the impingers. Because it is a well-known fact that NO$_2$-PAH can be formed under certain circumstances during sampling, this phenomena can be an explanation for the relatively high concentrations NO$_2$-PAH found for the S1 samples. Although a breakthrough was determined during sampling on S1, the results for the duplicate samplings are found to be in the same order of magnitude. PCDD/F as well as PCB levels were relatively low, while the PAH levels were significantly higher than those for the Blank. Due to the measured breakthrough it may be concluded that the amount of emitted PAH by S1 is probably higher than measured here.

For S3 and S5 less problems, besides the soot problems, were observed during the sampling. The results for these ships are well in line with those of other investigations.

Overall, he PCDD/F emissions are rather low. The PCB emissions (which are also very low) can perhaps be understood when the fuel samples have been analysed for PCB. Based on our findings a total PCB emission per year on the North Sea of about 20 kg can be calculated, which is low in comparison to the estimated 10 - 160 tons per year [7].

The nitro-PAH emissions are about two orders of magnitude lower than the PAH emissions, which could be expected from the literature. However, this literature also shows that nitro-PAH emission can be much higher for idling Diesel engines. The PAH emissions are not surprising.

If we take the maximum estimate of 5 million tons of fuel oil per year combusted on the North Sea [3], shipping with ships of the type studied here contributes about 16 tons of PAH per year to the atmospheric deposition on the North Sea. This is not much compared to the input estimates of 80 to 1500 tons/year [7].

However, we do not know whether the emissions from the S1 and the S5 can be considered to be representative for the combined shipping on the North Sea.

6.   CONCLUSIONS AND RECOMMENDATIONS

The emissions of HCB+PCB, PCDD/F, PAH and NO_2-PAH we have found for three cruising ships are in the order of magnitude which could be expected from the literature data on Diesel engines on land.

If the data found here are considered to be representative for the emissions of all ships on the North Sea, the contribution from shipping to the atmospheric deposition on the North Sea is relatively small.

With regard to future investigations we would like to make the following recommendations:

- perhaps ships with older engines should be included in the study,
- the fuel oil should be analysed for TOCl and PCB,
- PCDD/F should only be analysed when extremely high TOCl values have been found in the fuel,
- more attention should be paid to NO_2-PAH emissions during the stay and the movements of the ships in port,
- during sampling more precautions should be taken against reactive gases in the exhaust.
- Nitro-PAH analysis should be improved/extended, by introducing appropriate (labelled) internal standards and for the characterisation of (unknown) NO_2-PAH, analysis, probably with HRGC-(HR)MS, should be included.

7.   QUALITY CONTROL

Concerning the accuracy and precision, a general comment can be made with respect to the sampling. Because the concentrations of organic microcontaminants in smoke gases is normally not known, it is very difficult, if not impossible, to validate these sampling techniques. So, normally, the sampling train is spiked prior to sampling and in some cases breakthrough volumes are determined. By sampling in duplicate, not only the reproducibility of the sampling is determined but also those of the extraction and the analysis. So, the accuracy of the sampling alone is not known. The repeatability and the accuracy of the extraction as well as the analysis however, have been determined for a number of standards and samples during the last couple of years, and are reported here.

The analysis of PAH is carried out according to a validated method for the determination of PAH in extracts [29].
The accuracy of this method is controlled by a certified Standard Reference Material, SRM 1647A. The accuracy varies per component, and lies between 0.5% (pyrene) and 22% (Benz(g,h,i)perylene).
The repeatability of this method is expressed as the relative standard deviation, and varies also per component; 6% (benz(b)fluorene) till 12% (benz(b)fluoranthene). Qualification is based on the retention times of external standards.

For the analysis of NO_2-PAH, quantification was possible by means of a ten times diluted certified Standard Reference Material, SRM 1587. The repeatability, also expressed as the relative standard deviation, varies per component and lies between 3% (6-nitro-benz(a)-pyrene) and 13% (6-nitrochrysene). Qualification is based on the comparison of retention times of external standards, standard addition and analysis of the samples with and without the use of the reduction column.

The analysis of PCDD/F is carried out according to a validated method for the determination of PCDD/F [27]. Prior to the analysis of the samples the performance of the capillary fused silica column is tested by means of a fly-ash extract. The resolution between 2,3,4,8- and 2,3,7,8,-T4CDF is at least 0.45.
Quantification of PCDD/F takes place by means of internal and external standards. Percentages recoveries of internal standards are determined, and are at least between 20% and 120% at a signal to noise ratio of at least 10 for the corresponding native PCDD/F.

The repeatability and accuracy of the method is determined by means of a fly-ash extract, and is usually less than 10%.

Qualification of the PCDD/F congeners are based on the retention times, simultane detection on the specific molecular mass and adequate isotope ratios.

The analysis of PCB + HCB is carried out according to a validated method for the determination of PCB + HCB in fly-ash [28].

Although no recent data is available on the repeatability and accuracy of the method, the method used can be compared with the method for the determination of PCDD/F. So, the repeatability and the accuracy is probably less than 10%.

8. LITERATURE REFERENCES

1. Lloyd's Register of Shipping, Marine Exhaust Emissions Research Programme: Transient Operation. Lloyd's Register of Shipping, London, 1993.

2. Ministry of Transport and Public Works, The Netherlands, 1986, "Water Quality Management Plan North Sea"; 93 pages, see: pages 39 - 43.

3. Wulffraat K. 1991, (Rijkswaterstaat, the Netherlands), personal communication.

4. White C.M. (ed.), 1985, "Nitrated Polycyclic Aromatic Hydrocarbons"; Huethig Verlag, Heidelberg, New York; 388 p..

5. WHO, IARC, 1989, "Diesel and Gasoline Engine Exhausts and some Nitroarenes."; IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 46, IARC, Lyon, France; 456 p..

6. Schwind K.-H. et al, 1991, "Emission of halogenated dibenzodioxins (PXDD) and dibenzofurans (PXDF) from combustion engines, running on commonly available fuels."
Z.Umweltchem.Oekotox.,3[5],291-298. (In German)

7. Salomons W., B.L.Bayne, E.K.Duursma, U.Förstner (Eds.), 1988, "Pollution of the North Sea. An Assessment", Springer Verlag, Berlin, London, etc.; 695 pages.

8. Södergren A. et al, 1990, "Transport of incinerated organochlorine compounds to air, water, microlayer and organisms.", Mar.Poll.Bull.,21[1], 18-24.

9. Kranz H., V.Dethlefsen, 1990, "Liver anomalies in dab Limanda limanda from the southern North Sea with special consideration given to neoplastic lesions."; Dis.Aquat.Org.,9, 171-185.

10. Sato T. et al, 1985, "Nitroarenes in Suimon River sediment.", Mutation Research, 157, 135-143.

11. Walker M.K. *et al*, 1991, "2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) toxicity during early life stage development of Lake Trout (Salvelinus namaycush).", Canad.J.Fish.Aquat.Sci., 48, 875-883.

12. Reynolds G.L. & J.S. Carlton, 1990, "Test bed and operational routes to the assessment of the marine exhaust contribution to atmospheric pollution.", EMEP Workshop on Emissions from Ships, Oslo, Norway, 7-8 June, 12 pages.

13. Gros S., 1990, "Emissions and Emission Control Techniques for Medium Speed Diesel Engines.", paper distributed during the EMEP Workshop on Emissions from Ships, Oslo, Norway, 7-8 June, 16 pages.

14. Weitkamp C., *et al*, 1986/7, "Distribution of Hydrochloric Acid in Waste Gas Plumes from Incineration Ships: Remote LIDAR Measurement of Concentration Distributions and the Determination of Dilution and Degradation Parameters." GKSS Report 86/E/44, Geesthacht, Germany. (Copies available in German and in English)

15. Levsen K., 1988, "The analysis of Diesel particulate. A Review.", Fres.Z.Anal.Chem.,331, 467-478.

16. Martone J.A., 1978, "Subisokinetic sampling errors for Aircraft Turbine Engine Smoke Probes.", J.Air Poll.Contr.Assoc., 28[6], 607-609.

17. Rader D.J. & V.A.Marple, 1988, "A Study of the Effects of Anisokinetic Sampling.", Aerosol Sci.Technol.,8, 283-299.

18. Plomp A. & M.M.Rhemrev-Boom, 1989, "Validation of sampling techniques for organic (PAH) and inorganic particulate components, carried out on a combustion gas and aerosol generating circuit." Report ECN-89-88, November 1989. (In Dutch)

19. Oberg T. & J.G.T.Bergström, 1985, "Hexachlorobenzene as an indicator for dioxin production from combustion.", Chemosphere,14[8] 1081 - 1086.

20. Zorge J.A. van, *et al*, 1989, "Assessment of the toxicity of mixtures of halogenated dibenzo-p-dioxines and dibenzofurans by use of Toxicity equivalency factors (TEF).",
Chemosphere, 19[12] 1881 - 1895.

21. Beije B. & L.Möller, 1988, "2-Nitrofluorene and related compounds: prevalence and biological effects."
Mutation Res.,196, 177 - 209.

22. Fiedler H. & W.Mücke, 1990, "Nitro-PAH from Combustion Engines. Analysis and Emissions.",
Z.Umweltchem.Oekotox., 2[4] 231 - 235. (in German)

23. Mücke W. & H.Fiedler, 1990, "Nitro-PAH. Sources, Environmental behaviour and Effects.",
Z.Umweltchem.Oekotox., 2[3] 170 - 176. (in German)

24. Hagemann R. *et al*, 1982, "Polycyclic Aromatic Hydrocarbons in Exhaust Particles Emitted from Gasoline and Diesel Automobile Engines.",
Toxicol.Env.Chem.,5, 227 - 236.

25. Marklund S. *et al*, 1990, "Emissions of PCDDs and PCDFs in gasoline and Diesel fueled cars.",
Chemosphere,20, 553 - 561.

26. Bröker G. *et al*, 1989, "Chlorinated and Brominated Dioxins and Furans from Motorcars.", (in German),
"Aus der Tätigkeit der LIS 1989, Essen.", 31 - 34 ; Germany.

27. L.J.M. Rodenburg, 1990, "The determination of the 17 most toxic PCDD/F congeners in flyash and electrofilter ash by means of capillairy gaschromatography and mass selective detection", standard operation procedure
IMW-TNO, IMWA/SG/020 (in Dutch).

28. S.A.C.M. Walraven, 1989, "The determination of polychlorobifphenyls (PCBs) in tissue and sediment samples", standard operating procedure IMW-TNO, IMWA/SG/016 (in Dutch).

29. R.M. Hoefnagel, 1991, "The determination of Polycyclic Aromatic Hydrocarbons in extracts", standard operating procedure IMW-TNO, IMWA/SV/014 (in Dutch).

30. A. Lindskog *et al*, 1984,"Transformation of reactive PAH on particles by exposure to oxidized nitrogen compounds and ozone", Report Swedish Environmental Research Institute, Gothenburg, Sweden.

APPENDICES
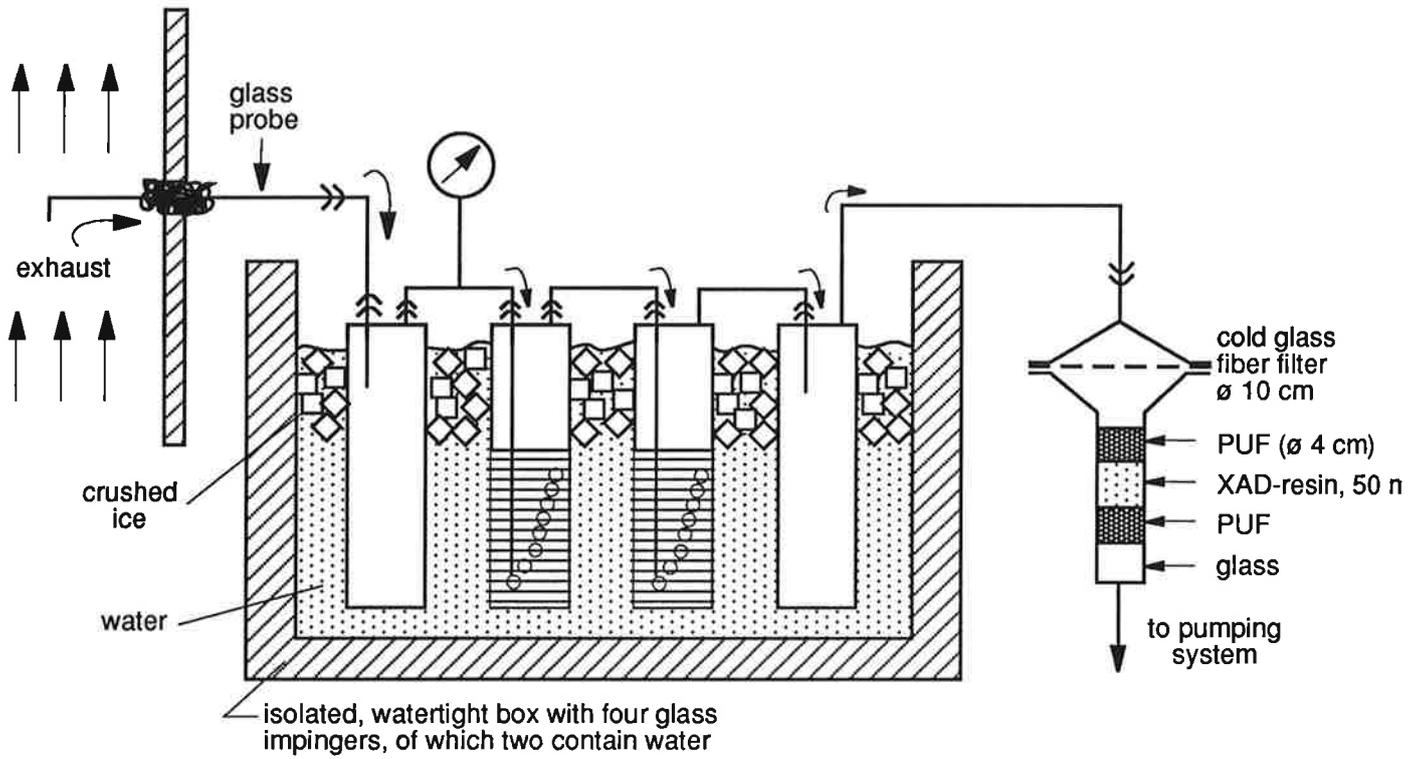
Figure 1   *The sampling equipment used on the ships.*
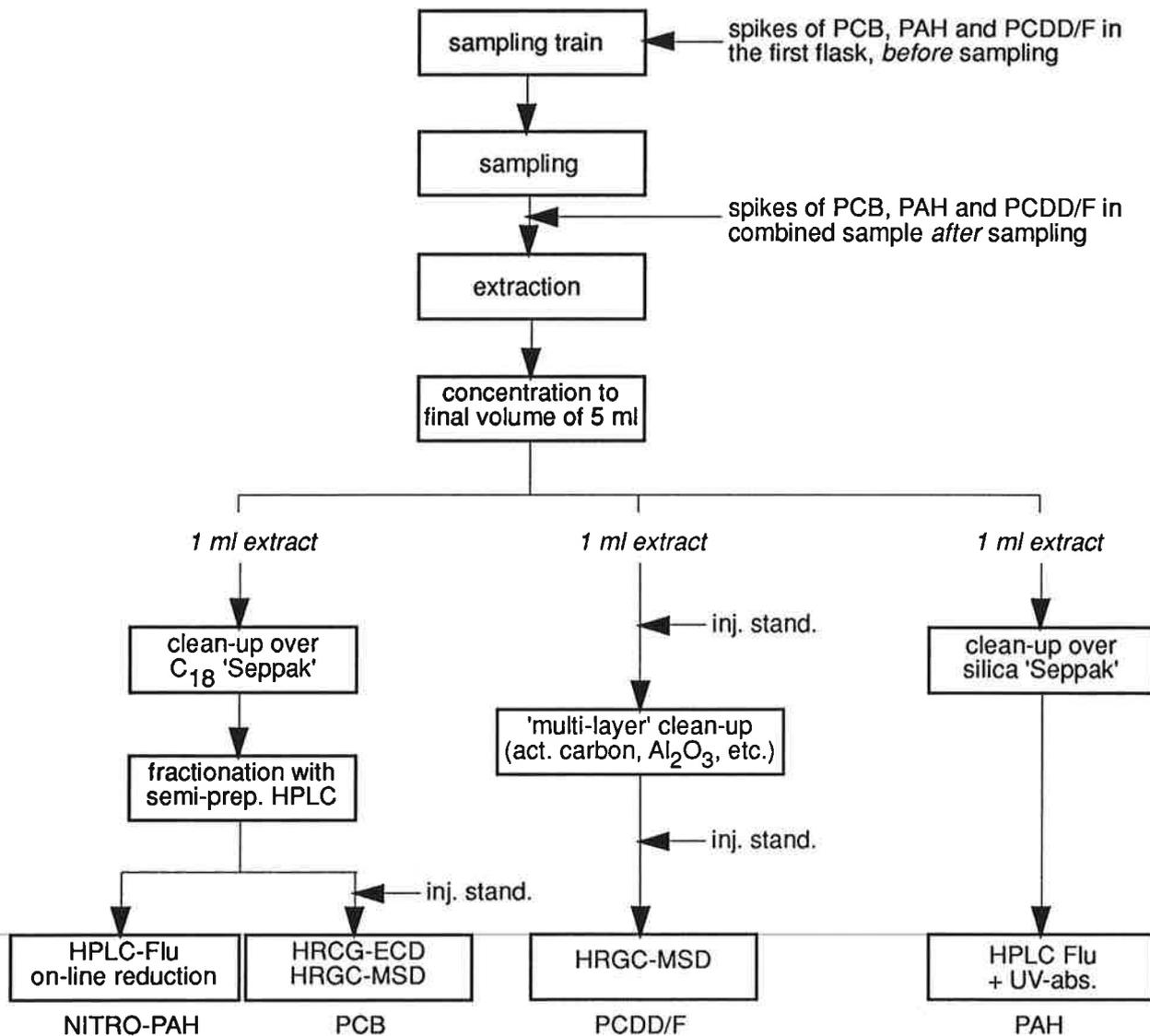
Figure 2   *Overall scheme of the analytical procedures*
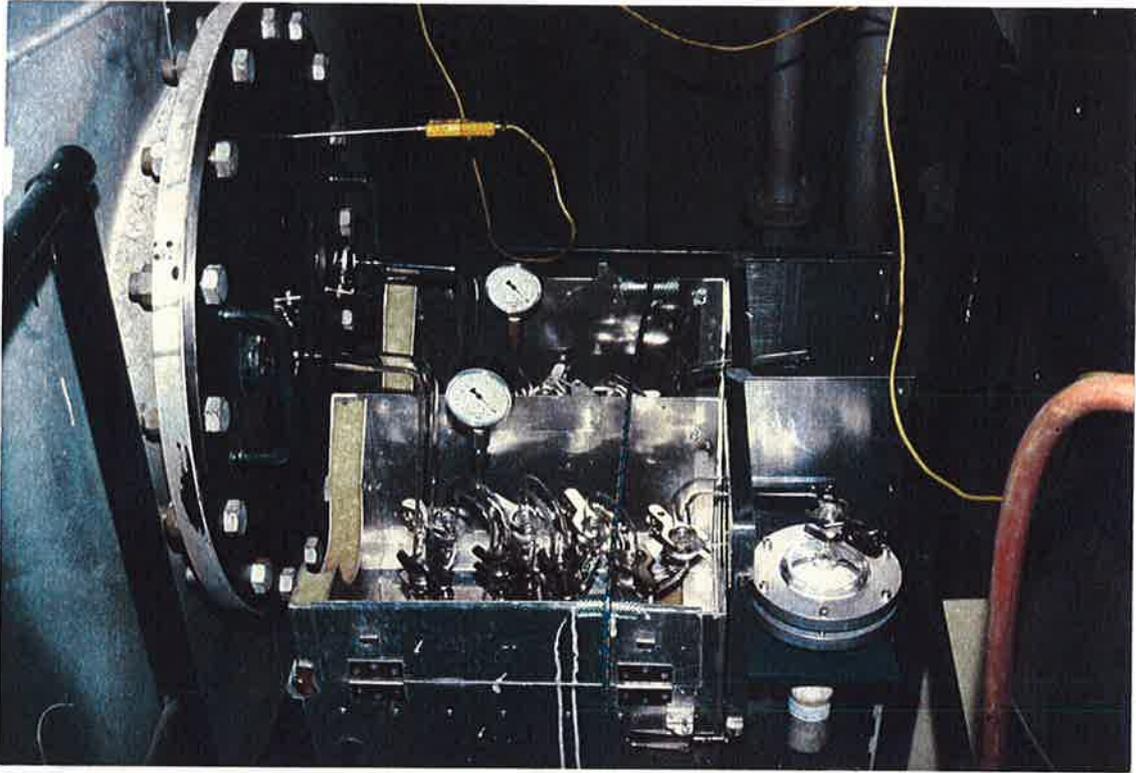
Photograph 1   *The glass sampling probe adapted on the S1*
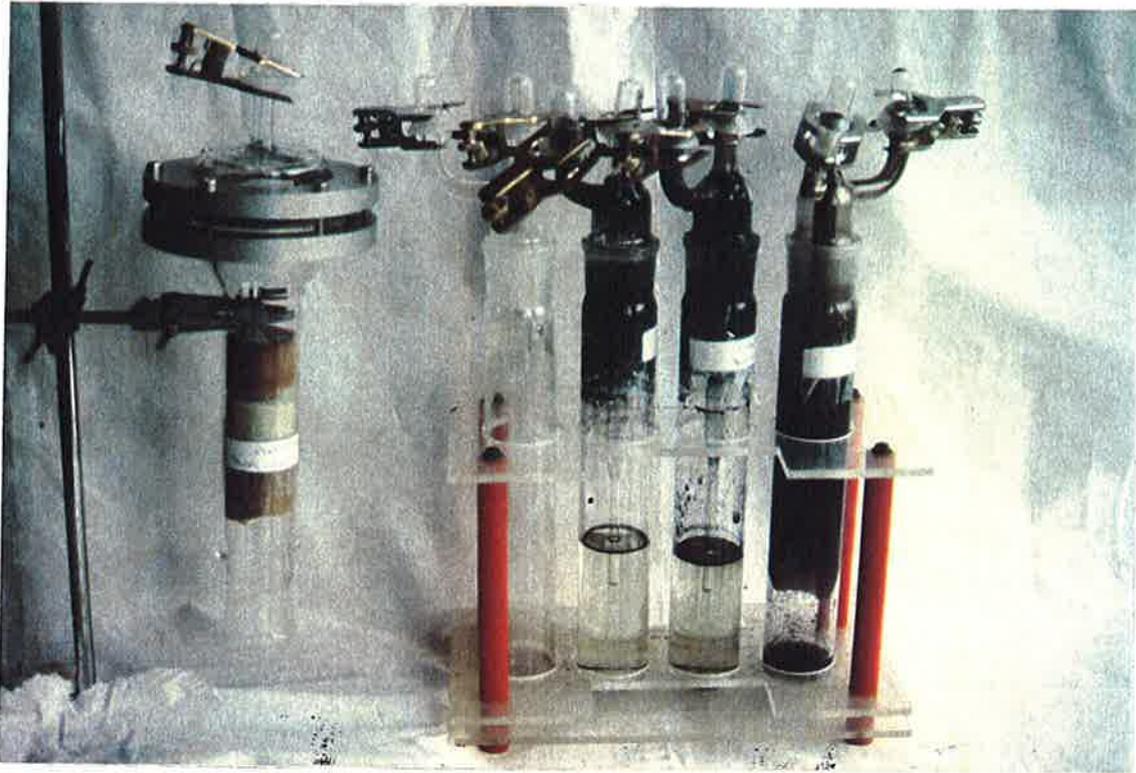
Photograph 2   *The sampling equipment after the sampling on the S1*
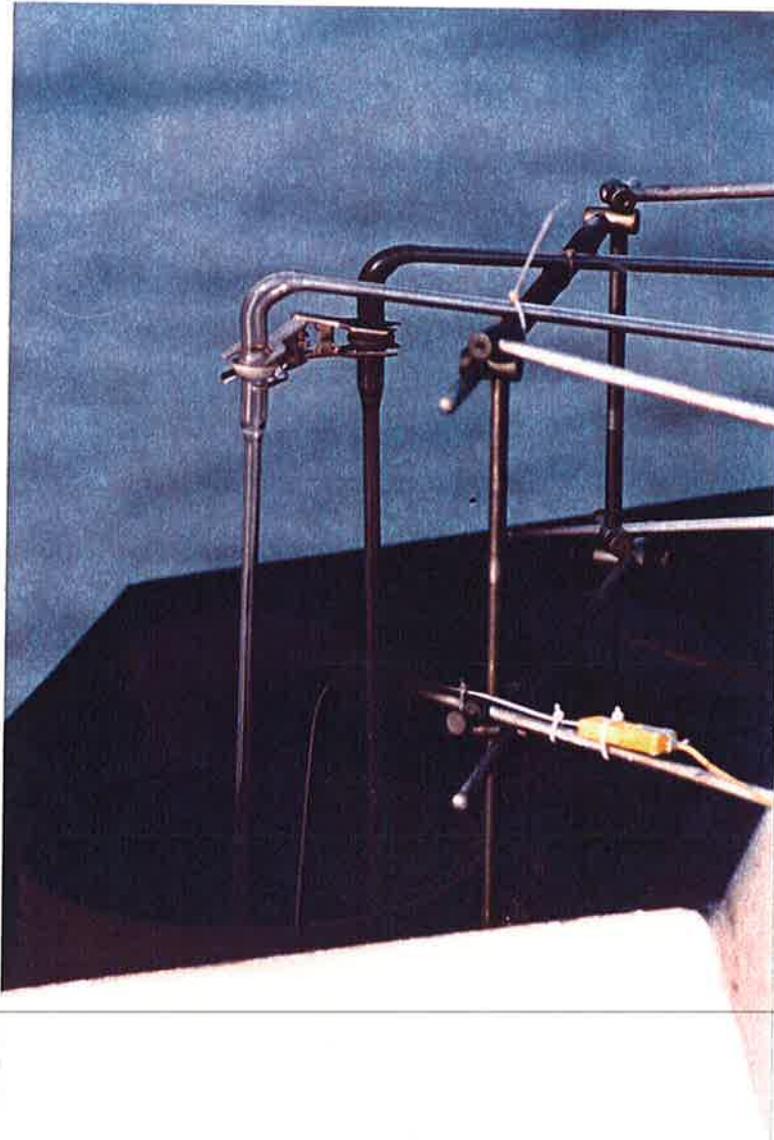
Photograph 3   *The glass sampling probe adapted on the S3*
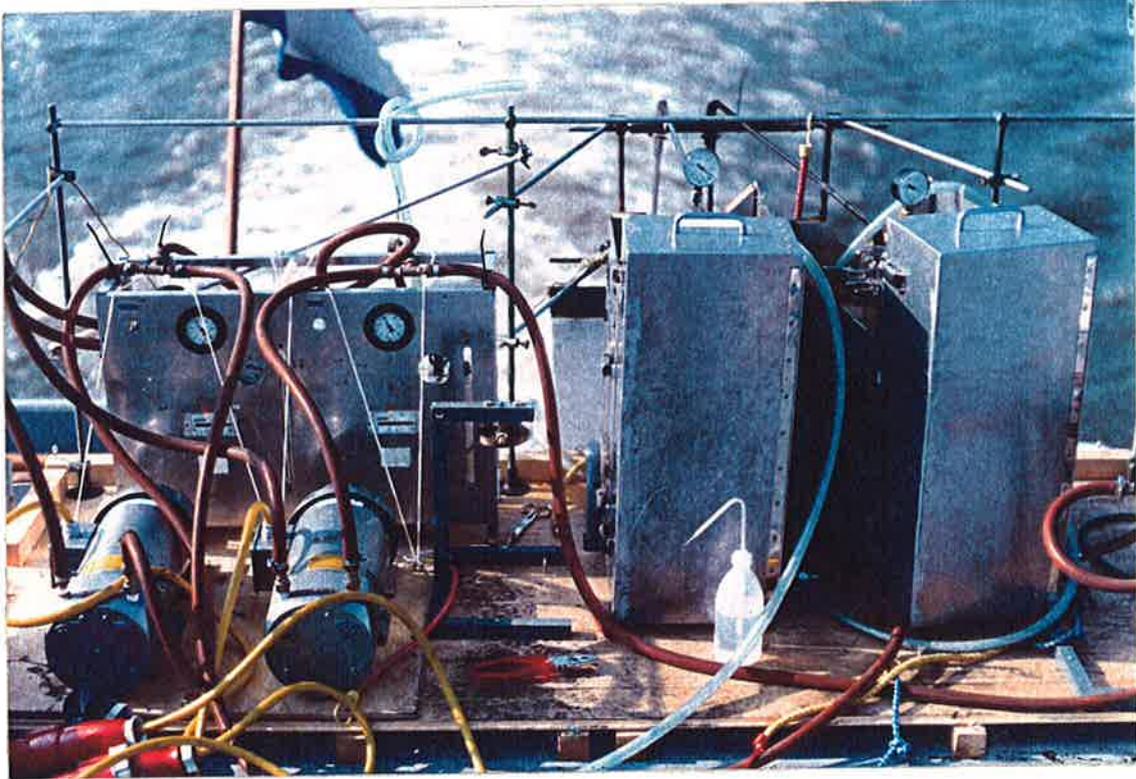
Photograph 4   *The sampling equipment used on the S3*
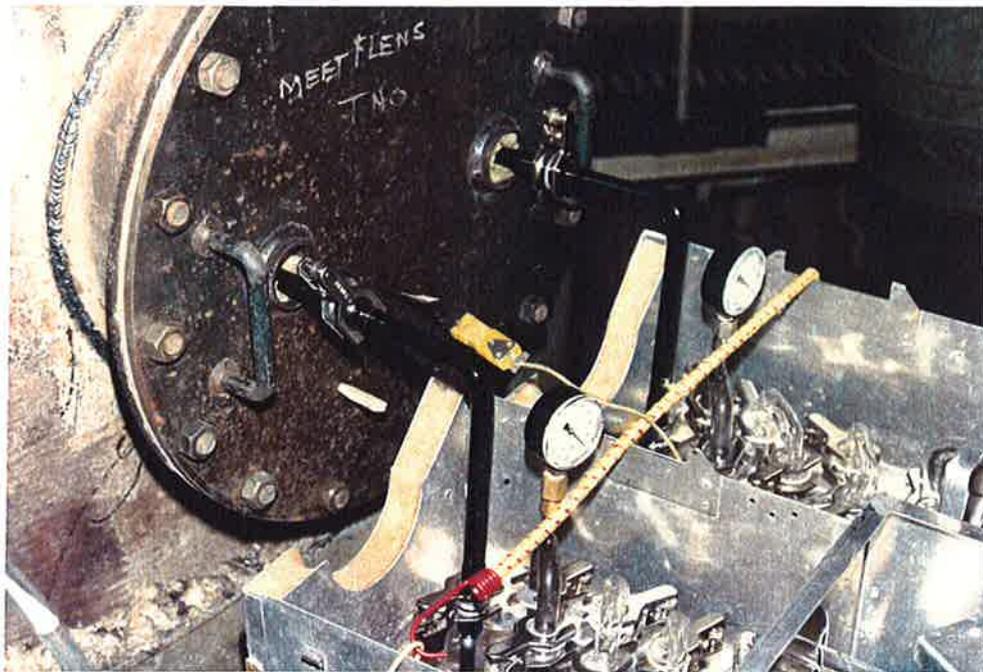
Photograph 5   *The glass sampling probe adapted on the S5*
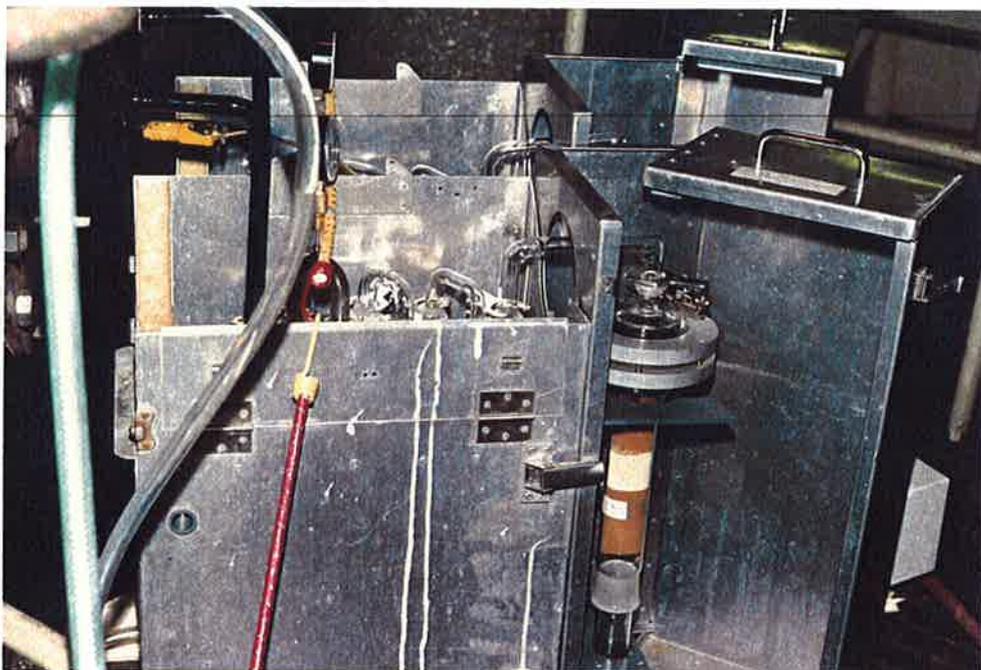
Photograph 6   *The sampling equipment used on the S5*