

Report on the Requirements for New Reactive Gas Calibration Techniques Relevant to the 1997-2000 Valid Analytical Measurement Programme

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ABSTRACT

This document outlines gases which could be measured using new reactive gas calibration techniques developed at NPL, and are required by UK or international regulatory bodies, or other organisations. The sources of the possible requirements are reviewed first, followed by an assessment of the different species that could be measured under Project 1.1(c) of the 1997-2000 Valid Analytical Measurement (VAM) Programme. Finally, there is a concise description on how the NPL Reactive Gas Calibration Facility will be employed to measure these gases, together with a conclusion justifying the selected species.

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by

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1. INTRODUCTION

There are a number of diverse UK and international organisations that are responsible for setting regulations, directives, and guidelines on air pollution. The most important ones are reviewed in Section 2, together with a brief summary of their roles. Important directives and recommendations on the concentrations of selected pollutants have also been identified. This is in order to determine which are the priority gases that could be developed as dynamic NPL standards under Project 1.1(c) of the 1997-2000 Valid Analytical Measurement (VAM) Programme. Section 3 contains a list of the possible target gases together with the recommended maximum exposure limits. Section 4 describes the method by which the selected dynamic standards may be analysed spectroscopically using the NPL Reactive Gas Calibration Facility. Finally, Section 5 gives the conclusions and justifications of the selected species.

2. SOURCES OF REQUIREMENT

2.1 UN/ECE CONVENTION ON LONG-RANGE TRANS-BOUNDARY POLLUTION

The United Nations Economic Commission for Europe (UN/ECE) is a body that encompasses a wide range of activities in Europe and the USA which include a Convention on Long-range Pollution. This Convention was adopted in 1979 to cover SO₂, NO_x (NO + NO₂), volatile organic compounds (VOCs), chlorine compounds, poly- aromatic hydrocarbons (PAHs), metals and particulates. There are various separate Protocols, binding their signatories to implement specified cuts in the stated pollutants. The European Monitoring and Evaluation Programme (EMEP) was set up to **monitor** the ambient levels of the various pollutants.

2.2 EC ENVIRONMENTAL INITIATIVES

The European Community (EC) has a number of environmental initiatives, of which the most relevant to the VAM Programme are listed below:

- i) The Ambient Air Framework Directive has now been agreed. Work is presently proceeding on a range of daughter Directives. These will involve the gases SO₂, CO, NO₂, and benzene.
- ii) Air Quality Standards have been set for some air pollutants making use of World Health Organisation (WHO) guidelines in a number of cases.
- iii) Reductions or phasing out of certain chemicals has been agreed, especially chlorofluorocarbons (CFCs) which are specified in the Montreal Protocol.
- iv) The Large Combustion Plant Directive ties the EC in with UN/ECE Trans-boundary Protocol. It sets (decreasing) limits on SO₂ and NO_x from combustion plants, on a national basis.
- v) The (**draft**) Solvents Directive defines “VOC” and “Solvents” in a general way, but makes no mention of individual compounds. It recognises “halogenated solvents”, but does not define them. The Directive sets limits on the total level of solvent emissions from specific types of process and requires **monitoring** of releases of solvents into the air.
- vi) The Municipal Waste Incineration and Hazardous Waste Incineration Directives requires measurements of a range of gaseous compounds.

2.3 WORLD HEALTH ORGANISATION GUIDELINES ON POLLUTANTS

In 1987 the World Health Organisation (WHO) produced a list of health-based limits for 27 air pollutants. These were re-assessed in 1996/7. The pollutants listed in the WHO document are all “classical” (CO, ozone, NO₂, SO₂), organic and inorganic species.

The organic compounds, together with limits, are classified by the WHO as:

non-carcinogens:

dichloromethane (3 mg/m ³)	formaldehyde (0.1 mg/m ³)
styrene (0.26 mg/m ³)	tetrachloroethylene (0.25 mg/m ³)
trichloroethylene	toluene (0.26 mg/m ³)

carcinogenic VOCs

benzene	1,3 butadiene	PAHs	trichloroethylene
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(The inorganic compounds are all metals and therefore are not listed here.)

2.4 MONTREAL PROTOCOL ON OZONE-DESTROYING SUBSTANCES

The following substances are **now** supposed to have been “phased out” because of their role in the destruction of stratospheric ozone:

chlorofluorocarbons (less developed countries can still use CFC compounds until 2010)
 halons (again, less developed countries may use these substances until 2010)
 carbon tetrachloride
 1,1,1 trichloroethane

In addition there is supposed to be a **limitation** in the use of methyl bromide, HCFCs and HBrFCs.

Since they are to be phased out, it should not be necessary to prepare the molecules listed above as standards, unless there is a future requirement to monitor infringements of the Protocol.

2.5 UK ACTIONS ON AIR POLLUTANTS

The most important legislation on pollution enforcement in the UK derives from the Environmental Pollution Act (EPA) of 1990. Under the Act, the main organisations that have the responsibility for enforcement are the Environment Agency (EA), the Local Authorities, and the Health and Safety Executive (HSE). Some of the most important roles are summarised below:

2.5.1 Integrated Pollution Control (IPC)

This activity started in the UK in 1990 when the Environment Act incorporated “Integrated Pollution Control (IPC)”, covering all emissions to air, water and land from “Part A” and “Part B” processes. The EA is responsible for enforcing Part A; ie, large plant emissions, and Local Authorities are responsible for Part B; ie, local emissions.

Guidance on control of Part A emissions is given in the EA “Integrated Pollution Regulation (IPR)” notes. These include “Achievable Release Levels (ARL)” for new plants using efficient abatement technology. There are also “Process Guidance (PG)” notes that are specific to particular types of plant, “Technical Guidance (TG)” notes on more general topics (“M” on Monitoring, “A” on Abatement, Environmental and Dispersion). There are also “Air Quality (AQ)” notes that are prepared by Air Quality Division of the Department of the Environment, Transport and the Regions (DETR), formally the Department of the Environment. These supplement or explain some of the TGs in certain specific areas.

Specific air pollutants mentioned by various IPR notes are:

S2 1.01 (Large Boilers and Furnaces): oxides of nitrogen, SO₂, HCl, CO,

	VOCs, dioxins, ammonia
S2 1.03 (Compression Ignition Engines):	oxides of nitrogen, SO ₂ , HCl, CO ₂ , CO, VOCs, dioxins, ammonia
S2 1.04 (Waste and Recovered Oil Burners):	HCl, oxides of sulphur, oxides of nitrogen, CO, dioxins, VOCs, PAHs
S2 1.05 (Combustion of Solid Waste Fuel):	HCl, HF, oxides of Sulphur, oxides of nitrogen, CO, dioxins, VOCs, formaldehyde, HCN,
S2 1.06 (Coke Manufacture):	SO ₂ , oxides of nitrogen, CO, ammonia, VOCs, PAHs, H ₂ S, dioxins
S2 1.07 (Carbonisation Processes):	oxides of sulphur, oxides of nitrogen, CO, H ₂ S, benzene, benzopyrene, VOCs, ammonia
S2 1.08 (Gasification of Feedstocks):	H ₂ S, oxides of nitrogen, SO ₂ , CO, dioxins, VOCs
S2 1.09 (Natural Gas Refining):	oxides of nitrogen, H ₂ S, SO ₂ , VOCs
S2 1.10 (Petroleum Processes):	oxides of nitrogen, sulphur dioxide
S2 1.11 (On-Shore Oil Production):	oxides of nitrogen, H ₂ S, sulphur dioxide, VOCs
S2 1.12 (Heat Treatment Furnaces)	oxides of nitrogen, SO ₂ , HCl, CO ₂ , CO, VOCs, dioxins, ammonia
S2 3.01 (Cement Manufacture etc.):	oxides of sulphur, oxides of nitrogen, dioxins, VOCs, HCl, HF, SO ₂ , CO (when burning 40% hazardous waste)
S2 3.02 (Asbestos Processes):	formaldehyde, phenol, HCl, ammonia, amines, VOCs
S2 3.03 (Glass Fibres, Frit Manufacturers.):	Cl ₂ , HCl, HF, VOCs, fluorides, oxides of nitrogen, chlorides, oxides of sulphur, H ₂ S, phenol, formaldehyde, ammonia, total amines,
S2 3.04 (Ceramic Processes):	oxides of sulphur, HF, HCl, CO
S2 5.01 (Waste Incineration):	HCl, CO, HF, SO ₂ , VOCs, dioxins, oxides of nitrogen, I ₂ , ammonia

S2 5.02 (Making Solid Fuel from Waste):	dioxins
S2 5.03 (Carbon Regeneration):	HCl, SO ₂ , oxides of nitrogen, CO, VOCs
S2 5.04 (Organic Solvents, Oil Distillation):	VOCs, ammonia, amines, H ₂ S, volatile organic sulphur compounds, halides/halogens
IPR 1/1 (Large Combustion Plant) :	SO ₂ , NO _x , ammonia, halogen compounds, VOCs
IPR 1/2 (Gas Turbines):	SO ₂ , oxides of nitrogen, CO
IPR 2/2 (Ferrous Foundry Processes):	dioxins, VOCs, fluorides
IPR 2/3 (Steelmaking Processes):	dioxins, fluorides, VOCs, HCl, NO _x
IPR 2/4 (Zinc Production):	oxides of sulphur, HCl, HF, VOCs, dioxins
IPR 2/5 (Lead Production):	oxides of sulphur, HCl, VOCs, dioxins
IPR 2/6 (Refractory Metal Production)	oxides of sulphur, VOCs, ammonia
IPR 2/7 (Melting and Recovery of Cd, Hg):	none
IPR 2/9 (Production of Copper):	oxides of nitrogen, oxides of sulphur CO, chlorides, dioxins, VOCs
IPR 2/10 (Precious Metal Producers):	chlorides, Cl ₂ , oxides of nitrogen, oxides of sulphur, dioxins, VOCs
IPR 2/11 (Ni Extraction, Ni and Co Alloys):	oxides of nitrogen, fluorides, VOCs, nickel carbonyl
IPR 2/12 (Tin and Bismuth Processes):	Cl ₂ , ammonia, VOCs
IPR 4/1 (Petrochemical Processes):	ammonia, benzene, CO, HCl, H ₂ S, oxides of nitrogen, VOCs
IPR 4/2 (Production of Amines, Nitriles etc):	total amines, ammonia, benzene, CS ₂ , CO, HCl, HCN, H ₂ S, organic sulphides and mercaptans, trimethylamine, VOCs
IPR 4/3 (Acetylene/Aldehydes Production):	ammonia, CO, Cl ₂ , HCl, HBr, HI, H ₂ S,

oxides of nitrogen, VOCs,
formaldehyde, total phenols cresols
and xylols, oxides of sulphur

IPR 4/4 (Organic Sulphur Production):	Br ₂ , CO, CS ₂ , HBr, HCl, HF, H ₂ S, I ₂ , oxides of nitrogen, organic sulphides and mercaptans, methyl mercaptan, oxides of sulphur, VOCs
IPR 4/5 (Manufacture of Organic Chemicals):	“active ingredients”, total amines, ammonia, benzene, Br ₂ , CS ₂ , CO, Cl ₂ , 1,2 dichloroethane, formaldehyde, HBr, HCl, HCN, HF, HI, H ₂ S, I ₂ , oxides of nitrogen, oxides of sulphur, organic sulphides and mercaptans, total phenols cresols and xylols, phosgene, trimethyl- amine, VOCs
IPR 4/7 (Manufacture of Organo-Metallics):	VOCs
IPR 4/8 (Pesticide Processes):	“active ingredients”, VOCs
IPR 4/9 (Pharmaceutical Processes):	VOCs
IPR 4/13 (Processes Releasing Halogens):	Br ₂ , Cl ₂ and oxy-Cl compounds, HF, HCl, sulphur oxides
IPR 4/14 (Hydrogen Halide Manufacture)	Br ₂ , Cl ₂ , HF, HCl, oxides of sulphur, vinyl chloride, 1,2 dichloroethane
IPR 4/15 (Halogenation of Organics):	amines, benzene, Br ₂ , Cl ₂ , ethylene dichloride, HF, formaldehyde, HCl, sulphur oxides, phosgene, vinyl chloride, 1,2 dichloroethane, VOCs
IPR 4/16 (Fertiliser Production):	ammonia, oxides of sulphur, NO _x , HCl, HF, H ₂ S
IPR 4/19 (Ammonia Use/Release):	ammonia, Br ₂ , HF, HCl, H ₂ S, NO _x , SO ₂ , oxides of sulphur, amines, formaldehyde
IPR 4/20 (Phosphorus Compounds)	carbon disulphide, Cl ₂ , HCl, H ₂ S, NO _x , oxides of sulphur, organic sulphides, formaldehyde, VOCs, alcohols
IPR 4/21 (H ₂ S and HCN Manufacturers)	ammonia, Cl ₂ , HCl, H ₂ S, VOCs

IPR 4/22 (Metals/Compounds):	ammonia, Cl ₂ , sulphur oxides, NO _x , HCl, HF, H ₂ S
IPR 4/23 (Use or Release of Cadmium):	H ₂ S, SO ₂ , VOCs
IPR 4/24 (Release of Mercury):	Benzene, VOCs
IPR 4/25 (Production of Cr, Mn, Mg, Ni, Zn):	ammonia, CO, Cl ₂ , HCl, HF, H ₂ S, oxides of nitrogen, oxides of sulphur, VOCs
IPR 5/9 (Ion Exchange Resin Waste Disposal):	none
IPR 6/1 (Tributyl-tin, Triphenyl-tin Coatings):	VOCs
IPR 6/2 (Tar and Bitumen Processes):	oxides of sulphur, oxides of nitrogen, CO, CS ₂ , H ₂ S, HCN, HF, ammonia, benzo(a)pyrene, VOCs
IPR 6/3 (Timber Preservation Processes):	VOCs
IPR 6/4 (Di-isocyanate Manufacture):	phosgene, HCl, formaldehyde, aniline, di-isocyanates, oxides of sulphur, oxides of nitrogen, VOCs
IPR 6/5 (Toluene Di-isocyanate, etc):	total amines, di-isocyanates, benzene, MbOCA, HCN, VOCs
IPR 6/7 (Processing of Animal Hides):	H ₂ S, VOCs, formaldehyde
IPR 6/9 (Papermaking and Related Processes):	VOCs, formaldehyde, chloroform, Cl ₂ , ClO ₂ , oxides of sulphur, oxides of nitrogen, dioxins

2.5.2 HSE: Health and Safety at Work Act (1974)

This Act set up the Health and Safety Executive (HSE) by an amalgamation of various other bodies. The HSE was originally partially responsible for lists of the industrial processes that had to be registered and substances that had to be controlled. Such lists are now incorporated in the general air pollution regulations attached to the Environmental Protection Act of 1990.

The HSE is responsible for investigation of industrial accidents and for drawing up the lists of Occupational Exposure Limits (OELs), under the 1994 COSHH regulations (Control of Substances Hazardous to Health). Some relevant OELs for **inorganic** species that might be prepared as standards are:

ammonia:	25 ppm (long term)	35 ppm (short term)
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NO ₂ :	3 ppm (long term)	5 ppm (short term)
HF:		3 ppm (short term only)
HCl:		5 ppm (short term only)
HBr:		3 ppm (short term only)
chlorine (Cl ₂):	0.5 ppm (long term)	1 ppm (short term)
sulphur hexafluoride (SF ₆):	1000 ppm (long term)	1250 ppm (short term)

SF₆, although virtually non-toxic, is one of the most powerful greenhouse gases (35,000 times greater than CO₂). Production is currently increasing, due to its use in electrical switchgear, magnesium foundries and aluminium casting. SF₆ presently accounts for about 1% of global warming.

Sulphur hexafluoride is often released into the air as a tracer gas in atmospheric monitoring experiments since it has a lifetime of 800 years. For instance, the United States Environmental Protection Agency (US EPA) has developed a number of techniques for monitoring hydrogen chloride, formaldehyde, phenol, methanol, carbonyl sulphide and carbon monoxide emissions. These are detailed in the various EPA "Test Methods" 318, 320, 321 and 322. Fourier Transform Infrared Spectroscopy or Infrared Gas Correlation Analysis are the employed to measure the listed species and sulphur hexafluoride is used to confirm the integrity of the extractive sampling system by "analyte spiking".

SF₆ is also employed as a tracer in a method developed to quantify fugitive (diffuse) emissions of hydrocarbons. The technique is based on concentration measurements with infrared remote sensing by Long Path Fourier Transform InfraRed (LPTIR), combined with tracer releases. The latest results show that LPFTIR is useful for flux measurements of both alkanes and alkenes in the vicinity of petrochemical plants and oil refineries.

There are over 300 compounds contained in the **organics** OEL list. For further information the reader should refer to document "EH40/98 Occupational Exposure Limits 1998", produced by the HSE.

2.5.3 Waste Incineration

Incineration is employed to reduce the weight of waste by about 65% and its volume by about 90%. However, inefficient combustion may produce hazardous gases such as HCl, HF, SO₂, CO, organics, dioxins, furans and metals.

There are various EC Directives on waste, largely implemented in the UK through the Environmental Protection Act of 1990 and the Waste Management Licensing Regulations of 1994. These require that HCl and CO must be continuously monitored in (large) incinerators, and HF and SO₂ periodically monitored. The EC has set emission concentration limits for the hazardous gases, mainly HCl (50-250 mg/m³), HF (2-4 mg/m³), SO₂, CO and organics (as total carbon).

2.5.4 EPAQS

EPAQS is the UK's Expert Panel on Air Quality Standards. This was set up by the DETR to recommend maximum limit values for pollutants in ordinary ambient air. The selected species for which there are now limits include:

SO ₂	benzene
NO ₂	1,3 butadiene
CO	lead
ozone	PM10

2.6 USA ACTIONS ON AIR POLLUTION

The US Environmental Protection Agency (US EPA) was set up to define and control all forms of pollution in the USA. The EPA publishes a list of "Hazardous Air Pollutants (HAPs)" that are known to be emitted by a variety of industrial / transport sources, or which could be released as a result of accidents, and which are known to cause health problems. Amongst the HAPs list of nearly two hundred compounds are:

acetaldehyde	HCl
carbon disulphide	HF
carbon tetrachloride	H ₂ S
chlorine	methyl ethyl ketone
chloroform	aromatic hydrocarbons
chlorobenzenes (various)	
chloroethanes and ethenes (various)	
formaldehyde	

2.7 NIST GAS STANDARDS

The National Institute of Standards and Technology (NIST) is the national standards laboratory of the USA. Their choices of gas standards are driven largely by the requirements of the US EPA, especially in the VOC area. In addition to the conventional gases like CO, CO₂, SO₂, oxides of nitrogen, methane and propane, NIST produce mixtures containing:

benzene	H ₂ S
toluene	hydrocarbon mixture (15 components)
chlorobenzene	toxics (hydrocarbons, inc. chlorinates; 19 components)
bromobenzene	toxics (hydrocarbons, inc. chlorinates; 43 components) (in future)
carbon tetrachloride	
vinyl chloride	

2.8 BOC SPECIAL GASES PLC

Discussions with BOC plc have indicated that the highest priority for which their customers will require standards, apart from those already supplied by NPL, are hydrogen fluoride, ammonia and chlorine.

2.9 SULPHUR GASES IN AMBIENT AIR

There is concern that carbonyl sulphide has the potential to influence the temperature structure of the lower stratosphere and to contribute to ozone depletion through the formation of sulphuric acid aerosols. OCS is the largest natural source of sulphur in the unpolluted troposphere and it is a precursor of SO₂.

The sources and sinks of OCS are not well understood but, since this molecule is relatively insoluble, it is the main sulphur species that enters the stratosphere. Molecules such as H₂S and CS₂ are too short lived to reach the stratosphere but the latter makes a contribution to the total OCS concentration through oxidation with the OH radical.

At ground level, aluminium production and automotive tyre wear have been implicated as the major anthropogenic sources of OCS. It is also emitted by the mineral wool and wool fibreglass industries. Carbon disulphide is mainly emitted by the chemical industry where it is used in the production of rayon, cellophane and methyl chloroform. These industrial sources are all expected to increase in the future. Both OCS and CS₂ have a characteristic odour of rotten eggs which is a concern to populations located near to plants emitting these pollutants.

3. POSSIBLE CANDIDATES FOR NEW GAS STANDARDS TO BE PREPARED WITHIN THE VAM PROGRAMME

The main inorganic gases noted in Section A that are not yet supplied as NPL standards are listed below, together with recommended maximum exposure levels and references to the relevant IPR guidance notes.

	HSE OELs (ppm)	EA Guidance Note maximum levels		
		(mg/m3)	(ppm)	
Ammonia	25 - 35	100	132	(IPR 4/11)
		50	66	(IPR 2/6)
				(S2 3.03)
		30	39	(IPR 4/19)
				(S2 1.06, 3.02, 1.07)
Chlorine	0.5 -	15	20	(IPR 2/12, 4/1, 4/2, 4/3, 4/5, 4/21, 4/22, 4/25, 6/2)
				(S2 1.01, 1.03, 1.12)
		10	13	(S2 5.01, 5.04)
		10	3.2	(IPR 4/3, 4/4, 4/5, 4/11, 4/12, 4/14, 4/20, 4/21, 4/22, 4/25, 6/8, 6/9)
				(S2 3.03)
		5	1.6	(IPR 2/8, 2/10)

Bromine	0.1 - 0.3	10	1.4	(IPR 4/4, 4/5, 4/11, 4/12)
Iodine	0.	10	0.88	(IPR 4/4, 4/5, 4/11, 4/12)
HCl	5	100	61	(SR 1.01)
		60	37	(S2 3.01, 5.01)
		50	31	(S2 1.12)
		30	18	(IPR 2/4, 2/5, 2/8, 2/9, 2/10, 2/12) (S2 1.04, 1.05, 5.03)
		10	6.	(IPR 2/3, 4/1, 4/3, 4/4, 4/5, 4/11, 4/12, 4/25, 6/4) (S2 3.02, 3.03, 3.04)
HBr	3	5	1.4	(IPR 4/3, 4/4, 4/5, 4/11, 4/12)
HF	3	5	5.6	(IPR 2/3, 2/4, 2/8, 2/12, 4/4, 4/5, 4/11, 4/14, 4/17, 4/19, 4/22, 4/25, 6/2) (S2 3.03)
		4	4.5	(S2 3.01, 3.04, 5.01)
		2	2.2	(S2 1.05)
HI	No HSE limit	5	0.88	(IPR 4/3, 4/4, 4/5, 4/11, 4/12)
HCN	10	5	4.	(IPR 6/2) (S2 1.05)
		2	1.7	(IPR 4/2, 4/5, 6/5)
H ₂ S	10 - 15	5	3.3	(IPR 4/1, 4/2, 4/3, 4/4, 4/5, 4/10, 4/11, 4/23, 4/25, 6/2) (S2 1.05, 1.07, 1.09, 1.11, 3.03)
			0.7	(S2 1.08, 5.04)
Methyl Mercaptan		2		(IPR 4/2, 4/4, 4/5)
CS ₂	10	5	1.5	(IPR 4/2, 4/4, 4/5, 4/20, 6/2)
OCS	No HSE limit yet set	US EPA "HAP"		
SF ₆	1000 (long-term)			

4. THE NPL REACTIVE-GAS CALIBRATION FACILITY

4.1 INTRODUCTION

A schematic of the NPL Reactive Gas Calibration Facility is given in Figure 1. A brief description follows of the existing spectroscopic facility which will be further developed to measure the concentration of a selected new range of reactive gases. It will be used to

dynamically generate gas mixtures at known concentrations for species that are too reactive to remain stable in cylinders for long periods of time.

4.2 THE FOURIER-TRANSFORM SPECTROMETER

The heart of the system is a high resolution Bomem DA8 Fourier Transform Spectrometer (FTS). This is capable of detecting a wide range of molecules (including minor impurities) from their absorption spectra, with high sensitivity and specificity. The FTS is designed to work mainly in the infrared (ir) spectral region where most molecules have absorptions at characteristic wavelengths. For homo-nuclear molecules, which are not infrared active, the spectrometer may be operated in the ultra-violet (uv) and visible spectral regions. This is done by replacing the KCl beamsplitter with a quartz beamsplitter, and changing the blackbody light source to a deuterium lamp.

Spectra are recorded at just above atmospheric pressure, with the gas flowing through a multiple-pass White cell of known pathlength. The light source from the FTS is passed into the White cell, where a small fraction may be absorbed by the gas. The transmitted beam is then focused onto an appropriate detector (a cryogenically cooled mercury-cadmium telluride or indium antimonide for the infrared region and a room temperature silicon detector for the uv/visible region) to obtain an absorption spectrum. Figure 2 shows an example of a spectrum of a 121 ppm HCl/N₂ sample recorded at 0.1 cm⁻¹ resolution. Here it is possible to clearly distinguish between the two different isotopomers of this molecule, ¹H³⁵Cl and ¹H³⁷Cl, and to observe that there are no nearby interferences due to other impurities.

A number of White cells have been developed at the NPL for the infrared (with gold mirrors) and uv/visible (with aluminium mirrors) spectral regions. Other than the mirrors, all the internal components of each cell are specially coated with teflon in order to minimise wall reactions with the reactive gases. The temperature and pressure of the gas flowing through the cell are monitored using calibrated gauges.

The concentration of the reactive gas present in each cylinder may be labelled directly using the spectroscopic facility. Alternatively, the dynamic blending system can be employed to generate a range of lower concentrations by further diluting the parent mixture with nitrogen. All gases are vented directly through an extraction system or may be passed through a customer's monitor that requires calibration.

4.3 SYSTEM PREPARATION

Each White cell may be evacuated using a rotary and turbo-molecular pump combination. The cell is normally flushed with dry nitrogen and pumped to remove contaminants prior to the introduction of a sample.

The cylinders containing the reactive gases are kept in a gas safety cabinet where flushing and dynamic blending systems are available. The high pressure pipework, valves and regulator are made from electropolished 316 stainless steel components. The tubing employed downstream

of the gas regulator is made from a perfluoroalkoxy (PFA) polymer to minimise adsorption of gases.

Before opening the target gas cylinder, care is required to ensure that water and other contaminants have been removed and do not deplete the concentration of reactive gas. This is particularly important in the stainless steel pipework because corrosion can easily be initiated when reactive gases come into contact with low concentrations of water. The method of flushing followed by pumping, outlined above, is employed for this purpose.

4.4 DETERMINATION OF SPECTROSCOPIC CONCENTRATION

The concentration of reactive gas species is related to the measured spectrum by the well known Beer-Lambert Law:

$$A = \alpha \cdot [c] \cdot d$$

where A is the absorbance (defined as $\ln\{I_0 / I_t\}$), $[c]$ is the concentration of interest, d is the pathlength of the White cell, and α is the absorption coefficient.

It is not generally possible to obtain a stable reactive gas standard from which a spectrum of known concentration can be recorded. In most cases it is necessary to generate synthetic calibration spectra from a well established spectroscopic database such as HITRAN. They contain the best available values of the absorption coefficient. It is then possible to determine the concentration of reactive gas from the measured spectrum.

5. CONCLUSIONS

This study shows that there is still a significant requirement for new dynamic gas standards to be developed for species that are too reactive to be maintained over long time periods with known stable concentrations in cylinders. The potential market covers a wide range of concentrations in order to satisfy the very diverse requirements of different industries, legislation enforcement bodies, and scientists involved in atmospheric research.

From the data presented in Section 2, it is apparent that potential candidates for calibration standards are: carbonyl sulphide, carbon disulphide, ammonia, chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen iodide, hydrogen cyanide, hydrogen sulphide, methyl mercaptan, and sulphur hexafluoride.

Work is already progressing in the NPL VAM Programme (Projects 1.2 and 1.4) on the development of new standards for certain of these species, covering ammonia, chlorine, carbonyl sulphide, hydrogen chloride, hydrogen sulphide and hydrogen fluoride. Some of this work will feed into VAM Project 1.1 (c) particularly in the case of hydrogen chloride, chlorine and ammonia. There are also plans to extend the work on odour standards to cover methyl mercaptan.

Surveys on possible customer requirements for the remaining compounds have been carried out in order to determine the market priorities for new dynamic reactive standards. Some of these gases, require a large investment of resources to overcome the technical difficulties of developing new calibration techniques. For example, bromine is highly reactive, corrosive, hazardous to health and would require the use of non-ferrous metals under rigorously dry conditions. Similar difficulties arise with hydrogen bromide, iodine, hydrogen iodide, and hydrogen cyanide which is extremely toxic. However, major demand for gas standards of Br_2 , HBr , I_2 , HI or HCN , has not yet been identified from the surveys, although this may change in the future. There is a requirement for SF_6 standards, for the various reasons described in Section 2.5.2, but this is exceeded by the demand for the more technically challenging molecules, OCS and CS_2 .

Carbonyl sulphide is emitted in aluminium production, and from manufacturing industries using phenolic resins (fibreglass production). EPA Test Method 318 suggests that OCS levels are sufficiently elevated (parts per million) in the latter process that a Fourier Transform Infrared Spectrometer can detect this species using a moderately short pathlength cell. In addition, a large source of OCS is believed to come from automotive tyre wear, the oceans and soils. OCS is also of concern to local populations near industrial areas because of its malodorous properties, and hence the additional requirement for standards to underpin the work on odour. The development of accurate OCS calibration gases through the reactive gases facility will ensure that the required wide range of concentrations can be produced efficiently.

There is an increased interest by atmospheric scientists (and industry) in high accuracy measurements of carbonyl sulphide. OCS is the most abundant sulphur compound in the atmosphere and has an almost uniform mixing ratio of 500 parts per trillion in the troposphere. It is thought to be an important precursor to sulphuric acid aerosols which have been implicated in stratospheric ozone destruction. Recent three dimensional global model studies of OCS in the troposphere and lower stratosphere indicate that there should be higher mixing ratios in the Southern Hemisphere than in the Northern Hemisphere. This interhemispheric gradient is the opposite of what is observed and demonstrates that the present knowledge of the distribution of sources and sinks is inadequate.

Carbon disulphide is also of concern since the main sources of production are from chemical industries producing rayon, cellophane and methyl chloroform. It is predicted that industrial emissions of CS_2 will increase in the future.

The oxidation processes of reduced sulphur compounds are not, in general, well established and there is frequent disagreement on the results of kinetic and mechanistic data. These species, which include OCS , CS_2 and H_2S , are all difficult to study because they are readily adsorbed on the walls of reaction vessels. This can often lead to heterogeneous reactions contributing to the overall oxidation process. The oxidation of carbon disulphide is complex but the final products are now believed to be OCS and SO_2 . The OCS component of this reaction is then free to enter the stratosphere where it is eventually converted into the sulphuric acid aerosols as described above.

In conclusion, the requirement to produce new gas standards which may be analysed spectroscopically in the Reactive Gas Calibration Facility under the 1997-2000 VAM

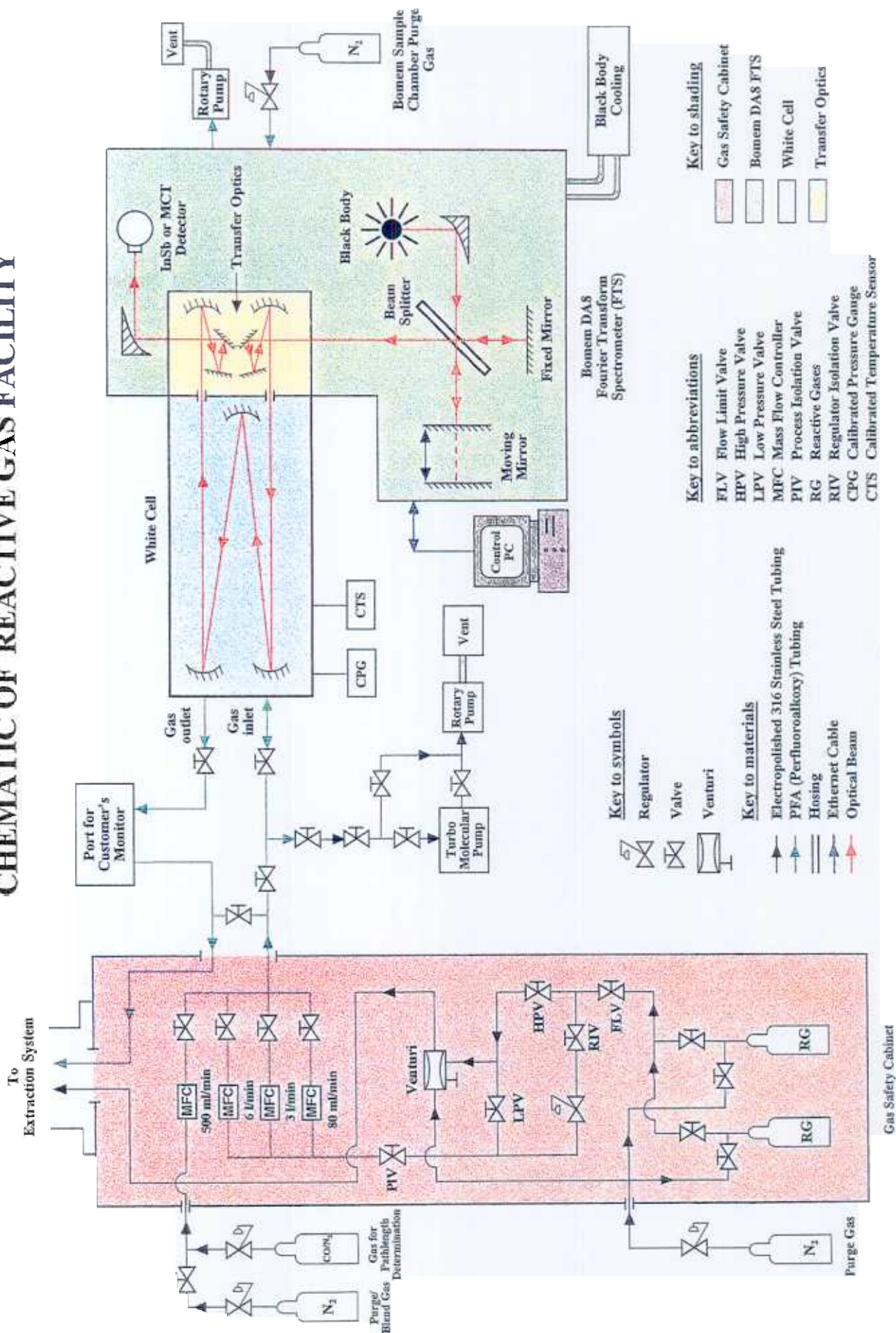
Programme has been reviewed. The proposed candidates, OCS and CS₂, have been selected for Project 1.1(c) by taking into account market demands, the scientific and technical merits, and the need to interface with other areas of development under Projects 1.2 and 1.4.

LIST OF FIGURES

Figure 1: Schematic of Reactive Gas Facility

Figure 2: HCl Infrared Spectrum

CHEMATIC OF REACTIVE GAS FACILITY



HCl Absorbance Spectrum

