

**Report on the Requirements for New Gas Standards to Calibrate Open Path and
Remote Monitoring Instruments
Relevant to the 1997-2000 Valid Analytical Measurement Programme**

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ABSTRACT

This document outlines gases which could be developed as new NPL standards for use in the calibration of open-path and remote monitoring instruments, 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 developed as gas standards under Project 1.1 (c) of the 1997-2000 Valid Analytical Measurement (VAM) Programme. Finally, there is a concise description on how the NPL Open Path Gas Calibration Facility will be used to measure these gases, together with the conclusions justifying the selected species.

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Approved on behalf of the Managing Director, NPL
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**REPORT ON THE REQUIREMENTS FOR NEW GAS STANDARDS TO
CALIBRATE OPEN PATH AND REMOTE MONITORING INSTRUMENTS
RELEVANT TO THE 1997-2000 VALID ANALYTICAL MEASUREMENT
PROGRAMME**

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 Open Path 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) An Ambient Air Framework Directive, which was agreed in 1996, and has now been signed. Work is presently proceeding on a range of daughter Directives. These will involve primarily 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 of 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), inorganic and organic 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 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 .01 (Large Boilers and Furnaces):	oxides of nitrogen, SO ₂ , HCl, CO, VOCs, dioxins, ammonia
S2 1.03 (Compression Ignition Engines):	oxides of nitrogen, SO ₂ , HCl, CO ₂ , CO, VOCs, dioxins, ammonia

S2 .04 (Waste and Recovered Oil Burners):	HCl, oxides of sulphur, oxides of nitrogen, CO, dioxins, VOCs, PAHs
S2 .05 (Combustion of Solid Waste Fuel):	HCl, HF, oxides of Sulphur, oxides of nitrogen, CO, dioxins, VOCs, formaldehyde, HCN,
S2 .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 10 (Petroleum Processes):	oxides of nitrogen, sulphur dioxide
S2 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):	NPL Report COEM 19 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)
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)
sulphur hexafluoride (SF ₆):	1000 ppm (long term)	1250 ppm (short term)

Sulphur hexafluoride, although virtually non-toxic, is one of the most powerful greenhouse gases (35,000 times greater than CO₂). Production is currently increasing, due to use in

electrical switchgear, magnesium foundries and aluminium casting. SF₆ presently accounts for about 1% of global warming.

SF₆ 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 (LPFTIR), 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, and 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 largely 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 small contribution to the total OCS concentration through oxidation. At ground level, aluminium production has been implicated as a new anthropogenic source of OCS. It is also emitted by the mineral wool and wool fibreglass industries.

3. POSSIBLE CANDIDATES FOR VAM GAS STANDARDS

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/m ³)	(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)
		15	20	(IPR 2/12, 4/1, 4/2, 4/3, 4/5, 4/21, 4/22, 4/25, 6/2)
Chlorine	0.5 - 1			(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)
		5	.6	(S2 3.03)
Bromine	0.1 - 0.3	10	.4	(IPR 2/8, 2/10)
Iodine	0.1	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	NPL Report COEM 19 (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	4.1	(IPR 6/2) (S2 1.05)
		2	.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	.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 OPEN-PATH GAS CALIBRATION FACILITY

4. INTRODUCTION

A brief description of the NPL Open-Path Gas Calibration Facility is given in the succeeding paragraphs. This facility will be further developed to provide the concentration of new gases that are required for the calibration of open-path and remote monitoring instruments. These new instruments are being brought onto the market to satisfy the need by industry and others to monitor industrial emissions, industrial fence lines, explosive hazards and air quality.

4.2 THE OPTICAL ABSORPTION CELL

The heart of the system is a specially developed stainless steel cylindrical optical absorption cell, of 0.5 metre, pathlength which can be filled with the target gas of interest at a known concentration. The internal surfaces of the cell have recently been coated in a perfluoroalkoxy (PFA) polymer to minimise possible gas-wall reactions. The two cell windows are made of high quality ir transmitting ZnSe. They have a thickness of 10 mm and a diameter which can deliver a clear optical beam aperture of 178 mm. The windows have a 1° wedge angle to minimise the possible formation of optical fringes.

The 0.5 metre cell can be placed into the optical beam of an instrument requiring calibration. The cell may be flushed with dry nitrogen and evacuated with a rotary and turbo-molecular pump combination to remove unwanted contaminants.

Gases can be introduced into this facility either in a dynamic or static mode depending on whether they are reactive or stable. There is a dynamic blending system which can also be employed to generate a range of lower concentrations by further diluting the parent gas mixture with nitrogen. The temperature and pressure of the gas in the optical cell can be monitored continuously throughout the experiment using calibrated sensors.

4.3 THE FOURIER TRANSFORM SPECTROMETER

A high-resolution Fourier-Transform Spectrometer (FTS) can be employed, in an open-path configuration, to measure the concentration of the target gases. The FTS is capable of detecting a wide range of molecules (including minor impurities) from their absorption spectra with high sensitivity and specificity. The instrument is configured to work in the infrared (ir) spectral region where most molecules have absorptions at characteristic wavelengths from which they can be identified and quantified.

The target gas is measured by passing the blackbody radiation from the spectrometer into the optical cell. After one pass, a small fraction of the light is absorbed by the infrared active gas. The transmitted beam is then focused onto a detector to obtain an absorption spectrum. A cryogenically cooled mercury-cadmium telluride or indium antimonide detector is employed depending on the exact spectral region required.

4.4 MEASUREMENT PROTOCOL

Since the FTS is used as a remote sensing instrument it is necessary to record three different spectra during each calibration. A reference spectrum of the evacuated cell is required. This is followed by a spectrum of the cell filled with the target gas at the desired concentration. The gas can either be in the static or dynamic mode depending on its reactivity. Finally, a spectrum is recorded with the blackbody infrared source switched off in order to determine the effect of ambient background radiation. If any small background contribution is found it is subtracted from the reference and target gas spectra. Finally, the corrected spectra are ratioed to give a transmission spectrum of the target gas. This is converted into an absorbance spectrum so that the concentration can be calculated.

It should be noted that open-path gas monitors operating in the field normally measure the atmospheric abundance as a product of the concentration and pathlength. Thus the calibration gas does not need to be uniformly dispersed along the total atmospheric path. It is necessary to have a high concentration in the 0.5 m length gas cell, since it is only a fraction of the typical total atmospheric path.

4.5 DETERMINATION OF SPECTROSCOPIC CONCENTRATION

The concentration of the target gas species can be related to the measured spectrum using 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 cell, and α is the absorption coefficient.

It is not always possible to obtain a stable gas standard from which a spectrum of known concentration can be recorded. In many 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. Using this method it is then possible to label the concentration of the target gas from the measured spectrum.

5. SUMMARY AND CONCLUSIONS

This short study shows that there is still a significant requirement for new gas standards to be developed in order to satisfy the demand for calibration and validation of new open-path and remote monitoring instruments. These instruments have to cover 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 3, it is apparent that possible 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 some of these species, and for external customers, on 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 standards. The majority of these species, require a significant investment of resources to overcome the technical difficulties of maintaining a stable concentration in the 0.5 metre absorption cell. 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. A major demand for gas standards of Br₂, HBr, I₂, HI or HCN, has not yet been identified from the surveys, although this may change in the future.

There is a requirement for CS₂ standards for the various reasons outlined in Section 2.9. This work will be undertaken using new developments to the NPL Reactive Gas Calibration Facility within Project 1.1 (c). The market demand which has been identified for calibration standards of the remaining priority molecules, OCS and SF₆, will be met by technical improvements to the NPL 0.5 metre open path cell.

It is known that 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 requirement for standards to underpin the work on odour under the above VAM Projects.

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.

The other target molecule is sulphur hexafluoride because of its role as a greenhouse gas. There is concern about its increasing anthropogenic production in electrical switchgear, magnesium foundries and aluminium casting. SF₆ is also deliberately released into the atmosphere, as a tracer, in certain tropospheric measurement studies. This is in order to gain a better understanding of the transport processes associated with the release of noxious materials from local industrial plants. Recent advances have shown that SF₆ tracer releases, combined with LPFTIR, are a useful optical technique to quantify fugitive hydrocarbon emissions from petrochemical plants and oil refineries.

Sulphur hexafluoride is also employed in the proposed US EPA Test Methods 318, 320, 321, and 322 for the detection of HCl, H₂CO, C₆H₅OH, OCS, CH₃CO₂H and CO emissions. In these applications SF₆ is introduced as a “spike gas” at approximately 10% of the total analyte flow rate. For example, in the case of HCl emissions in the 10-50 ppm range, this requires an SF₆ tracer concentration of about 2-5 ppm to be added to confirm that the analyte is not consumed before reaching the measurement system. This use as a tracer is important because remote monitoring instruments will need to detect efficiently the tracer in very dilute quantities.

SF₆ is used as a tracer gas by atmospheric scientists to “date” air samples. The persistent increase of this species in the troposphere and the lack of destruction processes in the stratosphere makes it possible to establish a clear relationship between time and concentration which is free from complicated seasonal variations as in the case of CO₂. This offers a valuable boundary condition for tropospheric/stratospheric mixing studies. For example, above 25 km SF₆ concentrations are lagging the tropospheric ones by several years: 4.5 years for the tropics, 6 years at mid-latitudes and 10 years in the Arctic polar vortex. This may indicate that the lag between the peak halogen concentration in the troposphere and polar stratosphere is longer than previously assumed.

In conclusion, the requirement to produce new gas standards to calibrate open path and remote monitoring instruments under the 1997-2000 VAM Programme has been reviewed. The proposed candidates, OCS and SF₆, have been selected for Project 1.1(c) by taking into account market demands, the scientific and technical merits, and the need to underpin other areas of development under Projects 1.2 and 1.4.