

Report on the Requirements for New Inorganic Gas Standards for the 1997-2000 Valid Analytical Measurement Programme

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ABSTRACT

This document outlines gases which could be developed as new inorganic gas standards by NPL, under Workpackage (A) of Project 1.2 in the 1997-2000 Valid Analytical Measurement (VAM) Programme. This follows a review of the requirements of UK and international regulatory bodies, and other organisations, that are concerned with the problems of air pollution. The sources of the possible requirements are reviewed first, followed by an assessment of the different standards that could be developed under the VAM Workpackage. Finally, a selection is made of suitable standards for development, with some consideration of the technical problems involved

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REPORT ON THE REQUIREMENTS FOR NEW INORGANIC GAS STANDARDS FOR TO THE 1997-2000 VALID ANALYTICAL MEASUREMENT PROGRAMME

by

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1. INTRODUCTION

A variety of UK and international organisations are responsible for setting guidelines on air pollution, and other organisations have interests in these. The most important ones are reviewed in Section A, together with a brief summary of their roles. Important directives and recommendations on the concentrations of selected pollutants have also been identified with a view to deciding which are the priority gases to be developed as NPL standards, prepared by gravimetric methods in high pressure cylinders under Workpackage (A) of Project 1.2 in the 1997-2000 NMS Valid Analytical Measurement (VAM) Programme. Section B contains a list of the priority target gases together with the recommended exposure limits. Section C assesses the inorganic gases that could be developed as static (ie retained in stable form in gas cylinders) gas standards under VAM Project 1.2, Workpackage 1.2(A). Finally, a selection is made of suitable standards, with some consideration of the technical problems involved

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 signed. 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 (WHO) GUIDELINES ON POLLUTANTS

In 1987 the 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 their recommended 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 should now 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 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 main legislation enforcement in the UK is performed by the Environment Agency (EA), the Health and Safety Executive (HSE) and Local Authorities. Some of the most important roles are summarised below:

2.5.1 Integrated Pollution Control (IPC)

This activity started in the UK with the Environmental Pollution Act (EPA) of 1990. 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 1.01 (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 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, trimethylamine, 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)	1250 ppm (short)

The environmental journal ENDS (No. 265, p4, Feb 1997) notes that SF₆, although virtually non-toxic, is one of the most powerful greenhouse gases (35,000 times > 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.

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 sampling system by "analyte spiking".

There are over 300 compounds contained in the **organics** OEL list. Further information is contained in the 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	PM ₁₀ Particulate

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 “usual” gases like CO, CO₂, SO₂, 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 (Future: hydrocarbons, inc. chlorinates; 43 components)
carbon tetrachloride	
vinyl chloride	

2.8 BOC SPECIAL GASES PLC

Discussions with BOC plc has indicated that the first priority gases for which their customers require standards, apart from those already supplied by NPL, are:

HF	ammonia	chlorine
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Multicomponent natural gas and chlorinated hydrocarbon standards.

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 NEW 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 (mg/m ³)	Note maximum levels (ppm)	
Ammonia	25 - 35	100	132	(IPR 4/11)
		50	66	(IPR 2/6)
				(S2 3.03)
		30	39	(IPR 4/19)
		15	20	(S2 1.06, 3.02, 1.07)
Chlorine	0.5 - 1			(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)
Chlorine	0.5 - 1	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	1.4	(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	4.1	(IPR 6/2) (S2 1.05)
			.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)
		1	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 GRAVIMETRICALLY-PREPARED INORGANIC GAS STANDARDS WHICH HAVE BEEN SELECTED

This study shows that there is still a significant requirement for new statically prepared inorganic gas standards to be developed. 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 A, it is apparent that some of the main gas candidates for calibration standards are: carbonyl sulphide, sulphur hexafluoride, ammonia, chlorine, bromine, iodine, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen iodide, hydrogen cyanide, hydrogen sulphide, methyl mercaptan, and carbon disulphide. From this list we have selected the following gases to produce as standards under Workpackage A of project VAM 1.2 :

4. AMMONIA

This gas is widely encountered in industrial plants under the following areas:

- Combustion of all types
- Coke production
- Furnaces
- Asbestos processes
- Glass production
- Waste incineration
- Organic solvent production
- Metal production
- Petrochemical processing
- Fertiliser manufacture

Ammonia is also commonly encountered in farming, where it often gives rise to odour complaints.

4.2 CHLORINE

This gas is found predominantly in:

- Glass production
- Organic chemical production
- Metal production
- Production of halogenated materials
- Phosphorous compound production
- H₂S/HCN production
- Papermaking
- Water treatment

4.3 HYDROGEN FLUORIDE

This gas is found predominantly in:

- Solid fuel combustion
- Ceramic production
- Glass production
- Cement / brick production
- Waste incineration
- Halogenation of organics
- Zinc production
- Petrochemical processing
- Fertiliser production
- Tar and bitumen processing

4.4 CARBONYL SULPHIDE

This gas is present, along with other sulphur oxides, in:

- Combustion of many types
- Coke production
- Cement production
- Ceramics production
- Waste incineration
- Organic solvent production
- Metal production
- Sulphur / phosphorous production
- Tar and bitumen processing
- Papermaking
- Tyre production
- Natural sources, especially the oceans and soils

Carbonyl sulphide is also of significant interest to atmospheric research. It is the most abundant sulphur compound in the atmosphere and has an almost uniform mixing ratio of 500 ppt in the troposphere. However, 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, thus demonstrating that the present knowledge of the distribution of sources and sinks is inadequate. It is thought that OCS is an important precursor to sulphuric acid aerosols which have been implicated in stratospheric ozone destruction.

OCS is also of concern to local populations near industrial areas because of its malodorous properties, and hence there is also an additional requirement for standards to underpin the work on odour.

OTHER GASES

From the information in Sections 1 and 2 a variety of other possible gases may be identified as possible candidates for static inorganic gas standards. These include gases such as bromine, iodine, hydrogen bromide, hydrogen iodide or hydrogen cyanide. However, surveys on possible customer requirements for the remaining compounds have not presently identified a major generic industrial demand for gas standards of these materials, although this may change in the future. In practical terms, it would be necessary to commit large resources to overcome the technical difficulties of, for instance, developing bromine standards. This compound is highly reactive, corrosive, hazardous to health and would require the use of non-ferrous metals under rigorously dry conditions. Similar difficulties arise with HBr, I₂, HI, and HCN.

5. CONCLUSIONS

The conclusion from the information presented in this Report is that the highest priority of inorganic gases that should be produced as gravimetric primary gas standards, in addition to those already offered by NPL, are:

Ammonia
Chlorine
Carbonyl sulphide
Hydrogen fluoride

This work would be carried out under the VAM Project 1.2 New Inorganic Gas Standards, [Workpackage 1.2(a)]. It will, for carbonyl sulphide, compliment work being carried out within VAM project 1.1(c) where known concentration gas mixtures will be produced dynamically over a very wide concentration range, to cover the different applications.

The production of primary standards of these gases will be technically demanding, since they are all reactive species which are difficult to maintain with stable concentrations in gas cylinders and difficult to measure accurately, due to cylinder problems of wall adsorption, solubility in water and analyser cross-interference effects. Therefore, as part of this project, discussions with gas cylinder manufacturers will be necessary to identify cylinders, and cylinder passivation treatments, that yield the required long-term gas stability.