CENTRAL ATMOSPHERE MONITORING SYSTEM (CAMS) FOR SUBMARINES

BY

M. J. WOOD, B.SC. (ENG.), C.ENG., M.I.E.E., R.C.N.C.
(Sea Systems Controllerate)

ABSTRACT

In the new Central Atmosphere Monitoring System, the concentrations of atmospheric constituents and pollutants in a submarine are measured automatically by mass spectrometer. Software recognizes each constituent from its characteristic peaks in the mass spectrum. The engineering of the very high vacuum required is also described.

Introduction

The composition of the atmosphere of a nuclear submarine must be controlled to ensure that the physical and mental performance of the crew is unimpaired and to ensure that health risks are minimized. To check that the control measures are effective, atmosphere monitoring must be provided, the aim being to keep the atmosphere within parameters agreed by the Institute of Naval Medicine and Flag Officer Submarines, and published in BR 1326[1], the submariner's 'bible' on atmosphere control.

The main requirements for atmosphere monitoring are:

(a) To provide a Central Atmosphere Monitoring System capable of continuous automatic surveillance of major atmospheric constituents, which can provide rapid warning of a problem or potential problem.

(b) To provide back-up monitoring instruments to cater for failure of the main central system or specific problem investigation.

(c) To provide special monitoring equipment for hazards beyond the capability of the central system, or where a separate system is deemed necessary, e.g. monitoring for weapon propellant leakage.

(d) To provide monitoring facilities for atmosphere pollutants that produce long-term health risks to the crew.

Monitoring can be of two types:

(a) Real Time. An instrument provides an analysis in a matter of minutes or less, on which the crew can take immediate action if necessary. In general, requirements (a), (b) and (c) above must be met by instruments of this type.

(b) Retrospective. Equipment is provided for the taking of samples for shore analysis and is used to meet the major part of (d) above.

Central Atmosphere Monitoring

This article concerns only the first of the four requirements listed above, the provision of a Central Atmosphere Monitoring System. Although this term is usually used for the equipment it also really encompasses the network of fixed small bore (6 mm) sampling pipes that transport atmosphere samples from each important compartment of the submarine to the analyser which identifies and quantifies their constituents. The sampling lines terminate together in a selector arrangement which enables the operator to select the compartment of interest for analysis.

The analyser installed in most nuclear submarines at present, the Pye Unicam Atmosphere Analyser, based on gas chromatography, is obsolescent and is being replaced by the Central Atmosphere Monitoring System (CAMS), based on mass spectrometry. This is an entirely different technology to that used in its predecessor, and one which is new to the Fleet.

Around 1975 consideration began of a replacement for the Pye Unicam Analyser which employed technology of the mid 1960s and was demanding in terms of downtime and on-board services (compressed air, carrier gas cylinders, and calibration gas cylinders). The downtime was associated with a corresponding maintainer commitment which, at times, was unacceptable, and a reliability figure of less than 500 hours mtbf. The system, too, had limited flexibility in that a requirement to monitor new gases meant mechanical modifications.

Requirements

TABLE I shows the list of gases to be analysed by the new analyser and the measuring ranges for each. The need to monitor oxygen, carbon dioxide, carbon monoxide and hydrogen are widely understood. R 12 (dichlorodifluoromethane), commonly known by the trade name Freon 12, is used in current refrigeration plants and is mildly toxic at

TABLE I—*Gases to be analysed*

Gas	Measuring Range
Oxygen	60–200 T
Carbon dioxide	0–30 T
R 12	0–5%
R 114	0–5%
Halon 1301	0–5%
Hydrogen	0–6% by vol
Benzene	0–10 mT
Aliphatic organics	0–100 mT
Aromatic organics	0–20 mT
Carbon monoxide	0–300 ppm

T: torr (= 1 mm mercury)
mT: millitorr
ppm: parts per million by volume

high levels, but breaks down into toxic and corrosive compounds when heated. Leakage of this heavy gas can form 'pools' in bilges and can present a suffocation danger due to exclusion of oxygen. There is a safety requirement for real-time monitoring as well as a requirement to give an early indication of refrigeration plant problems. R 114 (dichlorotetrafluoroethane—another member of the CFC group of compounds) will be introduced into service in the VANGUARD Class refrigeration plants. Halon 1301 will be used in automatic fire-fighting systems in VANGUARD and other classes. The reasons for monitoring R 114 and Halon are similar to those for R 12. The equipment is also required to have three channels dedicated to organic compounds, capable of monitoring at low ppm (parts per million by volume) levels. Organic vapours can get into the submarine atmosphere at these levels from a variety of sources, e.g. solvents, paints, lub oils, diesel fuel, cooking oil, etc. Because of the very large number of these compounds they have been divided into three groups, roughly related to their toxicity. Benzene, although very rarely detected in independent atmosphere trials, is highly toxic and thus has its own channel (the maximum level permitted is 0.5 ppm). Aromatic organics are also highly toxic (maximum level 2 ppm). Aliphatics are the least toxic (8 ppm). Although all organics are continuously filtered from the submarine atmosphere there is a need to monitor for them, to safeguard the long-term health of the crew.

Feasibility

At the time feasibility was being considered, four basic techniques were available for continuous analysis of a multi-gas sample:

(a) *Infra-Red Spectrometry*

Gases can be measured by the absorption of infra-red radiation, but this technique cannot be used for oxygen, hydrogen and other diatomic components. It is therefore ruled out as a single technique for submarine atmospheres.

(b) *Colorimetry*

Colorimetry employs paper tapes impregnated with chemicals that will react with the gases to be analysed, causing measurable colour changes. As with all chemical reaction techniques this can suffer from cross-sensitivity. It is dependent on electro-mechanical devices and would be large for the number of gases to be analysed. Detectors would be short-life and paper tapes subject to stringent quality assurance. This technique had too many disadvantages to be considered further.

(c) *Gas Chromatography*

In gas chromatography the sample mixture to be analysed is divided into its component gases by passing it through a column containing solid granules (sometimes coated with a liquid) which have different affinities to the substances in the gas sample. Component gases can be identified by their different transit times and a detector used to establish concentration. A second generation of the Pye system was technically feasible.

(d) *Mass Spectrometry*

This is a technique is which the sample gases are ionized and the different ions separated and measured (by either alternating electric or direct magnetic fields) according to the mass/charge ratio of the ions. Mass spectrometry is used for process control in industry and it was known that the U.S.Navy had successfully developed a mass spectrometer for use in submarines.

Three feasibility studies were placed. The first looked at a Mk. 2 gas chromatograph; the second and third were placed simultaneously with two mass spectrometer companies to examine the feasibility of a U.K.-developed mass spectrometer. It was concluded in 1977 that a Mk. 2 gas chromatograph would have similar disadvantages to its predecessor but that mass spectrometry offered a solution with lower on-board maintenance, space and weight, and could be more easily changed to monitor new gases by relatively minor software changes.

A development contract was placed with one of the mass spectrometer companies (VG Gas Analysis Systems Ltd.) to develop an analyser for U.K. nuclear submarines. This resulted in two prototypes developed to naval environmental standards, one of which was tested at sea in H.M.S. *Repulse* for six months in 1982. The first production units were built during 1983 and 1984 and the first installations in submarines took place in 1986.
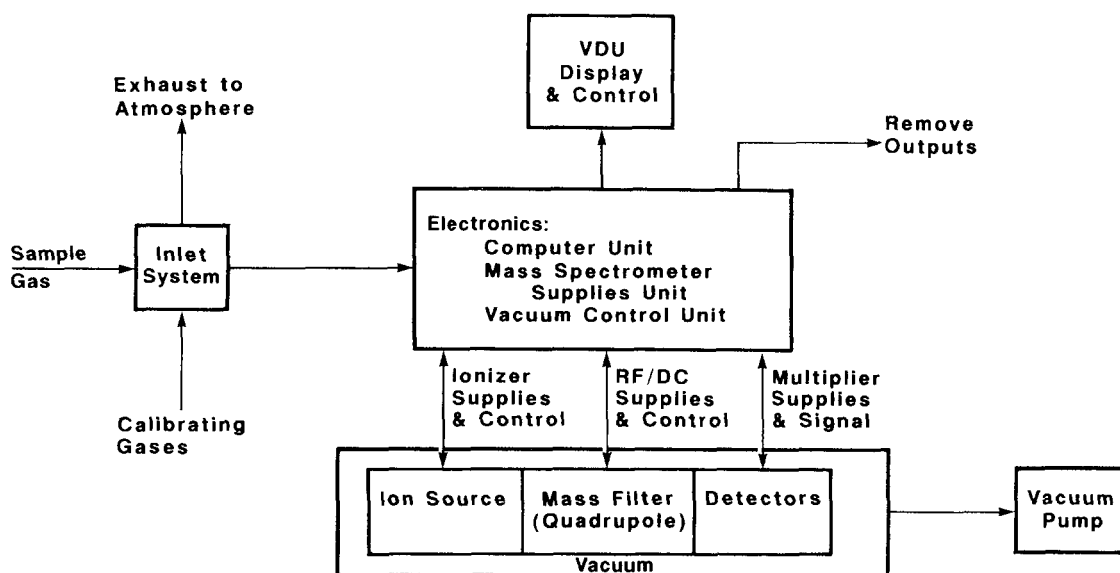

FIG. 1—THE MASS SPECTROMETER

Principle of Operation

The submarine mass spectrometer, known officially as The Central Atmosphere Monitoring System, is a 'quadrupole' mass spectrometer. FIG. 1 shows a much simplified block diagram of the system. The sample gas is drawn by a sample pump from a selected area of the submarine, past the inlet system, exhausting to atmosphere. A very small proportion of the sample is bled via a capillary inlet to the ion source where the sample gases are ionized by electron bombardment, the electrons being produced from a thermionic filament. The positively charged ions are focussed into a beam and pass into the quadrupole which acts as mass filter (or narrow band pass filter) allowing ions of only one mass (strictly mass/charge ratio) to pass through. The quadrupole comprises four parallel stainless steel rods in a close square array to which d.c. and r.f. voltages are simultaneously applied. An ion passing into one end of the quadrupole will oscillate about the centre line due to the r.f. electric field, whilst the d.c. field will deflect it from the centre line and cause it eventually to strike one of the electrodes where it will gain an electron and become neutralized. It can be shown that by selection of values of d.c. voltage and r.f. voltage amplitude and frequency, a narrow range of mass/charge (m/e) ratio ions will have a stable motion and emerge at the other

end of the quadrupole. By scanning the d.c. and r.f. voltages from zero to their maximum value the quadrupole filter can be made to scan, filtering ions sequentially in order of their m/e values. Ions are detected at the opposite end by either a Faraday cup (for abundant species) or an electron multiplier (for trace species). In summary then, the m/e ratios of the ions allow determination of what substances are present whilst the ion intensities determine how much is present.

During ionization, one (sometimes two) electrons are removed from a molecule; thus e in m/e is normally known and the instrument effectively measures the molecular weight of the gases in the sample. The ionization of a given type of gas molecule (whether an element or a compound) usually produces several different ions since the molecule is to some extent chemically fragmented as well as ionized. The number of ionic species is also increased by isotopes of elements in the molecule, since these affect molecular weight.

Mass Spectra

By connection of a suitable chart recorder or VDU, the instrument can produce a 'mass spectrum' of the sample gas, over the mass range of the instrument. In this spectrum the x axis represents m/e, and the y axis ion intensity. The mass spectrum of a single substance, known as its 'cracking pattern', is needed to enable the substance to be recognized within the mass spectrum of the sample. Fig. 2 shows a cracking pattern for carbon dioxide. As might be expected, the largest or base peak is at m/e 44 corresponding to the molecular weight of carbon dioxide. Peaks at m/e 13, 29 and 45 are associated with the mass 13 isotope of carbon. The peaks at m/e 12, 16 and 28 are due to the chemical breakdown of a small amount of carbon dioxide into carbon, oxygen and carbon monoxide respectively. A simple compound such as carbon dioxide can give rise to nine or more peaks. It follows that the more complex the molecule the more complex the cracking pattern since the number of permutations of combinations of isotopes and chemical fragments will increase rapidly. It should be noted that a small proportion of the sample molecules may have two electrons removed during ionization. In the case of carbon dioxide this produces another peak at m/e 22 (half that of the base peak) since e is doubled.

The spectrum of an atmosphere sample is the sum of the cracking patterns of its constituents. Where two or more substances each produce a peak at the same m/e the resultant peak height is the sum of the contributions from each substance.
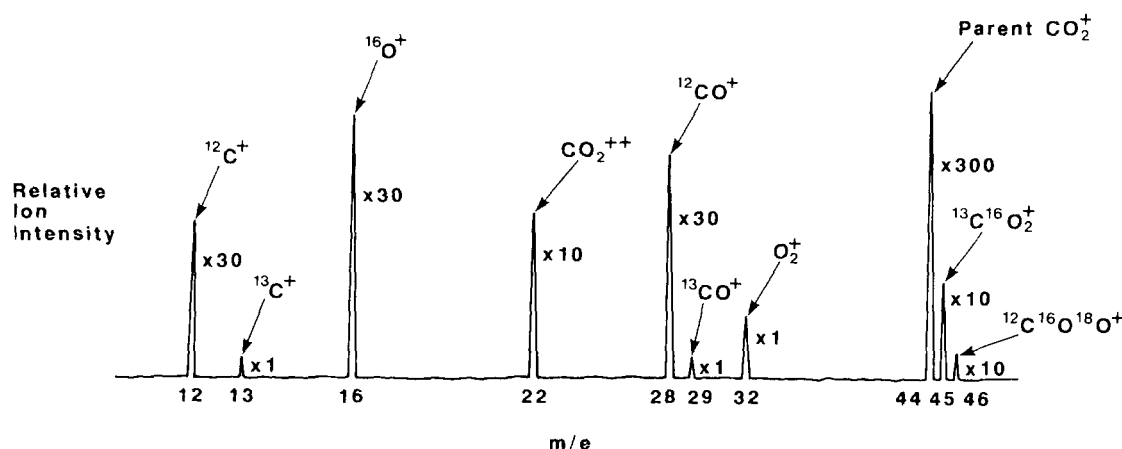

Fig. 2—Mass spectrum of carbon dioxide. The larger peaks have been scaled down (by factors between 10 and 300) so that all can be shown on the same diagram

212

Recognition of the substance is most easily achieved by arranging for the software to look for a unique peak (or at least unique for the range of substances expected in a submarine atmosphere). To achieve maximum accuracy of measurement the largest peaks should be taken. In the case of carbon dioxide the base peak at m/e 44 can be used, since the contributions from other sources to the m/e 44 peak (e.g. from breakdown of organics) in the overall atmosphere spectrum are insignificant. Recognition of the major constituents is relatively easy, using their base peaks. The peak at m/e 2 is hydrogen, m/e 32 is oxygen, m/e 28 is nitrogen, and so on.

Overlapping cracking patterns can be identified by measurement of a number of peaks and the use of simultaneous equations or a pattern recognition technique in the software. This requires increased computing power and so because of the limited computer capacity available at the start of CAMS development and in the interests of simplicity such techniques have been avoided except for CFCs and organics.

Unfortunately nitrogen and carbon monoxide have the same base peak, 28. Since nitrogen is about 78% of the sample and carbon monoxide only a few parts per million, separation of these peaks is impossible in this type of mass spectrometer. Thus carbon monoxide has to be measured on a separate (infra-red absorption) instrument within the CAMS cabinet.

High Vacuum Technology

Mass spectrometers will only operate at a very low pressure. Referring back to FIG. 1, it will be noticed that the ion source, quadrupole filter and detectors are enclosed within a 'vacuum system'.

For the quadrupole mass filter to operate correctly, the path followed by the ions must not be affected by collisions between ions and gas molecules. Thus the probability of collision between ions and gas molecules has to be very low. The molecules of a gas are in constant motion and constantly colliding with each other. As the pressure is reduced so the average distance travelled between collisions (the mean free path) increases. The pressure within the vacuum system is measured in torr (1 torr (T) is approximately equivalent to 1 mm of mercury). At atmospheric pressure the mean free path is less than 10^{-3} mm, increasing to 50 cm at a pressure of 10^{-4} T. In fact the mass spectrometer will only operate at a maximum pressure of 10^{-5} T.

This low pressure is also essential to prevent rapid ageing of the filaments in the ion source and the electron multiplier.

But how can such an extremely low pressure be achieved, and maintained? The vacuum is produced by two pumps. When the mass spectrometer is first turned on, a rotary (roughing) sliding vane vacuum pump takes the pressure down to 10^{-2} T. Below pressures of about 10^{-3} T the mechanical pump is no longer effective and an ion pump is used to take the pressure to 10^{-5} T and below. A high voltage is applied between the anode and cathode of the ion pump causing emission of electrons which, aided by a magnetic field from a permanent magnet, ionize gas molecules. The charged ions are accelerated by the electric field produced by the voltage and are buried in the surface of the cathode. The bombarding ions knock out titanium atoms from the cathode which are deposited on pump walls and anode at the same time combining chemically with gas molecules (the Getter effect).

Several practical problems are associated with a high vacuum. A microscopic air leak into the system will cause the pressure to rise and the instrument to shut down. Sealing between flanges is achieved by a knife edge machined into one flange. A copper gasket is placed between the knife edge and the opposite flange, and the flanges bolted together. Also at these low pressures traces of contamination on internal surfaces are instantly vaporized,

and will register as a false reading. All internal parts have to be specially cleaned before assembly, and must be made of materials such as stainless steel or ceramics which do not readily 'outgas' under high vacuum. Thus plastics and rubbers cannot be used. The mass spectrum obtained with no sample entering the instrument is known as the 'background'; it must be measured, stored in memory and deducted from actual readings to obtain the true values. A new instrument will have a high background until 'cleaned' by the ion pump. This is one reason why, once in service, the mass spectrometer should not be left unpowered for more than a few days, otherwise vacuum will be lost and the instrument's subsequent performance will be affected. The amount of gas absorbed onto the internals of the vacuum system is temperature-dependent, an increase in temperature causing the surfaces to outgas, increasing the background and causing a background error until background levels are automatically rechecked. The critical parts of the vacuum system are therefore enclosed in a temperature controlled oven. The precise temperature is unimportant; it is the temperature stability which is critical.

The inlet system is important since the tiny ingress of sample into the system must not destroy the vacuum. Gas is bled into the system from one of a number of inlets having a controlling solenoid valve at the high pressure end. Each inlet is a stainless steel capillary tube of 0.003 inch internal diameter which is further crimped down during manufacture to balance the input gas flow accurately against the ion pump capacity and so maintain the desired pressure.

The Complete System

The complete system is contained in a cabinet 1.9 m high, 0.6 m wide and 0.5 m deep, weighing 350 kg and it comprises a number of drawer units. The vacuum unit contains the ion source, quadrupole and detectors, roughing pump, ion pump, inlet system and calibration gas reservoirs. The vacuum control unit controls the pumps and solenoid-operated valves in the vacuum system. It also controls temperature stability.

The mass spectrometer supplies unit provides the special power supplies required for the quadrupole, ion source, and detectors. Sample gas entering the system passes through the carbon monoxide analyser before reaching the inlets. The carbon monoxide analyser unit provides the computer unit with a signal proportional to carbon monoxide level. The computer unit employing a DEC 11-73 central processor, controls all units in the system and provides gas analysis data to the VDU contained within the display and control unit.

Start-up sequence is fully automatic, and the instrument will sample from a pre-set sample point continuously with no operator intervention. Calibration, using gas from two bottles in the vacuum system, takes place every 24 hours with no operator input. Adjustable alarm levels are provided on each channel. A 24 hour trend display for each gas and a diagnostics mode can be called up.

Operational Experience

Favourable comments have been received from users regarding the fully automatic operation of CAMS and the lack of routine attention it needs.

Fault diagnosis and adjustment of the system by on-board maintainers has been a problem due to lack of knowledge and experience with the technology. It is hoped that the handbook and training course improvements will go some way to solving this problem. Course attendance as close as possible to taking up a maintainer post and taking full advantage of the refreshers now available are essential if the best possible reliability and performance are to be obtained.

Problems have been experienced with the hydrogen channel due to the ion pump's lesser ability to pump hydrogen than other gases, leading to an unstable background level and reduced accuracy of readings. The solution is to enclose the ion source and operate it at a higher pressure than the rest of the vacuum system so that the amount of background gases getting into the quadrupole is reduced. A modification to develop an enclosed source is under development.

There have also been problems with the organics channels. This is a difficult area. The aliphatics and aromatics channels each have to obtain a total value for a range of organic compounds. Each compound will have a complex cracking pattern and may have a concentration of a fraction of a part per million. Each individual compound will have its own 'response factor'. To obtain accurate results, the instrument would need to be calibrated with an accurately known concentration of each compound to determine each response factor. This can be done in a laboratory but not in a field instrument. Organics, especially at these trace levels, cannot be used in the calibration gas bottles used for auto-calibration since they both decompose and stick to the walls of the vessel. Identification of the compounds from the mass spectrum is also far from straightforward. Work is under way to improve organics performance by improved software.

Conclusion

In spite of the complexity of this equipment and the need for skilled personnel in support and maintainance, the mass spectrometer represents a powerful tool for meeting the continuing and expanding needs for the monitoring of submarine atmospheres at sea.

Reference
1. Air purification in submarines; *BR 1326 (revised)*, 1986.