

DEVELOPMENT AND PERFORMANCE OF THE GAS SENSOR SYSTEM

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Summary

The design, development, laboratory testing and production of the gas sensing instruments for the Heavy Gas Dispersion Trials are discussed in detail. The gas sensing transducer used in these instruments is an electrochemical cell which gives a signal proportional to the partial pressure of oxygen in the atmosphere. Any gas species is thus detectable by the reduction in oxygen partial pressure caused by its presence.

The specification of the instruments and the factors influencing the selection of the electrochemical cell are discussed. The principle of operation of the cell is described, together with the main conclusions of a mathematical analysis for diffusion of oxygen molecules through thin membranes. In order to achieve the required frequency response, an electronic signal-enhancement technique was developed. The basis of this technique is explained and experiments are described which confirmed its effectiveness.

The instruments were subjected to laboratory performance checks before delivery to the trials' site. Details of these checks and the results obtained are presented. In order to assure the accuracy of the data produced by the gas measuring system, the on-site performance of the instruments was checked at regular intervals by applying known gas mixtures. The performance of the instruments is discussed and certain design refinements are described.

The quality of the data produced by the gas sensing system is of key importance and techniques were developed to validate the data before their release to sponsors. The validation methodology adopted is described.

The instruments have performed reliably with minimum maintenance. They are low-cost devices and are capable of working over wide temperature and humidity ranges.

1. Introduction

The design and development of the gas sensing instruments used in the Heavy Gas Dispersion Trials (HGDT) was undertaken by HSE's Research and Laboratory Services Division (RLSD) once it became apparent that no commercially available instrument would meet the required specification. The transducer finally adopted for use in these instruments was a version of the electrochemical oxygen cell developed by RLSD some years ago

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[1]. The standard instruments employed a commercial version (Draeger Manufacturing Ltd., Blyth, England) of this electrochemical cell whilst the limited number of fast response instruments employed a prototype cell developed specifically for HGDT by HSE.

The factors, both technical and commercial, taken into account by the HGDT Technical Sub-Committee (TSC) in its decision to choose gas sensors based on the electrochemical cell are discussed in Section 3. This choice was of necessity a compromise due to constraints such as cost, commercial availability and limited time-span available for any development work. The decision to proceed with instruments based on the well tried and tested electrochemical cell was endorsed by an independent survey of gas sensing techniques and sensors carried out by Professor J.A. Lovelock and vindicated by the excellent service actually given by the instruments in the trials.

The choice of gas to be released in the trials and the instruments deployed to measure its concentration are, of course, closely inter-related. The TSC, taking into account available gas sensors and the cost of evaporation plants to produce gas at ambient temperature and pressure, concluded that the best choice of gas would be a mixture of Refrigerant-12 (Freon-12) and nitrogen. This mixture was non-toxic, non-flammable, and offered the possibility of carrying out trials with gas clouds having a density relative to air in the range 4.2 to 1 (neutrally buoyant).

The first part of this paper details the specification to which the gas sensors were produced, followed by a brief review of the types of gas sensors considered. The principle of operation of the electrochemical cell and its use as an oxygen deficiency sensor is explained, together with the main conclusions of a theoretical analysis of its behaviour. In order to achieve the required frequency response, frequency enhancement techniques had to be applied to the signal produced by the basic cell. The theoretical basis of these techniques is explained and details of their use in this application are given. The remainder of the paper describes the tests carried out to ensure that the instruments supplied met the required specifications. Finally, the techniques used to check the validity of the data produced by the gas sensors before its release to sponsors are explained.

2. Gas sensor specification

The specification for the gas measuring system was agreed by the HGDT Steering Committee on the recommendations of TSC in the light of what was reasonably attainable. Because of the constraints outlined above, the desired specification was relaxed in certain areas to produce the following working specification:

- (i) Number required: 180.
- (ii) Concentration range: 0.1% to 100% (mixtures of Freon-12 and nitrogen in air).

- (iii) Accuracy: $\pm 5\%$ of reading for concentrations $\geq 2\%$, $\pm 0.1\%$ absolute for concentrations $\leq 2\%$.
- (iv) Frequency response: 20 Hz (-3dB point). This requirement on the full quota of gas sensors was relaxed after considering the availability of suitable gas sensors and their cost. It was concluded that a limited number of 'fast response sensors' (say 10) was required for use in conjunction with the high speed anemometers to study the physics of the mixing process. For the remainder of the gas sensor array, 'standard sensors' with a frequency response of 1 Hz (-3dB point) were considered adequate for validating the various mathematical models.
- (v) Stability: Zero drift and stability should be consistent with the accuracy requirements over the experimental measurement period which was unlikely to exceed 30 minutes. The minimum requirement was that the zero drift should be less than 10% of scale over a 10 minute period.
- (vi) Cost: Should not exceed £250/instrument for the standard sensors and £1000/instrument for the fast sensors.
- (vii) Availability: A commercially available proven instrument was preferred because of the limited time available for the development work.
- (viii) Operational requirements: The instrument must be rugged, able to withstand prolonged exposure to weather encountered at the trials' site from April to November and be available for use within a few hours of the time the decision to go for a release is made. It must therefore be fully waterproofed and able to withstand wind, rain, direct sun and a temperature range from -5°C to $+35^{\circ}\text{C}$.
- (ix) Response to smoke: Since the released gas was to be marked with smoke so that its progress down the range could be visually observed, the gas sensors must be unaffected by smoke.

3. Selection of the gas sensors

It was recognised at an early stage in the selection process that the gas detection instruments could either be used to detect the source gas or to detect a marker gas added to the source gas before its release. An extensive computerised database covering many types of gas sensing instruments is maintained by HSE and this was searched, making the assumption that the released gas contained a mixture of Freon-12 and carbon dioxide or Freon-12 and nitrogen and that marker gases such as chlorine, sulphur dioxide, sulphur hexafluoride or krypton-85 could be used. The output from this search was huge and covered a wide range of techniques including thermal conductivity, electron capture, infrared absorption, spectrophotometric, electrochemical, flame ionisation and acoustic. The majority of instruments listed by the search were rejected on the grounds of poor response time, high cost or unsuitability for field trials work. Similarly,

the use of marker gases was rejected on the grounds of cost, limited dynamic range of the measuring system, and the problems associated with handling the markers and ensuring uniform seeding. Additionally, there was a strong possibility of raising public disquiet by proposing to release toxic or radioactive material into the atmosphere.

Those instruments or techniques which offered the possibility for use in HGDT were then subjected to a further detailed investigation by RLSD. Additionally, Professor J.A. Lovelock was commissioned to review the most promising gas sensing techniques. The overall conclusion agreed by all parties and subsequently endorsed by the HGDT Steering Committee, was that the oxygen electrochemical cell offered the best compromise in terms of response time, cost, reliability and sensitivity. Gas sensing instruments using this cell would operate as oxygen deficiency sensors and the presence of the released gas would be detected by the displacement of atmospheric oxygen. This gives the additional advantages of ease of calibration and independence of the composition of the released gas.

4. Operating principles of the oxygen electrochemical cell

A diagram illustrating the construction of the electrochemical cells used in the standard sensors (and with slight modification, the fast-response sensors) is shown in Fig. 1. The external atmosphere diffuses through a metal sinter (not present in the fast-response sensor) and then through a PTFE membrane to the cathode which is a thin layer of silver evaporated onto the inner surface of the PTFE membrane. The PTFE membrane is mechanically supported by a dialysis membrane. This also serves to keep the cathode 'wet' with molar sodium chloride electrolyte which fills the body of the cell.

A silver wire anode is inserted into the electrolyte and, in operation, a potential of about 1 volt is applied across the cell. At this potential,

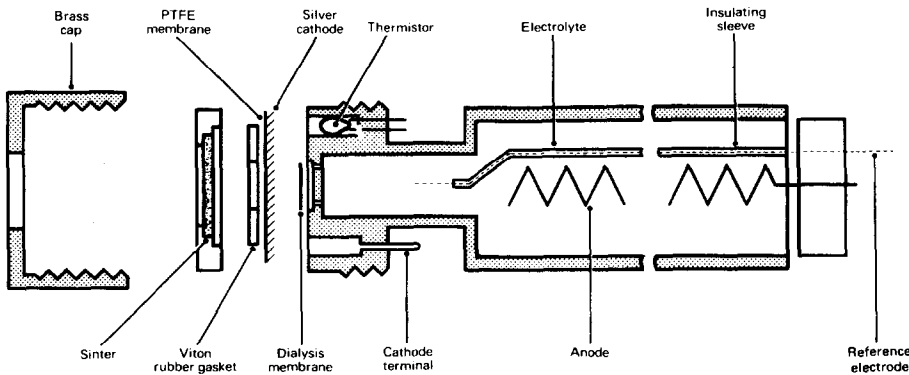


Fig. 1. Schematic diagram showing the construction of the oxygen electrochemical cell.

electrons with sufficient energy are available to quickly changes the state of any oxygen molecules which arrive at the cathode, probably into the super oxide ion O_2^- , which then reacts with the water of the electrolyte, accepting further electrons until it is finally converted into an hydroxyl ion. Because of the speed of the electrochemical reaction, the partial pressure of oxygen at the cathode is effectively zero and the current through the cell is dependent on the partial pressure of oxygen in the atmosphere and the diffusion characteristics of the sinter and membrane.

In operation, silver chloride is deposited on the anode causing an increase in the electrical resistance of the cell with use. If this resistance becomes too large the effective potential across the cell is reduced and proper operation ceases. A third electrode can be inserted into the electrolyte to overcome this problem. By means of this third electrode, the effective potential can be sensed and held constant using an electronic feedback circuit.

A plot of the variation in output voltage (i.e. the voltage generated by the cell current across a fixed resistance) with bias voltage is known as a polarogram. Figure 2 shows a typical polarogram for air (curves (a)) produced by ramping the bias voltage between the minimum and maximum values shown. Different curves are produced when the bias voltage rises or

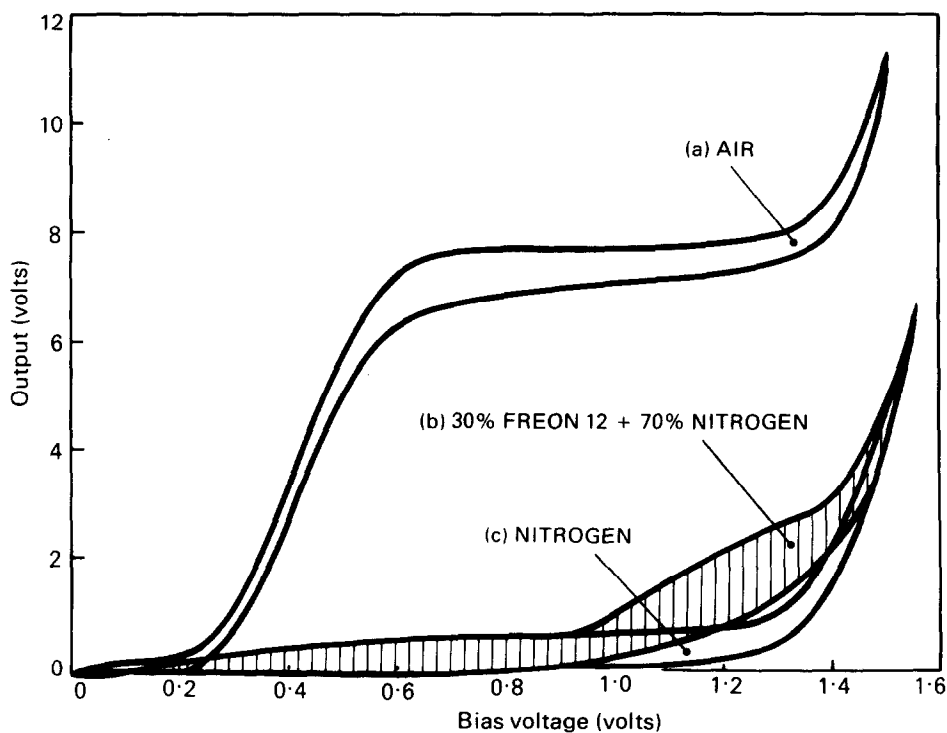


Fig. 2. Typical oxygen cell polarograms; (a) normal air; (b) 30% Freon-12 in nitrogen; (c) 100% nitrogen.

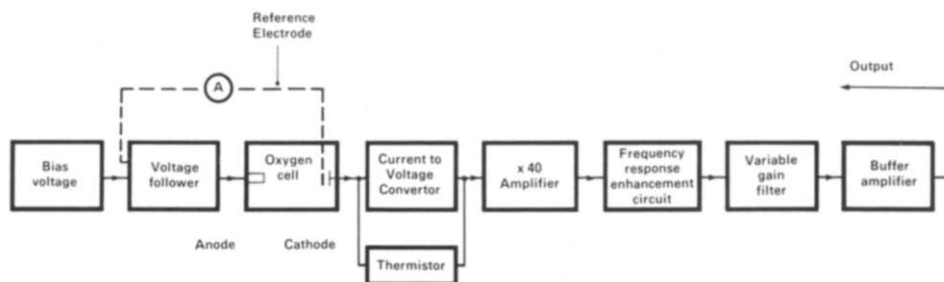
falls due to a hysteresis effect produced by the operation of the cell. If oxygen is present, the output voltage increases with bias voltage until a level plateau is reached. To function correctly the cells must be operated on this plateau, where the variation of output voltage with oxygen partial pressure is at its most linear. The mid position of the plateau (which corresponds to a bias voltage of about 1.1 V) is normally chosen to give maximum cell life. Early experiments showed, however, that the presence of Freon-12 caused an additional contribution to the output voltage. This is clearly illustrated in Fig. 2 (curves (b)). Operation at a bias of 1.1 V in the presence of Freon-12 would have made the cell response non-linear and, accordingly, the cells were operated at 0.9 V.

In practice, it is found that the variation in output voltage with partial pressure of oxygen deviates negligibly from a perfectly linear characteristic. The background voltage from an atmosphere totally deficient in oxygen is typically less than two percent of the voltage given by normal air and very stable. Since the cells are operated as oxygen deficiency sensors their calibration is particularly easy. If normal air is taken to have an oxygen content of 21% then 1% oxygen deficient air would have an oxygen content of 20%. This is equivalent to about 5% concentration by volume of released gas (i.e. Freon and nitrogen mixture) in normal air.

5. Basic details of the gas sensing instruments

The standard instruments employ a commercial electrochemical cell manufactured by Draeger Manufacturing Ltd. This cell has a six micrometer thick PTFE membrane and two electrodes. As will be described later, during the course of the Phase I trials these cells were modified to incorporate a third electrode. The fast-response sensors employ a custom-made cell with a three micrometer thick PTFE membrane, no sinter and three electrodes. Additionally, the fast-response sensors have an aspirator, driven by a small pump, to prevent dead volumes of gas accumulating near the membrane. In both instruments the cells are used in a constant-voltage circuit and low-noise amplifiers are used throughout. To improve the frequency response of the instruments, signal enhancement techniques as described below are used in both instruments. As a result, the standard instrument has a frequency response of about 1 Hz and the fast-response instrument about 10 Hz.

A block diagram of the standard instrument is given in Fig. 3; the fast-response instrument is similar in concept. A constant bias voltage is applied to the cathode of the electrochemical cell and, as described above, oxygen molecules coming into contact with the cell cathode produce an electrical current. This is changed into a voltage by means of the current-to-voltage converter. A thermistor, located close to the cell membrane, is used to compensate for changes in cell sensitivity caused by temperature variations. The voltage is amplified by a factor of 40 and then passed



The link "A" and reference electrode were added to the instrument during the 1983 trials

Fig. 3. Block diagram showing component parts of the standard gas sensor.

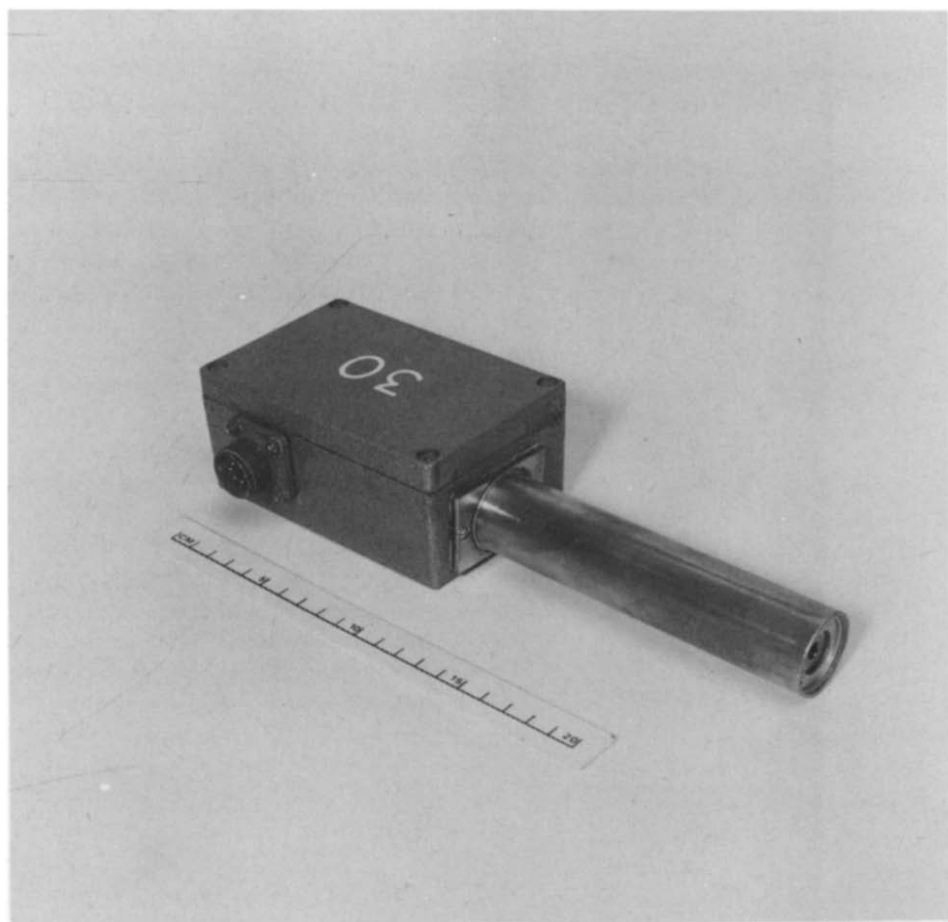


Fig. 4. Photograph of standard gas sensor.

through the frequency response enhancement circuit. Finally, the signal passes through a variable gain active filter and buffer amplifier to the output. The output voltage of the instrument is set to about 8 V in air, the output dropping to a few tenths of volts when the sensor is immersed in nitrogen. The instruments are powered from a ± 12 V supply, typical power consumption being less than 1 W.

The electronics for the instrument were assembled on a printed circuit board, which was subsequently encapsulated in a silicon rubber compound. To ensure that the complete instruments would withstand harsh climatic conditions, the circuit board and cell were housed in a waterproof case. Sunshields were also provided to protect against overheating by direct sunlight. Photographs of the complete instruments are shown in Figs. 4 and 5.

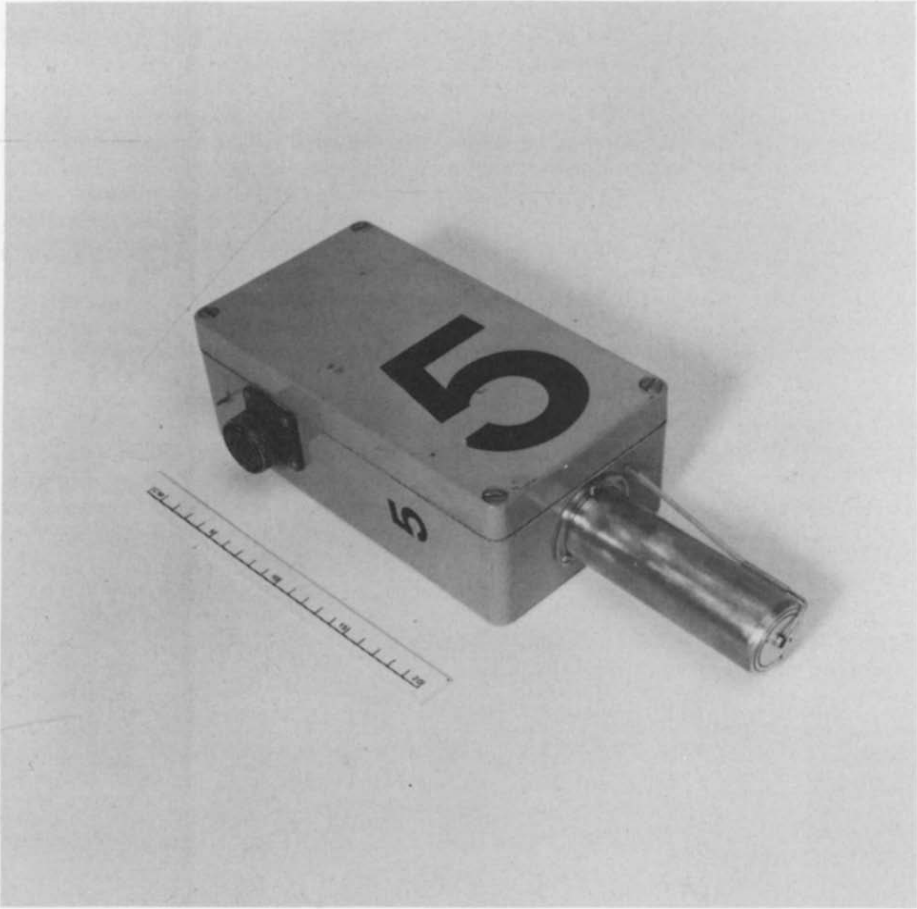


Fig. 5. Photograph of fast-response gas sensor.

6. Electronic enhancement of frequency response

As already mentioned, the signal enhancement techniques were used in both the standard and fast-response instruments to meet the required specifications of 1 Hz and 10 Hz, respectively. A theoretical analysis of the spectral characteristics of the cell was carried out on the assumption that these were determined by the transport of oxygen through the PTFE membrane. This diffusion limited model has been used previously by McCallum and Pletcher [2]. The analysis was also extended to incorporate the effects of the brass sinter in front of the membrane. The analysis showed that a diffusion limited electrochemical cell has a transfer function which can be expressed as follows:

$$H(\omega) = \prod_{n=1}^{\infty} (i/T_n)(i/S_n)/[(\omega + i/T_n)(\omega + i/S_n)]$$

where T_n and S_n are time constants associated with the transport of oxygen through the membrane and the sinter respectively, and $T_n = L^2/Dn^2\pi^2$, $S_n = 4L_s^2/(2n-1)^2\pi^2D_s$, D = diffusivity of oxygen in the PTFE membrane, D_s = diffusivity of oxygen in the sinter, L = thickness of the PTFE membrane, L_s = thickness of the sinter, ω = angular frequency of the input signal.

In the case of the fast-response instrument, which did not have a sinter, the transfer function becomes:

$$H(\omega) = \prod_{n=1}^{\infty} (i/T_n)/(\omega + i/T_n)$$

Thus the spectral characteristics of the cell can be represented by a series of exponential terms at angular frequencies dependent on the diffusivities of oxygen in the membrane and the sinter and on the thickness of both. In a well designed cell one would expect $T_n > S_n$, i.e. that the lower frequency terms would be associated with the transport of oxygen through the membrane.

On the basis of the above it was concluded that frequency enhancement techniques based on pole cancelling techniques could be applied. The enhancement technique depends on filtering the electrical output of the transducer in such a way as to cancel poles in its transfer function. It follows that, to improve the performance of a diffusion limited electrochemical cell, the first stage of filtering (1st order enhancement) should be designed to cancel the pole at $\omega = i/T_1 = iD\pi^2/L^2$, the second stage (2nd order) to cancel the pole at $\omega = i/T_2 = i4D\pi^2/L^2$, and so on.

Experiments were carried out to determine the step function response of the fast-response electrochemical cell with 0th-order (direct output), 1st order and 2nd order enhancement. The cell had a 3 micrometer thick PTFE membrane. During the experiments the cell and valve assembly were placed inside a climatic chamber and the temperature held constant at 20°C.

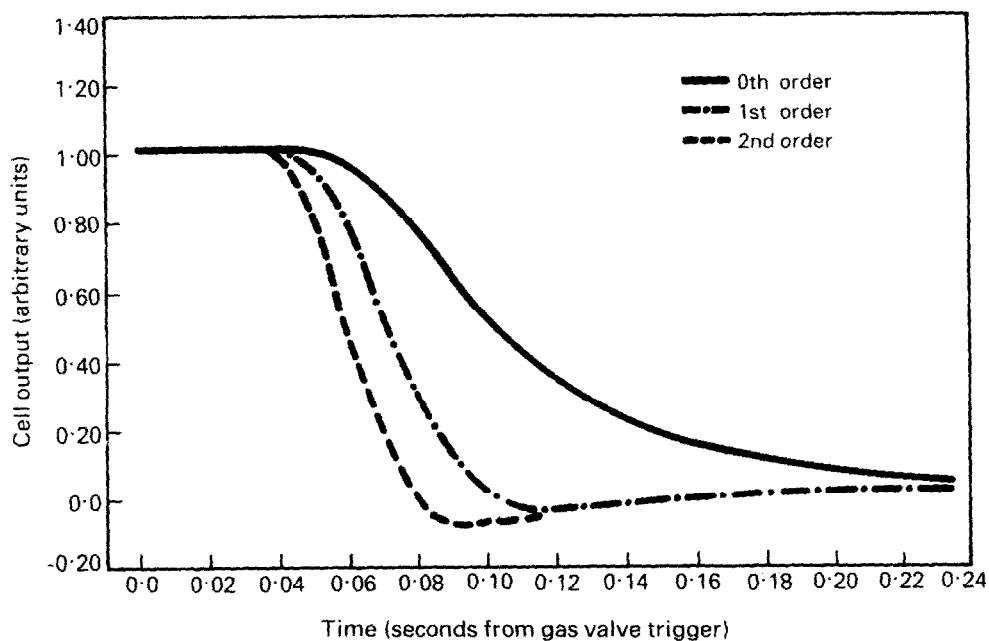


Fig. 6. Effect of frequency response enhancement on an electrochemical cell (at constant temperature).

To generate a step function change in gas concentration at the cell, a jet of gas was directed at the PTFE membrane via a fast, solenoid-operated, spool valve. The valve was used to switch between two gas mixtures with different proportions of oxygen, the first consisting of one part oxygen to ten of nitrogen and the second, one part oxygen to five of nitrogen. Using a TSI hot wire probe with a frequency response of about 30 kHz it was determined that the transition time (10% to 90%) between gas mixtures at the surface of the PTFE membrane was 14 milliseconds. This is much faster than the actual response of the cell and can be considered, as a first approximation, to be equivalent to a step change in oxygen concentration. Besides the inherent transition time due to the valve there is a delay time of about 30 milliseconds between the trigger pulse being applied to the valve and the valve actually operating. A computer was used to trigger the valve and sample the various voltage outputs at 4 millisecond intervals. The results are plotted in Fig. 6.

A second series of experiments were carried out to determine the effects of temperature changes on the cell performance with various orders of enhancement. The experimental set-up was as before except that measurements were taken at 15°C, 20°C, and 25°C. The results are plotted in Fig. 7, Fig. 8 and Fig. 9.

If the cell response to the step function input is approximated by a single exponential function as follows:

$$r(t) = \exp(-t/T)$$

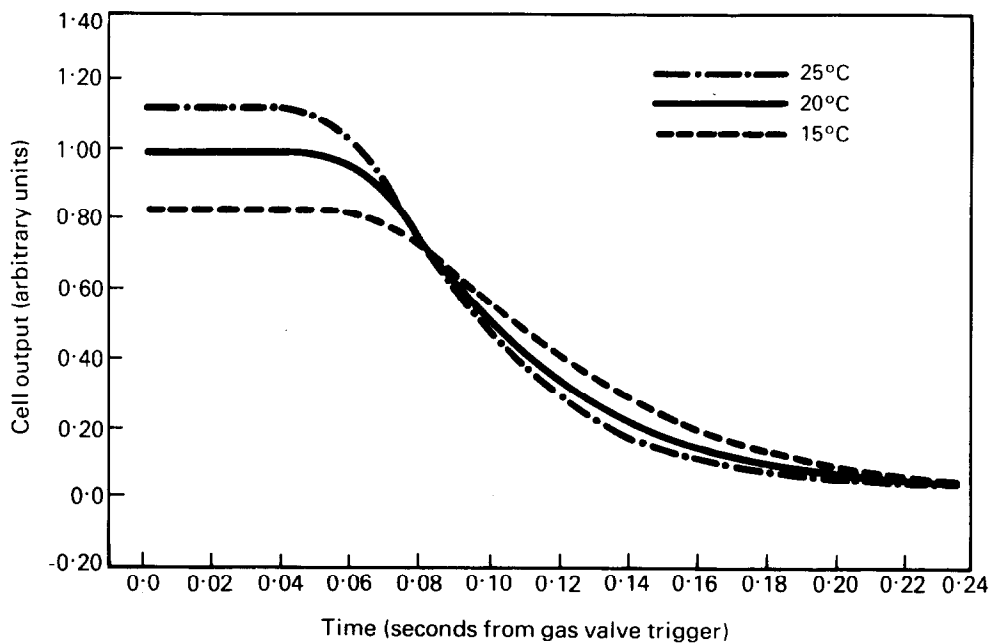


Fig. 7. Zeroth order enhancement at three temperatures.

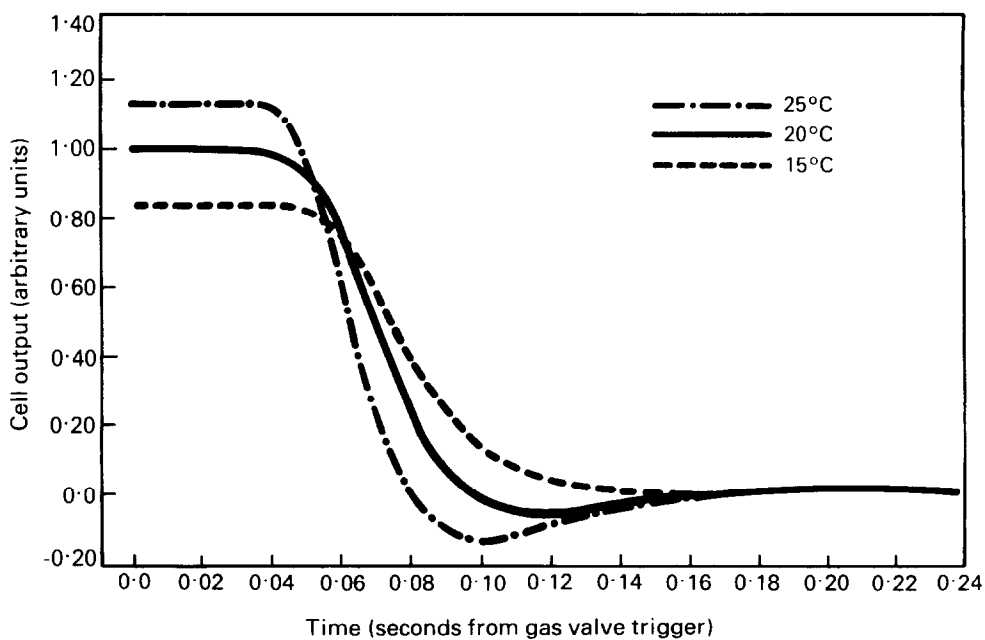


Fig. 8. First order enhancement at three temperatures.

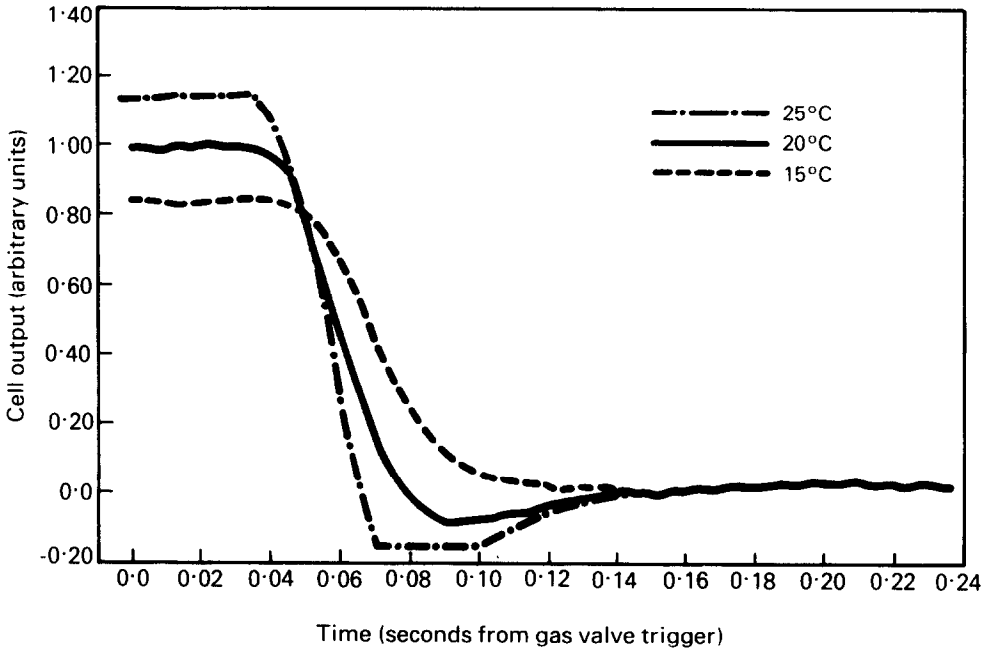


Fig. 9. Second order enhancement at three temperatures.

then it can be shown that 10% to 90% rise time is equal to $2.2T$. This rise time can be measured to show that:

$$[0\text{th order}]_{90}^{10} = 0.116 \text{ s}, T = 52.7 \text{ ms}$$

$$[1\text{st order}]_{90}^{10} = 0.038 \text{ s}, T = 17.3 \text{ ms}$$

$$[2\text{nd order}]_{90}^{10} = 0.026 \text{ s}, T = 11.8 \text{ ms}$$

By using the single exponential approximation the relationship between rise time and frequency response is $[\text{rise time}]_{90}^{10} [\text{freq resp.}(-3\text{dB})] = 0.35$.

The frequency response of the fast-response cell with the different orders of enhancement may now be determined:

$$0\text{th order} = 3.0 \text{ Hz } (-3\text{dB})$$

$$1\text{st order} = 9.2 \text{ Hz } (-3\text{dB})$$

$$2\text{nd order} = 13.5 \text{ Hz } (-3\text{dB})$$

This represents a 3-fold improvement in frequency response between 0th and 1st order and a further 1.5 times improvement between 1st and 2nd order. The frequency response of the electrochemical cell enhanced to 2nd order is therefore some 4.5 times better than that of basic cell.

The diffusivity of oxygen in the PTFE membrane varies with temperature and pole cancelling will only be exact at a fixed temperature. At higher temperatures the oxygen diffuses more rapidly giving a faster response, resulting in overshoot of the frequency enhanced output in response to a change in oxygen concentration. At lower temperatures the output will undershoot.

An estimate of the change of diffusivity with temperature can be made from the data in Fig. 7. The overall cell output is proportional to the diffusivity and any change in the magnitude of the cell signal is directly proportional to the change in diffusivity.

Normally, this change in sensitivity with temperature is compensated electronically by means of a thermistor. However, the cell used for these tests was not compensated in this way. Between 20°C and 25°C the diffusivity increases by 12.5% and between 20°C and 15°C it decreases by 17%.

The change in diffusivity with temperature implies that the frequency response of the cell will change with temperature. Thus, frequency response will be proportional to diffusivity. The pole-cancelling filters were set up at 20°C so that at other temperatures exact pole-cancellation will not be encountered. Slight undershoot or overshoot is to be expected at lower and higher temperatures respectively.

In summary, these experiments showed that an electrochemical cell with a bare 3 micrometer thick membrane (i.e. the design ultimately adopted as the fast-response sensor) has a basic frequency response of 3 Hz. Two stages of enhancement would result in a frequency response of 13.5 Hz which is adequate to meet the specification for fast-response gas sensors. The standard gas sensor, with a 6 micrometer thick PTFE membrane and sinter has a basic frequency response of 0.3 Hz. Thus a single stage of enhancement should give a frequency response of 1.1 Hz, which meets the specification for the standard sensors. As will be seen later this figure was subsequently borne out by tests on the standard sensors themselves. Clearly, only with these enhancement techniques could the electrochemical cell meet the HGDT gas sensor specification.

7. Laboratory controlled performance tests

7.1. Preliminary instrument evaluation

Once the decision was taken to base the gas sensors on the electrochemical cell, ten prototype instruments were built and subjected to laboratory controlled testing in a climatic chamber. These prototypes were also subjected to the outside environment over a period of many months at HSE's Explosion and Flame Laboratory at Buxton, on the weather station at Thorney Island and on the roof of HSE's Safety Engineering Laboratory at Sheffield.

In all they were subjected to rain, wind, sunshine and temperatures in the range 30°C to -10°C. Throughout this evaluation period the prototype instruments showed good long-term stability well within the specification and the ability to withstand climatic conditions more severe than those likely to be encountered at Thorney Island.

Several proving trials were also carried out in a ventilated underground gallery in which the prototype sensors were exposed to smoke-marked

highly-turbulent Freon-12 releases. During these tests the instruments were exposed to high concentrations of smoke; no adverse effects were observed and the zero level and sensitivity remained unaffected.

7.2 Linearity checks

All the oxygen electrochemical cells supplied for use in the gas sensors were individually tested for linearity of response. Following initial tests to confirm linearity of the cells, linearity checks at air/nitrogen mixtures of 0%/100%, 25%/75%, 75%/25% and 100%/0% were adopted as standard laboratory checks for all the gas sensors prior to distribution to the site.

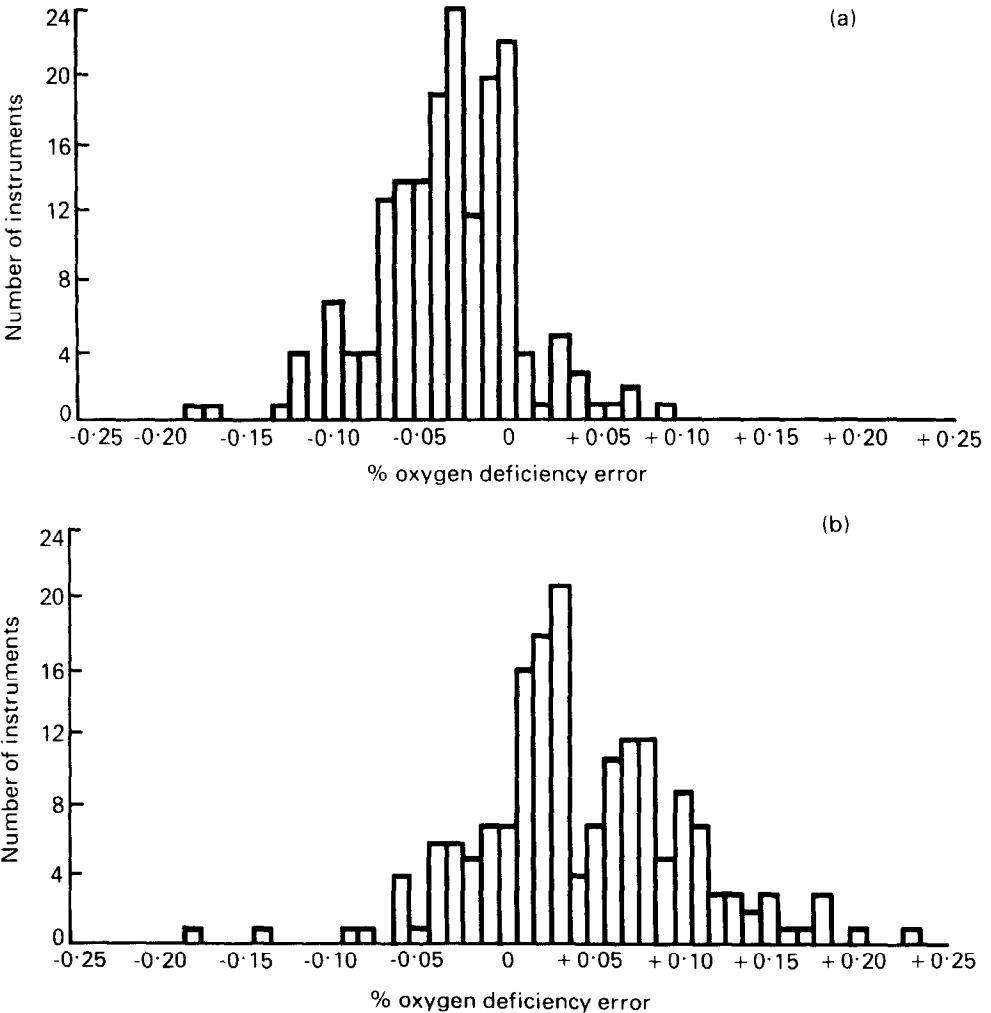


Fig. 10. Histograms showing distribution of linearity errors for a batch of 170 cells at: (a) 75% air/25% nitrogen and (b) 25% air/75% nitrogen.

The air and nitrogen were supplied from gas cylinders and blended using a mixing pump having an accuracy of 0.05% of reading. The resulting mixture was supplied to the cell under test by means of a gas-tight sampling head.

Histograms of the linearity errors at (75%/25%) and (25%/75%) for a batch of 170 cells are shown in Fig. 10(a) and Fig. 10(b) respectively. The results are expressed in terms of % oxygen deficiency error relative to air and show that the linearity of the cells is well within the specified tolerance. The maximum linearity error observed was -0.2% oxygen deficiency (equivalent to -1% gas concentration) for a gas concentration of 25% in air. For example, with a 25% concentration of nitrogen in air the mean linearity error is -0.03% oxygen deficiency with a standard deviation of 0.04%. In terms of a percentage gas concentration this mean error is equivalent to -0.15% gas. Using three standard deviations to determine the 99% confidence interval (assuming a normal distribution of errors) results in an error bar ± 0.45 and -0.75% gas. These results are more usefully expressed as a percentage error of reading. Any measurement of concentration of nitrogen in air plotted with an error bar encompassing +2% and -3% of reading should include the true concentration 99 times out of 100.

Similar linearity tests were also carried out using various mixtures of air, nitrogen and Freon-12 produced by two mixing pumps working in series. These tests showed that the linearity of the cells was adversely affected by the presence of Freon-12. The percentage of reading error in the (air/nitrogen/Freon-12) mixture as compared to the (nitrogen/air) mixture for a batch of 10 cells is given in Table 1. In each case the nitrogen and Freon were mixed in a 2:1 proportion. Over the range 0% to 30% gas mixture in air the mean linearity error was found to be -4.2% of reading with a standard deviation of 2.3%. Thus, for gas mixtures including Freon-12, measurements of the concentration should be plotted with an error bar encompassing +1% and -9% of the reading to be sure of including the true concentration with 95% confidence.

The reasons for the Freon-12 induced non-linearity are at present not clear. The results indicate, however, that Freon-12 in proportions of up to 30% in mixtures of (nitrogen/Freon) reduces the sensitivity of the oxygen electrochemical cell to oxygen. The effect is quite slow, taking approximately four minutes before the sensitivity stabilises. The maximum effect appears to occur at concentrations of about 30% of the 2:1 nitrogen/Freon mixture in air (70% air). As illustrated by Fig. 11(a), at higher concentrations of the mixture the deviation from the linear characteristic becomes less until at 0% air/100% mixture the cell output returns to its expected value. This suggests that the linearity error is not due to a signal from Freon-12 but rather the effect of Freon-12 on the response of the cell to oxygen. One possibility is that the presence of Freon-12 affects the diffusivity of oxygen in the PTFE membrane. However, the important

TABLE 1

Percentage reading error between (air/nitrogen) and (air/nitrogen/freon) mixtures for a batch of 10 cells.

Instrument Serial Number	Percentage of reading error (100% air used as baseline)						
	100% Air	96% Air	94% Air	92% Air	90% Air	80% Air	70% Air
19	0	-1.28	-3.057	-3.945	-5.544	-4.478	-3.057
50	0	-8.454	-3.82	-4.283	-7.898	-4.561	-3.412
59	0	1.774	-1.395	-2.662	-5.197	-5.197	-4.352
77	0	-7.379	-8.297	-8.759	-7.93	-4.075	-2.423
83	0	-0.711	-0.711	-2.192	-3.081	-2.489	-1.896
85	0	-5.322	-5.322	-5.322	-5.322	-4.213	-2.735
118	0	-3.184	-4.167	-4.659	-6.133	-5.543	-3.381
151	0	-3.486	-5.302	-4.848	-7.844	-5.12	-3.849
157	0	-8.454	-5.673	-5.673	-6.786	-5.673	-3.82
180	0	4.761	-0.53	-1.852	-3.704	-3.704	-2.646
MEAN	0	-3.173	-3.827	-4.42	-5.943	-4.500	-3.157
S DEV	0	4.412	2.472	2.00	1.71	0.95	0.74

The gas mixture used to dilute the air for the Freon 12 tests = 67% Nitrogen + 33% Freon 12.

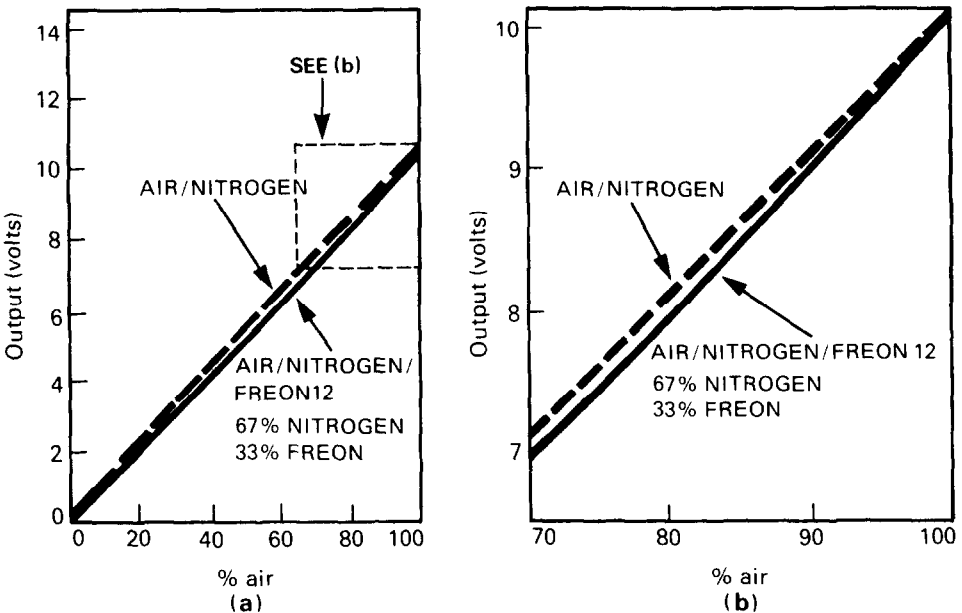


Fig. 11. Comparison of the linearity errors in (air/nitrogen) and (air/nitrogen/freon) mixtures.

point is that the 1% to -9% error band quoted above seems to represent a worst case situation. For the very low concentrations of Freon likely to be detected in the trials the error band is likely to be much narrower.

7.3 Frequency response checks

The frequency response of all instruments was optimised and checked before their despatch to the HGDT site. This involved adjusting preset potentiometers associated with the frequency enhancement circuit whilst pulses of gas were passed over the cell membrane via a fast-operating solenoid valve. The 10% to 90% rise and fall times of the gas concentration at the cell membrane were 14 ms as determined by a hot-wire probe. This is essentially instantaneous when compared to the response time of the cell. The rise time between 10% and 90% of full scale was recorded for each instrument and Fig. 12 shows a histogram of the results for a batch of standard sensors. Both the standard and fast sensors were tested in this fashion.

The relationship between frequency response f (at -3dB) and the 10% to 90% rise time T_r is approximately $f = 0.35/T_r$. Thus a rise time of 350 ms would correspond to a 1 Hz bandwidth. From Fig. 12 the mean rise time T_r is 290 ms with a standard deviation of 24 ms. Assuming a normal distribution it follows that 99% of the standard sensors have a frequency response in the range of 0.97 Hz to 1.6 Hz, in other words well within the specification.

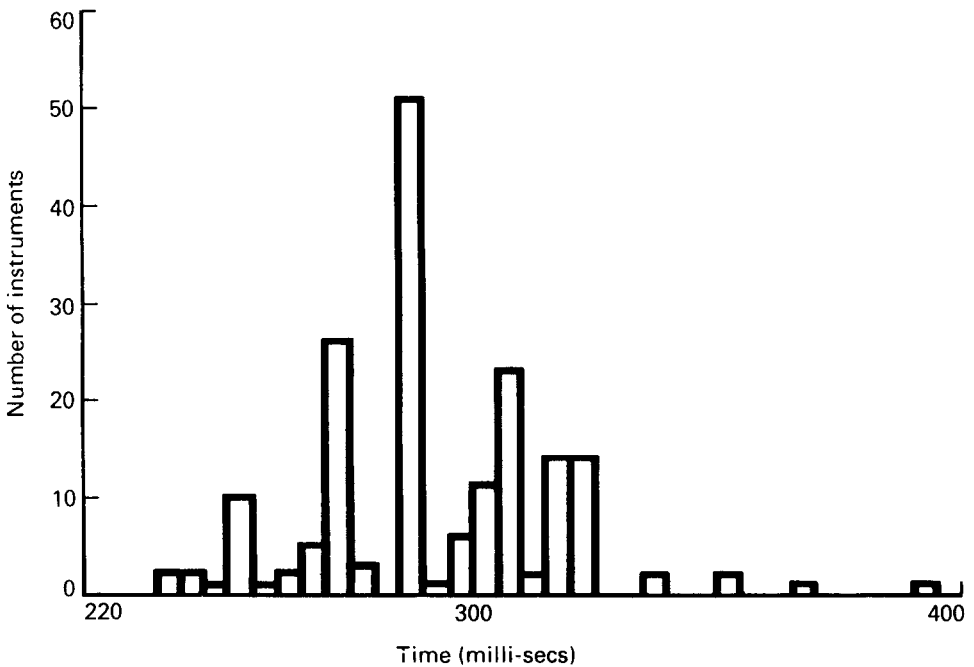


Fig. 12. Histogram showing distribution of 10% to 90% rise times for a batch of standard sensors.

7.4 Effect of temperature and humidity changes

All instruments were compensated for changes in membrane diffusivity with temperature by adjusting the feedback from the thermistor in close contact with the membrane to give constant sensitivity to oxygen between 5°C and 30°C to better than 0.02% oxygen deficiency/°C (static). Each instrument was then cycled repeatedly between these temperatures in an environmental chamber to check the accuracy of the compensation.

Typical graphs for a portion of the temperature cycling for seven of the instruments are reproduced in Fig. 13. Note that there are both dynamic and static errors, the former reducing as the rate of change of temperature decreases. Further investigation showed that the dynamic error was due to a slight mismatch in the temperature characteristics of the membrane and compensating thermistor. Histograms of the dynamic and static temperature drift errors based on all the instruments supplied for Phase I HGDT are shown in Fig. 14(a) and 14(b) respectively.

Initially it was assumed that relative humidity (RH) would have a negligible effect on the performance of the oxygen cell apart from the relationship between humidity and partial pressure of oxygen. A change of RH from 0% to 100% reduces the oxygen partial pressure by less than 1% (i.e. equivalent to less than 5% concentration of gas) and the tests on the prototype instruments bore out these figures. However, further tests on the production instruments (which employed a different batch of cells),

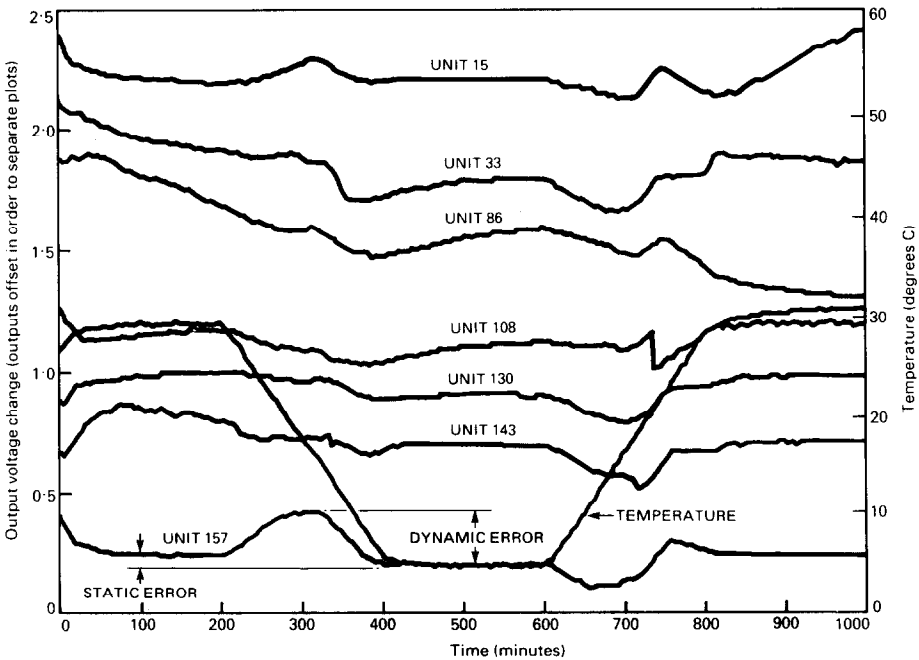
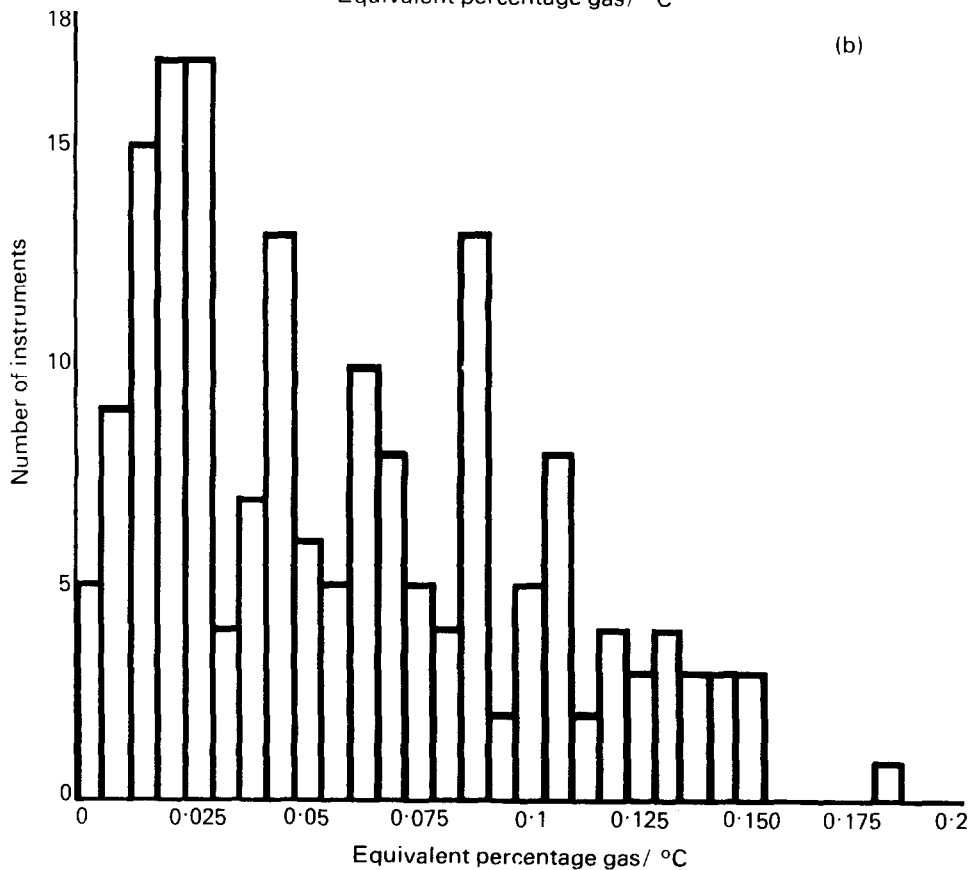
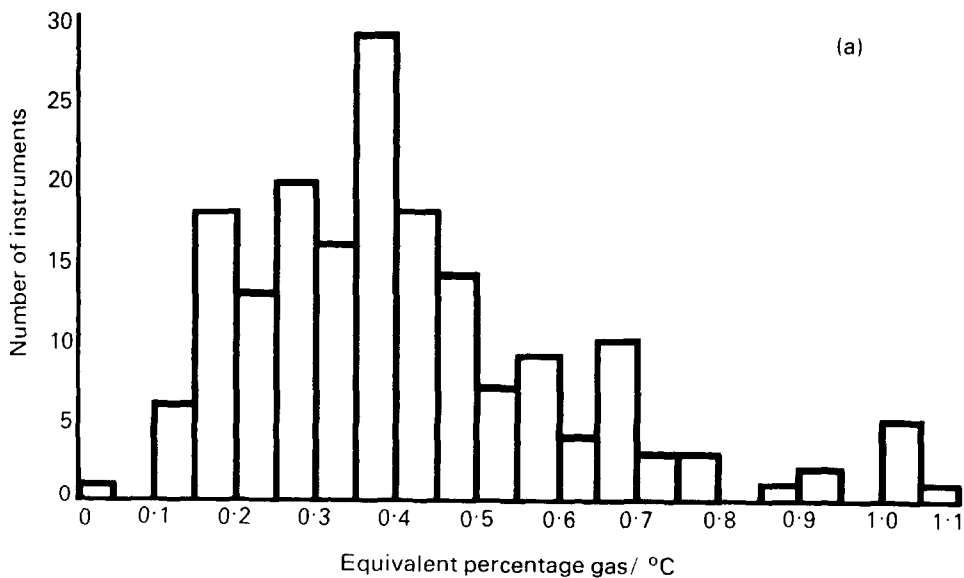


Fig. 13. Typical graphs illustrating the effect of temperature changes on the output of the standard gas sensors.



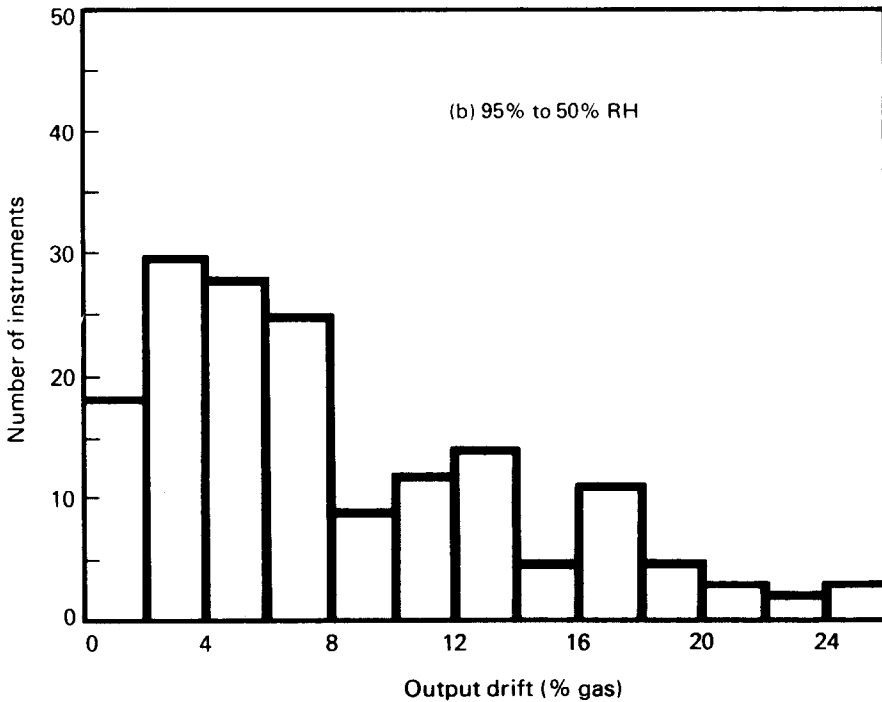
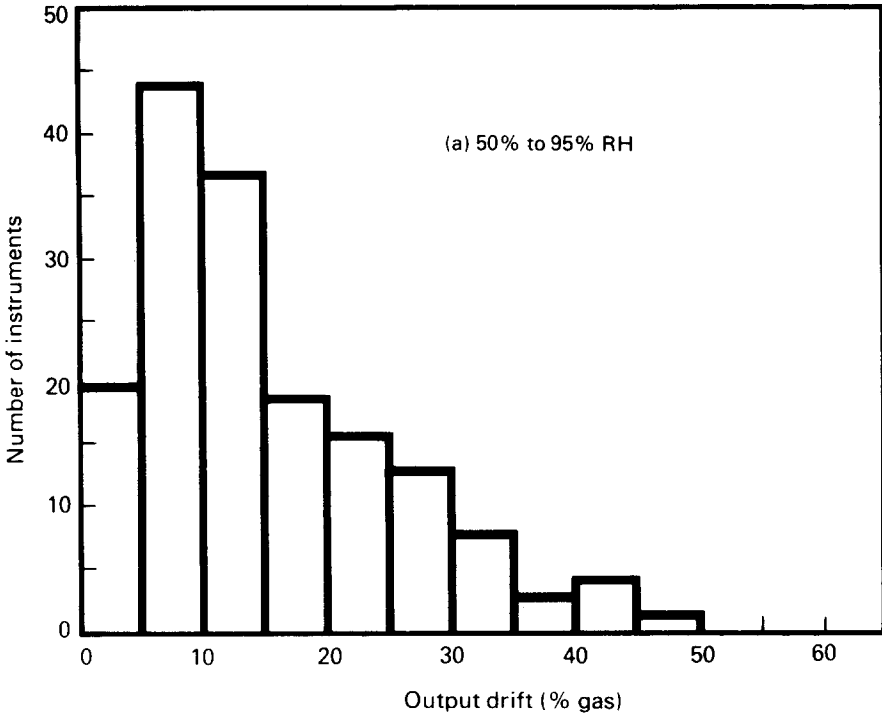


Fig. 15. Histograms showing the distribution of errors caused by changes in relative humidity: (a) dry to wet transition, (b) wet to dry transition.

carried out simultaneously with the Phase I trials, showed that errors due to RH changes were greater than expected. These tests involved cycling the instruments between 50% and 95% RH in an environmental chamber. It was observed that some of the oxygen cells had a larger error (output drift) on the first half of the cycle (i.e. 50% to 95% RH) than on the second half (i.e. 95% to 50% RH). Subsequent humidity cycling of the oxygen cell, however, produced similar errors for both parts of the cycle and the large errors found on the first half of the first cycle did not recur. Histograms showing the spread of errors during both halves of the first humidity cycle are shown in Figs. 15(a) and (b) in terms of equivalent gas concentration.

Other than selecting oxygen cells with errors less than a set value of, say, 12% gas equivalent there is no practical solution to this shortcoming. Indeed all the oxygen cells supplied for the Phase II trials were subjected to a relative humidity cycle test and the results from the wet to dry transition were used to determine the error due to the change in humidity. Only those which had an error of less than 12% gas equivalent for a 50% to 95% change in RH were selected for use in the trials. In practice 90% of gas sensors judged to have detected gas in the trials drifted by less than 1% equivalent gas concentration.

7.5 Noise tests

All the instruments were tested by sampling their outputs for one minute and checking the maximum peak to peak noise level that occurred. This was found to be equivalent to 0.05% gas over this interval.

7.6 Vibration tests

During the initial testing of the instruments it was observed that some of the standard oxygen cells were effected by mechanical vibration. This fault was traced back to the manufacturer who found that a defective batch of cells had been produced. Therefore to ensure reliability of the instruments a vibration check was included in the test program. This consisted of shaking the unit by hand for one minute and recording the maximum error produced. For all units tested the maximum error observed was less than 0.05% gas equivalent.

8. On-site performance of the gas sensors

The gas sensing system at the trials site was normally switched on several days before a trial or, if the weather conditions indicated that a sequence of trials was possible, left on continuously. Since the specified tolerance of the sensor outputs was between 7 and 9 V in normal air, dropping to roughly 0 V in 100% gas, the identification of faulty gas sensors was particularly straightforward using the diagnostic printouts available from the data gathering system. Whenever possible, faulty sensors were

identified before a trial was carried out and were replaced from a pool of spare sensors. Faulty sensors were returned to HSE's Sheffield Laboratory for fault diagnosis and repair. Details of the commonest faults encountered are given below. Thus on most occasions a full complement of sensors was available on-site to monitor the release.

In addition to this simple check on sensor operation, regular on-site span and linearity checks were also carried out by NMI staff. The span check involved supplying 100% nitrogen to each sensor on the site. The whole gas sensor field was checked in this fashion at monthly intervals or more frequently if a number of trials were carried out in close succession. As will be explained in the next section the 100% air and 100% gas readings were used to determine the calibration factor for each sensor on site. This information was subsequently used to convert the raw voltage output from each sensor into engineering data in terms of gas concentrations at the end of each trial.

Although the regular voltage output and span checks gave considerable confidence in the sensor integrity it was also considered necessary to obtain some information on the actual linearity of response of the sensors on the site. Early after Trial 6 it was established that a number of the standard sensors have become non-linear due to premature ageing of the original two-electrode electrochemical cells. At that stage the instruments had operated for just 54 days out of an expected lifespan of six months. An increasing anode resistance moves the operating point towards the knee of the plateau of the polarogram causing a non-linear characteristic to develop. There was no firm evidence as to the cause of the premature ageing but the problem was quickly rectified, by converting all the standard sensors to the three-electrode design. No further linearity problems were encountered in either the Phase I or Phase II trials.

Clearly regular checks on the linearity of all 200 on-site gas sensors was a formidable task and one prone to some considerable errors due to the location of the sensors on masts at up to 15 m above ground level. Various schemes were proposed and tried, each of necessity being a compromise between cost and thoroughness. The scheme finally adopted involved choosing a random sample of 10 sensors from the on-site population (each sensor had its own serial number) and carrying out a detailed linearity check on these whenever the span checks were carried out. A new random sample was chosen for each span check. The linearity check involved applying a nominal 10% Freon/90% air mixture to each of the chosen sensors. These linearity checks helped confirm that after the initial problems early in Phase I the sensors maintained their original linearity. Indeed, during the winter period between 1982 and 1983 when all sensors were returned to HSE for service and refurbishment their linearity was carefully checked and found to be within the original specification.

The major problems encountered with the gas sensors during the Phase I trials were due either to electrolyte leakage around the brass cap of the

electrochemical cell or to circuit board failure due to lightning strikes. Electrolyte leakage could result in earth loop problems and consequent zero drifting of the instruments. This could be detected during the periodic 100% nitrogen calibration checks or on catastrophic failure of the instruments. The effect of lightning strikes was also readily detectable in the field. In the former case the faulty cells were replaced and, during the Phase I/Phase II refurbishment, new cells having an improved construction which largely eliminated the leakage problem were installed. During the refurbishment, improved protection circuitry was incorporated into the sensors to minimise the damage from lightning.

After servicing, each instrument was tested to ensure it fully met the specification before it was returned to the HGDT site. Similarly, after the full refurbishment of all gas sensors, each one was subjected to the same rigorous test procedure as had been carried out originally.

9. Validation of the gas sensor data

A considerable amount of checking and validation of data produced by the gas sensors was carried out before data tapes were finally issued to sponsors. The initial data collected from the gas sensors were simply the raw voltage outputs from the gas sensors. After a trial, the next stage in the process was to prepare tapes containing engineering data, with the voltages converted into gas concentrations using the span and 0% gas baselines determined just before a trial. The 0% gas level is, of course, just the output from a sensor in ambient air — typically 8 V.

The next step was to examine the engineering data to determine which sensors had detected gas and whether those particular sensors had functioned correctly during the trial. This validation process was carried out at HSE's Sheffield Laboratory. To determine which sensors detected gas, all sensor outputs were checked as a function of time and position on the site, taking into account the known cloud position. In this way those sensors which could have potentially detected gas could easily be identified. The aim of the process was to ensure a consistent interpretation of the data, particularly at low gas concentrations. The gas sensors, like all other instrumentation, would occasionally give a small signal due to electrical noise or some other random process. The validation procedure ensured that any potentially misleading information was removed from the data-base before issue to sponsors. In fact only the outputs from the gas sensors which detected gas were retained on the validated tapes, the remaining sensor outputs being set to zero.

The second stage in the validation process was to correct for any residual shift in the zero gas baseline during the course of a trial. This could be caused by variations in relative humidity or ambient temperature. A simple linear correction was applied, as illustrated by Fig. 16. This process was carried out using HSE's mainframe computer and some interactive

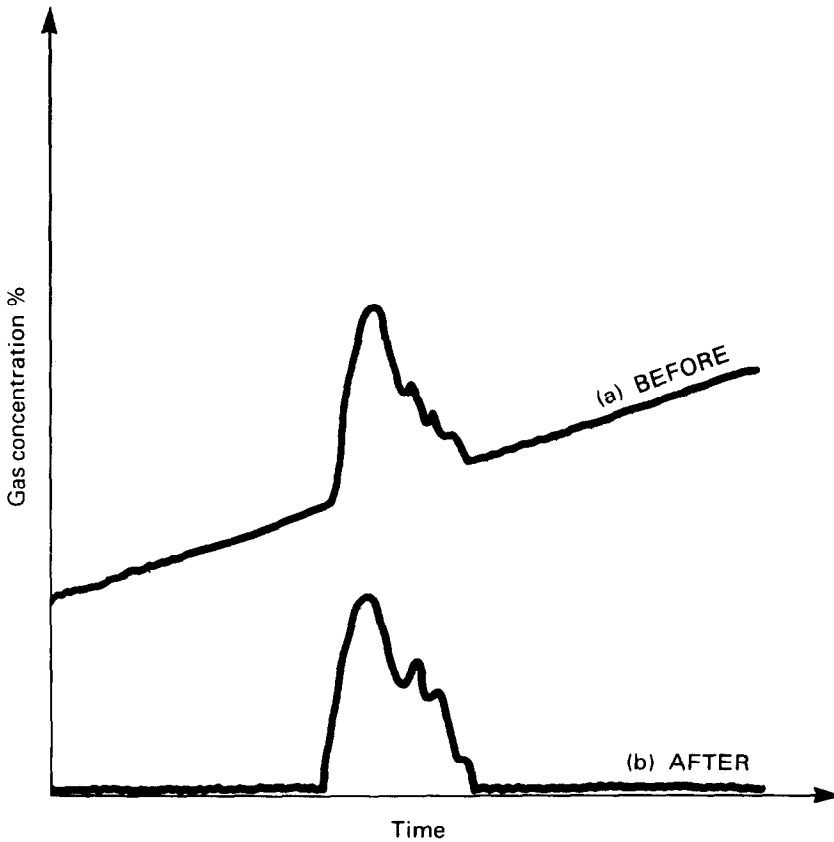


Fig. 16. Illustration of the baseline conversion of a typical gas sensor output: (a) before validation, (b) after validation.

graphics software. The computer would first attempt to do the correction automatically by an iterative least squares method with the largest residuals being removed at each stage in the iteration. In most cases the automatic method worked adequately but occasionally it was necessary to apply a correction by eye using the graphics package.

At the end of the validation process, tapes containing information on those sensors which detected gas during a particular trial and the zero and drift correction which had to be applied to these sensors were sent to NMI Ltd. The final validated engineering tapes were then produced by NMI using this information.

10. Conclusions

The oxygen electrochemical cell instrument has shown itself to be an excellent choice for the Heavy Gas Dispersion Trials at Thorney Island. The instruments have operated with a minimum of maintenance and have provided a vast amount of data.

The theoretical and experimental evaluation of the frequency response of both the standard and fast-response sensors has shown that with the help of signal enhancement techniques the required frequency specification has been met. The sensors have an excellent linear response over the 0% to 21% oxygen range, and the experimental air/nitrogen results show that the instruments were within the specified accuracy of $\pm 5\%$ of reading before delivery to the trials. It is recommended that an error range of $\pm 0.1\%$ gas is used for all gas sensors results where the peak gas concentration measured was less than 2%. For higher concentrations or where the percentage of Freon is greater than 1% an error band of $+1\%$, -9% is recommended to take account of Freon induced non-linearity (See Section 7.2). Although there were problems concerning linearity in the early stages of the trials, the modification described in the report overcame these problems and the spot check system confirmed that the sensors maintained their original linearity. Variations in temperature and humidity result in long term drift of the instrument output in air. This problem has been overcome by using the ambient air voltage level immediately prior to each release for instrument calibration. The temperature and humidity changes over the period of the trials were not sufficient to cause errors outside the ranges given above.

The wide dynamic measuring range of the oxygen electrochemical cell coupled with a minimum electronic requirement has produced an instrument of exceptional flexibility. It is small, weather proof, capable of producing accurate results over wide temperature and humidity ranges, requires minimum maintenance and the unit cost is low.

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