A METHYL BROMIDE MONITOR

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Abstract - A sensitive and accurate instrument is described for monitoring concentrations of methyl bromide in the range 1 - 20 ppm at numerous points in large work-areas. Its operation is entirely automatic, micro-computer management being used to continuously standardise and calibrate the instrument, monitor its performance, gather, process and record concentration data, and actuate alarms.

INTRODUCTION

Where toxic substances are used in industry there is a need to continually monitor their levels in the working environment. Methyl bromide (MeBr) is widely used as an insecticide in the grain storage industry, and current standards call for human exposure levels not to exceed 15 ppm, and average levels to be less than 5 ppm during each working day (American Conference of Governmental Industrial Hygienists, 1981). To be effective, such standards must be supported by suitable monitoring equipment, which, must itself meet rigorous standards.

To be suitable for monitoring MeBr in large workspaces, such as those associated with grain stores, instruments must operate continuously and be reliable, accurate, flame and tamper-proof, insensitive to likely contaminants and capable of monitoring at a number of representative points (or being cheaply replicated). Laboratory techniques (e.g. spectroscopic, photometric, chromatographic, infrared absorption) are generally too costly or their operation too complex for such industrial use. Some (e.g. thermal conductivity or interferometric) are not sufficiently sensitive or specific (Wohlgemuth, 1971). Chemical sensing using glass encapsulated or cassette packaged reagents, though ideal for spot checking, is unsuitable for continuous monitoring. Several instruments for detecting or measuring MeBr have been described in the literature (Call, 1952; Olah *et al.*, 1966; Avera, 1966; Nelson and Shapiro, 1971) but none adequately meets the above requirements.

A promising technique, combining economy and simple continuous operation with suitable sensitivity and robustness, uses platinum filament detectors, commonly used for detecting halogenated hydrocarbon refrigerants. The instrument described uses this sensing technique, coupled with frequent standardisation, to achieve high accuracy and reliability. It includes a sampling system whereby the concentration of methyl bromide may be determined at numerous points remote from the instrument. It meets the requirements listed above, with the exception that it responds to other halogenated hydrocarbons, including chloropicrin and dichlorvos.

THE MONITORING SYSTEM

The monitor uses a proprietry G.E.C. device (Catalogue number 1250K46700) consisting of an electrically heated platinum filament helically wound to form a cylinder approximately 2 mm in diameter and 4 mm long, surrounding an axial cathode maintained several hundred volts negative with respect to the filament (Anon., undated) Gas is passed axially through the sensor at a rate of 7.5-8.5 mL s^{-1} (a linear velocity of about 0.5 m s^{-1}) which conducts a small (microamp) current in the presence of gaseous halogens or halogenated hydrocarbons, including MeBr. Sensor current is proportional to halogen concentration, but the proportionality constant varies widely and is strongly influenced by previous exposure to halogenated compounds and to gas flow rate and filament power (Figs 1, 2, 3). Sensitivity is inversely related to cumulative exposure to halogens; new sensors display high sensitivity which deteriorates

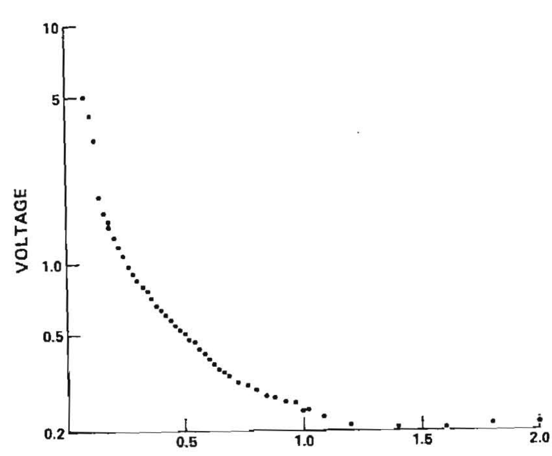

Fig. 1. Response of new sensor, to continuous exposure to 24 ppm MeBr v. time. (From Banks (1975) with permission)

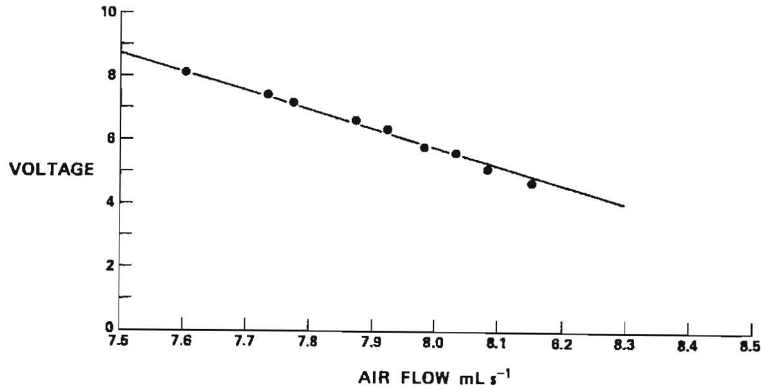

Fig. 2. Sensor response to constant 0.3 mL s^{-1} of 780 ppm MeBr diluted with varying air flow.

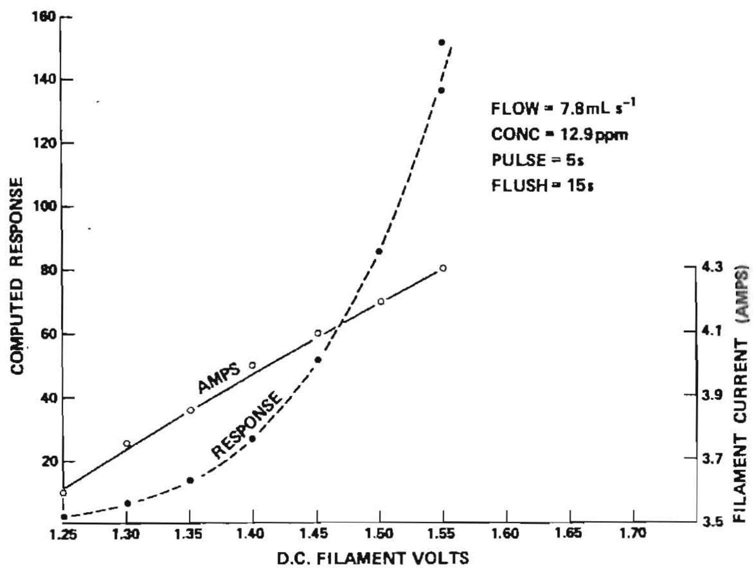

Fig. 3. Response and filament current v. filament voltage.

very rapidly with early exposure to MeBr (Fig. 1). After an initial stabilising period, short term sensitivity variation may be ignored if gas flow rate and filament power are held constant.

The detector is exposed cyclically to zero, sample and reference concentrations of MeBr. The measurement cycle consists of a period of 15 s during which the sensor and its plumbing are flushed with clean air, and a measure made of the sensor's response to this zero MeBr concentration, then a 5 s period in which it is exposed to the gas whose concentration is to be determined and a measure taken. This gas is drawn alternately through one of a number of sampling lines (12 in the prototype) leading to representative points in the work area or from a known reference concentration of MeBr used to calibrate the sensor.

Two diaphram pumps are used, one drawing samples through selected inlet lines, the other providing clean air for flushing the sensor and for use as a zero concentration MeBr standard. A reference concentration of MeBr is obtained by adding a small constant flow of a known high (around 1000 ppm) concentration to the air supplied by the latter pump.

Solenoid operated valves are used to switch gas streams. A bank of twelve selects the required one of twelve sample lines, and a bank of three selects sample, zero or reference gas. The configuration of valves and pumps is shown in Fig. 4.

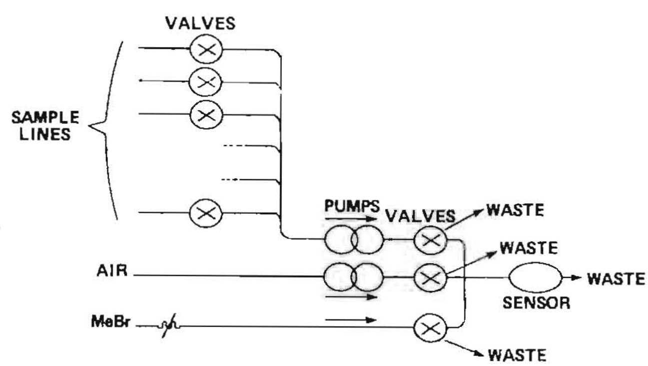

Fig. 4. Configuration of valves and pumps.

To correct for drift, the most recent 'zero' value is subtracted from each sample reading and from the most recent calibration value. The sample concentration is then calculated using the equation:

$$(\text{Sample concentration}) = \frac{(\text{Sample - zero})}{(\text{Reference - zero})} \times (\text{Reference concentration})$$

The system is managed by a Rockwell AIM 65 microcomputer which provides flexible control and calculating capability. It produces printed records, keeps time, generates alarms and monitors system performance. Upgraded from its minimum configuration by the addition of 1 K of random access memory (RAM) and the manufacturer's Maths Package chip, it costs around \$400 - \$500. The operating routines occupy part of an additional read only memory (EPROM) chip.

The AIM 65 controls a data acquisition chip (National ADC0816) comprising an 8 bit analogue to digital converter (ADC) and a separable 16 channel multiplexer. The ADC is connected without the multiplexer to the gas sensor, and the multiplexer used to operate the solenoid controlled gas valves through suitable drivers (Fig. 5). All switching is achieved using optically coupled solid state devices, so as to avoid the danger of mechanical switches arcing in potentially explosive environments.

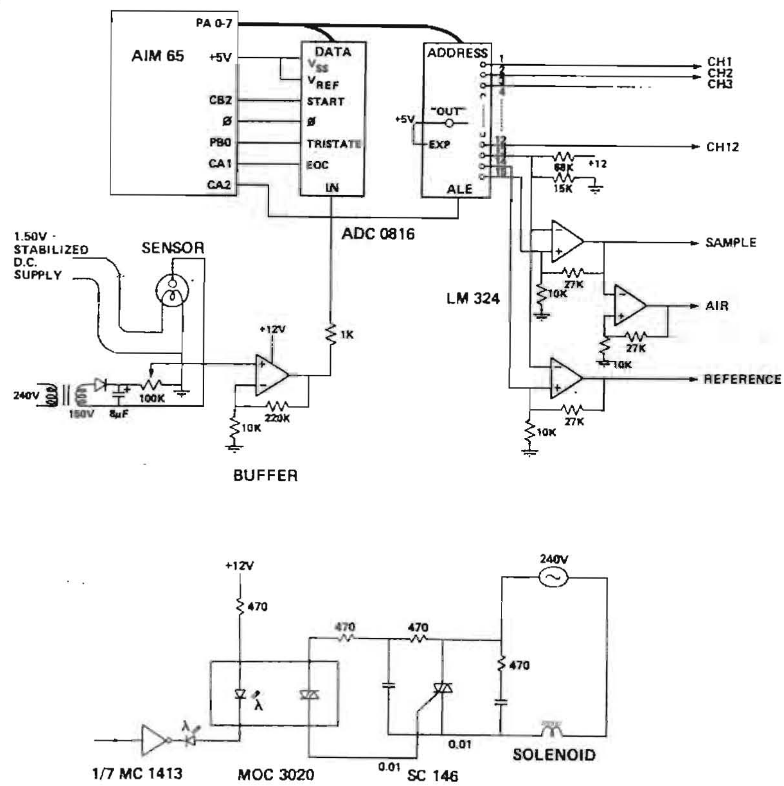

Fig. 5. (a) Measurement and valve control circuitry.
(b) Opto-isolated solenoid driver circuitry.

Various arithmetic and system checks are made:

1) To guard against the possibility that values lie outside the range of the ADC, the minimum and maximum ADC readings are considered invalid.
2) Since the sensitivity of the sensor varies widely, its response to the known reference concentration is checked to ensure that it is within acceptable limits. Out of bounds readings may also point to lack of reference gas or, because the reference

is obtained by dilution, improper adjustment of the dilution ratio.

3) Since the readings are obtained by subtraction of one ADC reading from another, and signals may be noisy, negative results are not uncommon when very low or zero concentrations are sampled. Slightly negative values of the unknown concentration are considered to be zero and printed as "-Ø". Significantly negative values are indicative of system malfunction, usually associated with variation in pumping speed.

4) Provision is made for two alarms, actuated when measured concentrations exceed predetermined thresholds.

Measured values of unknown concentrations are printed, together with time, day and channel number. Should system malfunction prevent the determination of a concentration, the nature of the malfunction is printed, details are retained in memory, and a system alarm actuated.

OPERATION

Only two mechanical operations are required to maintain the monitor, replacement of the sensor (perhaps weekly) and approximate adjustment of sensitivity (daily). Both are simple, the latter being guided by the AIM 65.

The prototype provides for sampling at up to twelve remote points, the present software allowing any of the twelve channels to be independently included or excluded from the monitoring programme. With additional valves, valve decoding and drivers, and after minor software changes, additional points may be monitored. The monitor takes 40 s to take each reading, so that monitoring large numbers of points may slow the reading rate of each unacceptably. Where greater channel capacity is required it may be preferable to use additional instruments rather than expanding a single unit. The Appendix lists the available machine commands, most of which are used to set operating parameters. If the initialising routines are amended to provide the parameters appropriate to each machine or fixed installation, the only input required from the operator will be the occasional setting of the clock.

The following are examples of a typical data printout (day number, time, channel number, measured concentration and alarm status), the range of system malfunction messages, and a listing of typical operating parameters:

128	12:14	3	8.7 *		
128	12:14	5	5.6 *	ADC TOO SLOW	REFERENCE CONC 10.0
128	12:15	6	-0	NEGATIVE REFERENCE	LO LEVEL ALARM 5.0
128	12:16	8	3.2	NEGATIVE SAMPLE	HI LEVEL ALARM 10.0
128	12:17	1	3.7	LOW SENSITIVITY	MIN SENSITIVITY 0.3
128	12:18	2	17.3**	HIGH SENSITIVITY	MAX SENSITIVITY 8.0
128	12:18	3	8.8 *		

PERFORMANCE

Fig. 6 is a plot of concentration measured by the system against concentration obtained by adding various small flows of 780 ppm MeBr to a constant flow of 7.8 mL s^{-1} of air. The flow rates of the two components were measured using variable area (gapmeter) flow meters. A MeBr concentration of 19 ppm was used as the reference.

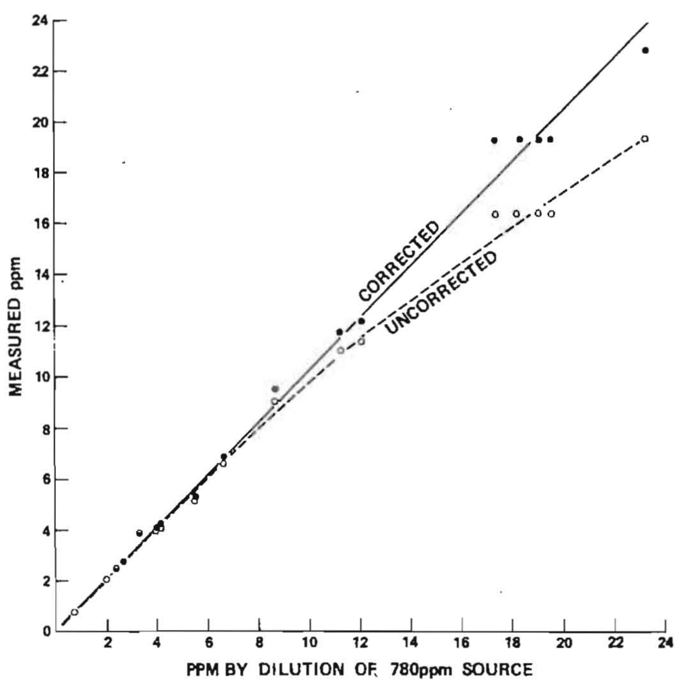

Fig. 6. Measured v. actual MeBr concentration.

The uncorrected curve in Fig. 6 illustrates the effect of the small change (less than 3%) in flow rate due to the varying dilution ratio. At these flow rates the detector response is reduced by about 6% for each 1% increase in flow (Fig. 2). The second curve in Fig. 6 is corrected for this flow variation and demonstrates well the sensitivity and accuracy of the instrument, even at concentrations below 1 ppm.

The ADC is capable of distinguishing between about 250 different levels, which for samples of up to 20 ppm limits accuracy when using a reference of around 10 ppm, to about $\pm$ 0.2 ppm. When the sensor has deteriorated to its worst acceptable level, accuracy is reduced to about $\pm$ 0.5 ppm. Although the sensor itself, given stable operating conditions, is capable of much better precision, its responsiveness to variations in flow rate and filament power renders this precision unattainable in a simple system such as that described here.

The life span of the sensor is dependent on cumulative exposure to halogenated compounds, and in low level monitoring applications is expected to be at least a working week. Various means described below may be employed to extend this life.

FURTHER DEVELOPMENT

A ratiometric measurement process, in which an unknown is compared with a reference using a linear instrument, is very robust. It does however rely on the linearity and short term stability of the sensing element. The sensor employed in the present instrument displays exceptional linearity, and sensitivity, but its stability is very poor, as indicated by Figs 1, 2 and 3. Cumulative exposure to halogens, increased flow rates and reduced filament power all reduce sensitivity.

It is likely that sensor temperature is a primary determinant of short term sensitivity to MeBr, and that flow rate and filament power affect sensitivity by varying sensor temperature. Since filament power may be readily controlled stability may be improved by maintaining constant temperature. Variation in filament temperature might be reduced by monitoring it using an infrared sensitive diode or other device positioned with a view of the filament, or using the very slight change in filament resistance with temperature, and varying filament current accordingly. (Although the effect of varying flow rate will be considerably reduced, the rate of delivery of halogenated molecules to the sensor will continue to be flow dependent.) Control of filament temperature may also permit the excessive sensitivity of new devices to be reduced to acceptable levels. The different cooling effects of alternative atmospheres, particularly those rich in carbon dioxide, will also call for control of filament temperature in some applications.

The quantities of reference gas (around 10 ppm) required dictate that it be obtained by dilution. The use of a dilute source (about 800 ppm in the prototype), further diluted in the instrument is unsatisfactory however, since both dilution ratios are subject to uncertainty. Adding the already dilute source to the zero concentration air stream also changes flow rate significantly, detracting from the instrument's standardisation. The use of a far smaller flow of 100% MeBr, precisely determined by a permeation device or calibrated leak, diluted with the existing air stream would enhance accuracy and reliability.

The sensor life is determined largely by cumulative exposure to halogens, the reference gas often constituting the major source. In such cases less frequent standardising will directly increase operating life. The sensor may need calibrating only rarely, other than when a significant level of MeBr is detected. Depending on the levels of MeBr in the samples gases, better calibrating strategies may increase operating life considerably.

In view of the excellent performance of the sensor under ideal conditions there may be advantage in diluting the sample gas stream and using a reference of far lower concentration. Sensor life span will be increased thereby, and stability enhanced.

CONCLUSION

The system described measures MeBr concentrations in the range from zero to greater than 20 ppm with an accuracy better than $\pm$ 0.5 ppm, and the measures are directly traceable to standards. It also monitors its own performance.

The system is suitable for monitoring concentrations at numerous points in large work areas, and actuating alarms when predetermined levels are exceeded. It produces permanent printed records of all measured concentrations, system malfunctions and alarm states, and is easily operated and controlled by unskilled users.

ACKNOWLEDGEMENTS

The sensor was initially appraised by H.J. Banks who also proposed the zeroing and referencing procedure, the subject of Australian Patent Application No 78722/75.

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APPENDIX I - OPERATING PROCEDURES

The software routines were written to operate on a standard AIM 65 microcomputer with 4k of RAM and the Rockwell AIM 65 Maths Package chip. The following operations are provided. More details, including program listings, are available from the author.

(1) Initialise
- Clock is reset to time zero, day zero
- Monitor reverts to sampling all twelve channels
- Operating parameters are set to: -
  - (a) Nominal reference concentration : 10 ppm
  - (b) Low level alarm : 5 ppm
  - (c) High level alarm : 15 ppm
  - (d) Minimum detector sensitivity : 0.3 times nominal
  - (e) Maximum detector sensitivity : 8 times nominal.

(2) Display and print current operating parameters

(3) Change nominal reference concentration

(4) Change low level alarm

(5) Change high level alarm

(6) Change minimum detector sensitivity

(7) Change maximum detector sensitivity

(8) Continue (Return to normal operation after any disruption. The system must have been initialised previously.)

(9) Set clock.

(10) Individual channels are enabled or disabled by storing ØØ or Ø1 respectively at address locations OFA1 to OFAC, corresponding with channel 1 to channel 12.