

Low-cost detector for the continuous monitoring of phosphine fumigation

R. Ryan*, S. Waddell*, P.W. Alexander†, K. Bowles†, L. Cherkson†, J. Morgan† and D. B. Hibbert†

Abstract

The general model $Ct = k$ describes the toxicity of phosphine when used as a fumigant in grain storage, where C is the concentration of phosphine, t is the exposure time, and k is a constant. This factor can be calculated only if data are available on the fate of phosphine gas after initial injection into grain storage silos. A simple handheld phosphine monitor capable of continuous monitoring of phosphine levels is proposed. It could be installed in silos and used to monitor the phosphine levels over long periods with data-logging capability and connection to telemetry systems for remote viewing of real-time data. The monitor consists of a solid-state semiconductor sensor which has been shown to give a linear response to phosphine gas in the concentration range 0.1–300 ppm using standard gas dilution procedures to calibrate the sensor. The response of the sensor is rapid (2 second response to steady-state readings) and with little drift below 300 ppm phosphine. Exposures over 20 minutes showed little drift in the above range, but drifts occurred at 1000 ppm. An alarm can be fitted to indicate when limits reach predetermined concentrations, and feedback control of phosphine injection could be introduced. The monitor developed in this work is capable of continuous operation over long periods and can be controlled from an external computer with very rapid response times. It is of low cost and could be fitted into storage facilities to improve fumigation efficacy, cost efficiency and safe use of phosphine gas. Carbon monoxide produced during storage interferes only at concentrations above 200 ppm.

Introduction

Phosphine is an important gas for use in commercial agriculture. The major commercial use of phosphine is as a fumigant in grain storage. Traditionally, the phosphine was produced by simply throwing tablets of metallic phosphide into the grain. The tablets react with atmospheric moisture to form phosphine gas. There is now an interest to introduce phosphine gas directly from gas cylinders (2% phosphine in carbon dioxide) and there is a need to be able to monitor the level of phosphine in the storage areas to ensure the concentration is kept at an effective level. An appropriate sensor should be able to detect phosphine in the 100–200 ppm range for this application. Phosphine, however, is a highly toxic gas with a TLV (thresh-

old limiting value) of 0.3 ppm. Therefore, there is an obvious need for a low-cost, reliable sensor to detect this gas at low concentrations for safety reasons.

Several gas sensors are currently available to detect phosphine. These include common badge types for personal exposure monitoring as well as photoionisation and infrared detectors. In addition, sensors sensitive to reducing gases, such as electrochemical types, Taguchi sensors (Figaro Engineering Inc. 1990; Alexander et al. 1993) and Langmuir-Blodgett film sensors may be applicable. Much work has been reported on gas sensors, particularly for the determination of O_2 , CO_2 , SO_2 , H_2S , NH_3 , CO , NO_2 , HCl , H_2 and Cl_2 (Shurmer et al. 1987; Watson 1984; Mosely et al. 1991). The Taguchi types of tin-oxide semiconductor sensors are obvious candidates for phosphine sensors due to their high resistance to poisoning and low cost. The present paper describes a study of Taguchi sensors for continuous monitoring of phosphine and other potentially interfering gases such as hydrocarbons, CO , and CO_2 .

Instrumentation

Preliminary studies were conducted with a Taguchi TGS825 sensor purchased from Figaro Engineering Inc. (Osaka, Japan). Single and multi-sensor studies were also conducted using a dual sensor gas analyser designed and manufactured at the Department of Chemistry, University of New South Wales, Australia (UNSW), and presently under a provisional patent by Unisearch Limited (Alexander et al. 1993). This analyser incorporated TGS813 and TGS822 sensors, purchased from Figaro Engineering Inc., attached to a printed circuit board via 6-pin connectors, and incorporating a small piston pump for aspiration of gas samples through the sensor cells. A glass T-piece was used to split the gas flow equally between two compartments containing the two sensors. The gas analyser was connected to a notebook computer via a 12-bit analog-to-digital converter for data logging on the computer. The system displays sensor voltages on an LCD with a switch to show the response of either sensor. Calibrations and calculations of gas concentrations detected by the sensors were performed on the notebook computer. The computer can also be used to control the monitor from a remote location.

Gas dilution apparatus

Gas dilutions for ethylene and phosphine calibrations were conducted using an Ecotech Model 8370 Gas Diluter on loan from The Commonwealth Industrial Gases (CIG). This is a portable system which allows mixing of two gases into precisely controlled gas flows to generate required concentration values. The system works by using a laminar flow device to force part of the gas stream through a section of heated capillary tube. The change of temperature (ΔT) between the ends of the capillary is a measure of heat absorbed by the gas. The amount of heat absorbed depends on the mass of the gas. Since mass is independent of temperature and pressure, the instrument is unaffected by temperature and pressure variations.

* The Commonwealth Industrial Gases Ltd, Chatswood, NSW 2067, Australia.

† Department of Analytical Chemistry, University of NSW, Kensington, NSW 2033, Australia.

Dilution gas (air) readings were given in L/minute and span gas (ethylene or phosphine) readings were given in mL/minute. The relationship for converting flow rates to concentrations is:

$$\text{Output concentration (ppm)} = \frac{\text{Input conc. (ppm)} * \text{span gas flow (mL / min.)}}{\text{Diluent gas flow (mL / min.)} + \text{span gas flow (mL / min.)}}$$

Ecotech quote the repeatability at 0.2% of full-scale readings for gas flows and $\pm 1\%$ full scale for electrical accuracy and linearity.

Data acquisition and processing

The gas monitor unit developed at UNSW (Alexander et al. 1993) incorporates an LED readout and may be used as a stand-alone device or may be interfaced to a computer via an analog-to-digital converter (ADC). An RS232C serial output is incorporated for direct connection to computer and telemetry systems. The system has been programmed with the 'Think C' Compiler for Apple Macintosh® computers. In the multi-sensor studies the raw data may be displayed in real time in one window. Another split screen is used to display the calculated values for the two different gases, also in real time. The data can be stored as an ASCII text file and transferred subsequently to a scientific spreadsheet for data processing.

The data were processed using the IGOR® program. IGOR® stores the data as waves which may be displayed as graphs. Mathematical functions such as smoothing and integration are available, as well as provisions for labelling and annotating axes.

Reagents

The preliminary studies involved calibration and precision experiments with standards of ethyl acetate in water. The ethyl acetate was analytical grade and was purchased from Pronalys®. Single and multi-sensor studies involved calibration with phosphine and ethylene. Ethylene was obtained in a cylinder from CIG. Standards of 2 ppm and 1053 ppm ethylene in nitrogen gas were used. Phosphine was also obtained in cylinders from CIG. Standards of 300, 1000 and 2000 ppm were used.

Procedures for sensor calibrations

Ethyl acetate

The TGS825 sensor was calibrated with ethyl acetate in water at the following concentrations: 10, 50, 100, 200, 400, 600, 800 and 1000 ppm. The standards were made up in 100 mL volumetric flasks. The flasks were stoppered to allow ethyl acetate to accumulate in the headspace. The TGS825 sensor was allowed to warm up for 15 minutes before measurements, to ensure a stable baseline. Measurements were made by holding the inlet tube of the sensor apparatus at the top of the flask immediately after removing the lid. An Apple II computer programmed with a software package entitled MV/FILE was used to collect the data. As soon as the trace of the response on the computer screen peaked and started to drop, the sensor inlet tube was removed from the flask. The flask was then resealed, shaken, and allowed to stand to allow the headspace gases to re-equilibrate. The trace on the screen was allowed to return to the baseline before a repeat measurement was made. Multiple measurements of each standard were made. The standards were measured from low to high concentration to avoid the possibility of memory effects.

Precision was tested with the TGS825 by taking replicate measurements of the 800 ppm standard using the same sampling procedure stated above. The effects of response time,

sampling time and positioning of the sensor inlet tube were tested by following the same procedure as above.

Calibration of the sensor response to phosphine and ethylene

TGS813 and TGS822 sensors were calibrated for various concentrations of phosphine. The phosphine from the standard gas cylinder of appropriate concentration was diluted with compressed air using the Ecotech Model 8370 Gas Diluter. The sensors were contained in the dual sensor gas analyser and could be calibrated simultaneously. The analyser and the dilution apparatus were turned on 15 minutes before measurements were to be taken, to ensure a stable baseline. Data points were acquired using a Macintosh® Powerbook computer. The compressed air was turned on and adjusted to the desired flow rate. The phosphine supply was then turned on at a very low flow rate. After the trace on the computer screen flattened out, the flow rate of the phosphine was increased in order to increase the concentration of the ethylene. This resulted in a series of stepwise increases in the voltage output. After the measurement with the maximum flow rate of phosphine, the flow supply was disconnected to allow the trace to return to the baseline. This procedure was repeated using a lower compressed air flow rate, allowing a series of measurements at higher phosphine concentrations. The above procedure was repeated for ethylene using the standardised gas cylinder containing 1053 ppm ethylene in nitrogen gas.

Results on the response of Taguchi sensors to phosphine

Figure 1(a) and 1(b) show the response for increasing concentrations of phosphine against a background of compressed air. Both sensors showed a significant response to the phosphine gas but higher response was achieved with the TGS822 sensor. Figure 1(c) shows that at higher concentrations of phosphine both sensors are subject to poisoning and do not give a steady-state response. At moderately high phosphine concentrations, it was found preferable to use the TGS813 rather than the TGS822 since it gave a lower response and was less prone to poisoning, as shown in Figure 1(c).

Figure 2(a) shows the response of both sensors to a stream of CO₂ gas. This is important since phosphine gas is commonly diluted in cylinders with CO₂ gas. The TGS822 shows very low response to the CO₂ which makes it useful as a phosphine sensor. The response of the TGS813 is possibly due to CO₂ displacing O₂ at the surface of the sensor and thus changing the conductivity.

Calibration plots were prepared from the data in the 0–125 ppm (Fig. 2(b) and 2(c)) and 0–600 ppm ranges (Fig. 3(a) and 3(b)). At low concentrations (0–125 ppm), a linear response was obtained for the TGS822 with a correlation coefficient of 99.9%. The TGS813 gave a linear plot with correlation of 99.1%. The log–log plot of the TGS813 results gave marginally improved linearity with a correlation of 99.2%. The log–log plot for the TGS822 resulted in decreased linearity due to the effect of logarithms near zero. Over a wider concentration range, both sensors gave curved calibration plots. Curves of best fit were obtained with the following general equation:

$$\text{Sensor voltage} = K_0 + K_1 \cdot \exp[-(\text{conc.} - K_2)/K_3]^2$$

where K₀, K₁, K₂ and K₃ are constants. Log-log plots in this case resulted in improved linearity. These results were successfully fitted to the same form as above.

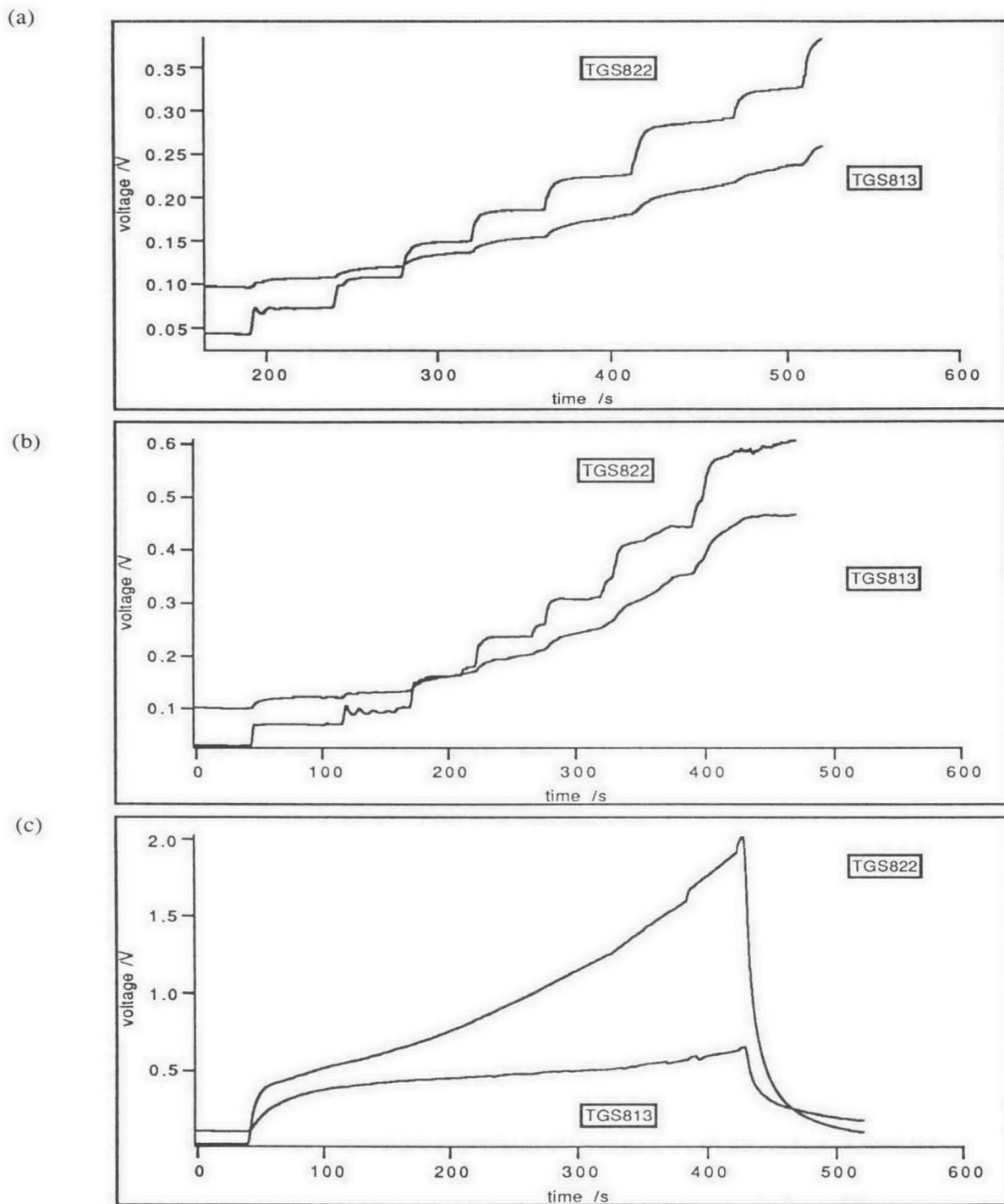


Fig. 1. (a) is the response of the TGS813 and TGS822 sensors to phosphine gas at various concentrations between 0–125 ppm. (b) is the response of the TGS813 and TGS822 sensors to phosphine gas at various concentrations between 0–600 ppm. The stepwise response is due to increases in the phosphine flow against a constant flow of diluent gas (compressed air). (c) is the response of the two sensors to phosphine at a higher concentration (1000 ppm).

Detection limits and sensitivity of each sensor

The sensitivity of the two sensors used indicated different response characteristics to phosphine, carbon monoxide and ethylene. The TGS813 responded well to ethylene but was less sensitive to phosphine. The TGS822 had a more sensitive response to phosphine but showed a definite effects of poisoning at higher phosphine concentrations. Conversely, the TGS822 was very insensitive to ethylene. Carbon monoxide

showed very little response at either sensor when the concentration was below 200 ppm. Detection limits were calculated on the basis of the noise level observed for the background readings for each sensor. For the TGS813 sensor, the baseline noise level was 1 mV which was calculated to correspond to detection limits of 0.125 ppm for ethylene and 10.1 ppm for phosphine. For the TGS822 sensor, the response was insensitive to ethylene concentrations below 500 ppm, but gave a detection limit of 0.1 ppm for phosphine. It appears therefore

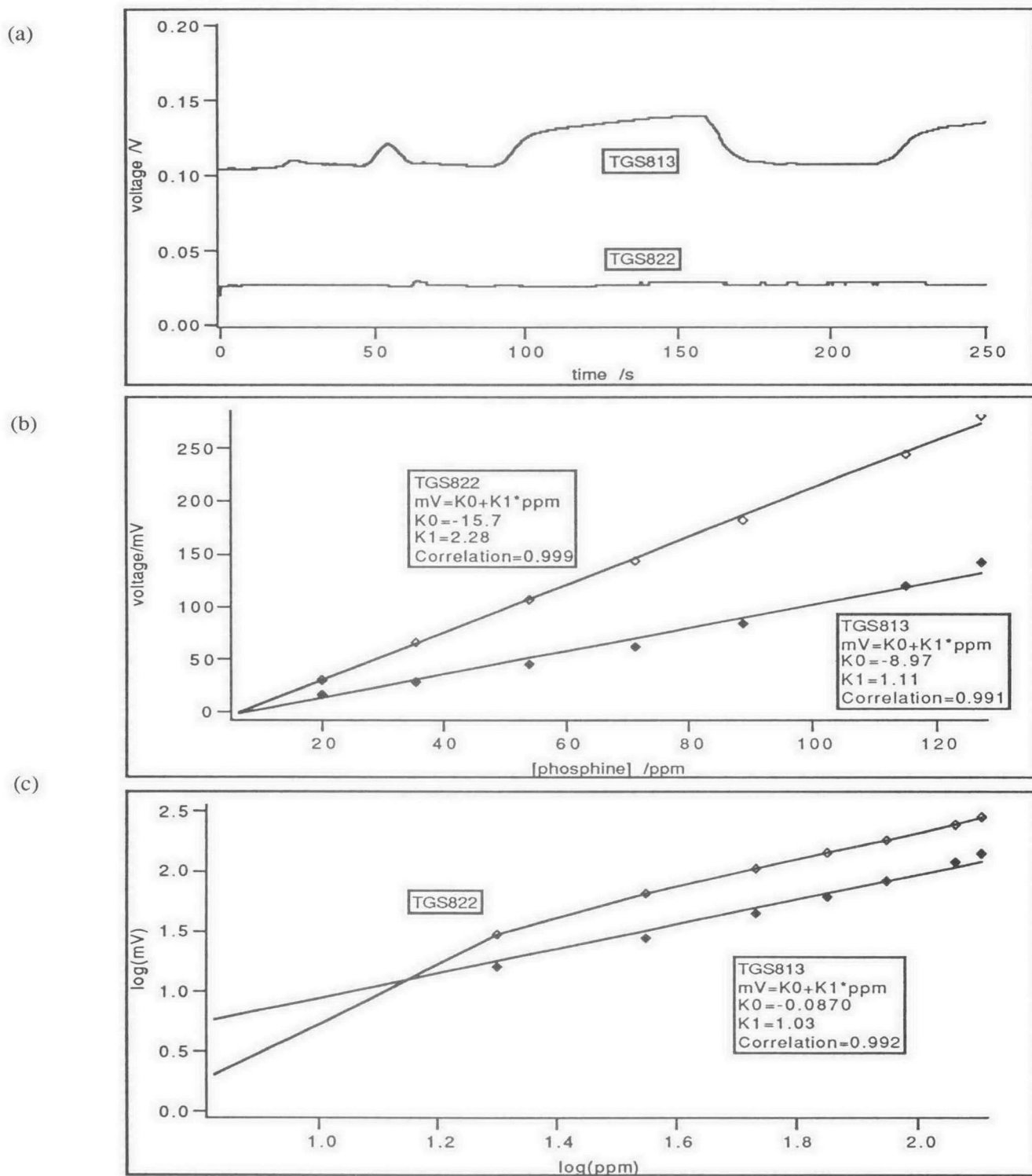


Fig. 2. (a) is the response of both sensors to a stream of pure CO₂. (b) is a plot of the results for the TGS813 and TGS822 sensors to phosphine at concentrations between 0–125 ppm. The line of best fit was calculated with constants as annotated. (c) is a log–log plot of the same data.

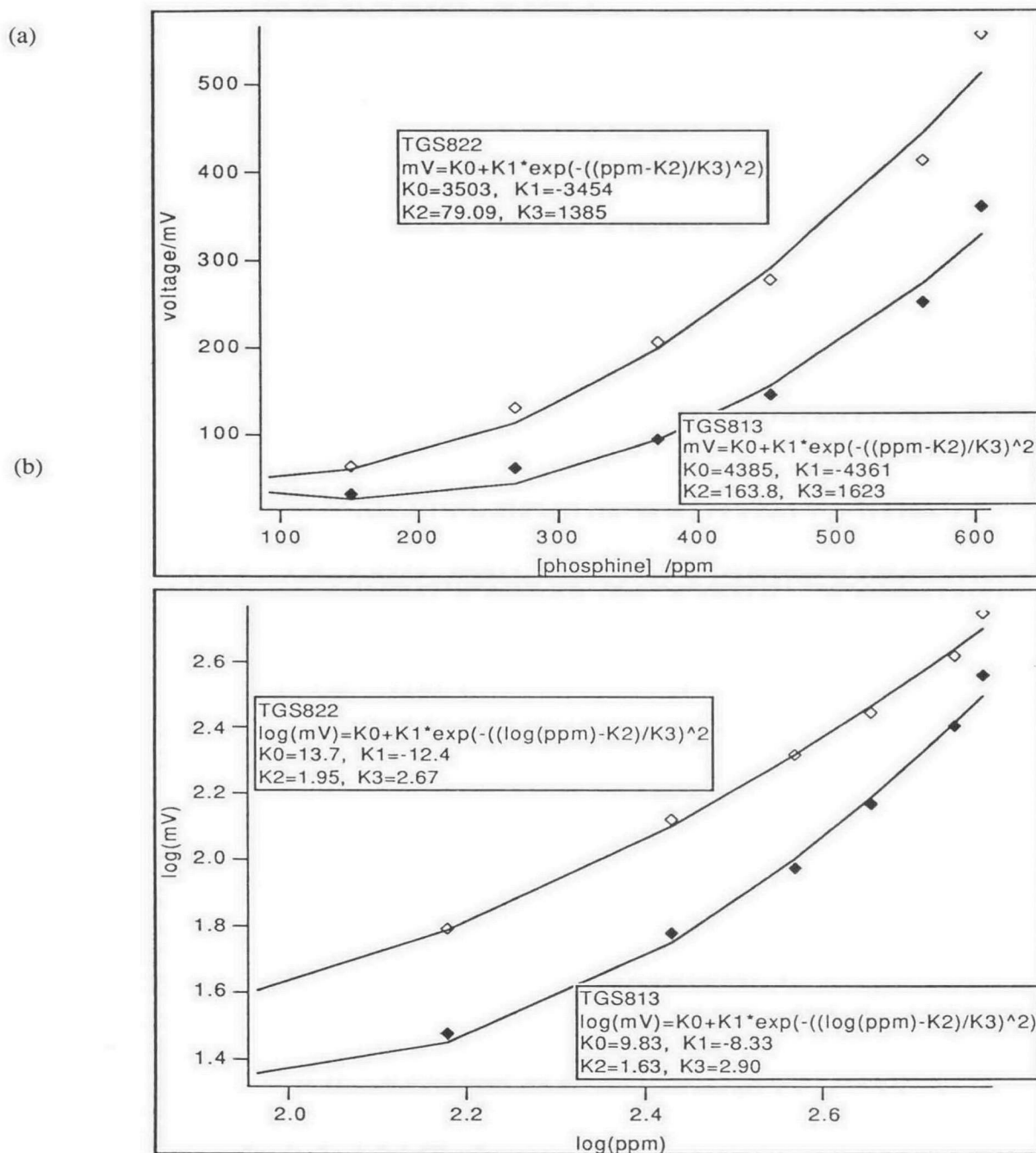


Fig. 3. (a) shows the calibration plots of the response of the TGS813 and TGS822 sensors to phosphine at concentrations between 0–600 ppm. The line of best fit was calculated with constants as annotated. (b) is a log–log plot of the same data.

that both sensors will be of use for measuring phosphine concentrations in grain storage, depending on the concentration of phosphine applied in the grain storage situation.

Conclusions

The monitor developed in this study has advantages over existing phosphine monitors for several reasons. It provides linear response in the range up to 300 ppm phosphine, it has a low detection limit, and rapid response times without poisoning problems below 300 ppm, and it is useful for data logging with computer control from a remote site.

References

Alexander, P.W., Hibbert, D.B., Cherkson, L. and Morgan, J.T. 1993. Australian Provisional Patent: Multi-sensor gas analyser. Unisearch Ltd, February 1993.

Figaro Engineering Inc. 1990. Figaro Gas Sensors, Product Document. Osaka, August 1990.

Mosely, P.T., Norris, V.J. and Williams, D. 1991. Techniques and mechanisms in gas sensing. Adam Hilger Series on Sensors, IOP Publishing.

Shurmer, H., Fard, A. Barker, J., Bartlett, P. Dodd, G. and Hayat, U. 1987. Physics in Technology, 18, 170–176.

Watson, J. 1984. Sensors and Actuators, 5(1), 29–42.