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THE USE OF A SULPHUR DIOXIDE PROBE FOR MEASUREMENTS IN GASEOUS STREAMS

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Introduction

The analysis of mixtures of gases is in many instances a difficult problem especially when the information is required for on-line treatment. As a rule it is more satisfactory to analyse the products of a chemical process by a physical method and to allow for the electronic transmission of the results.

There are a number of chemical and physical procedures which may be used to determine the concentration of sulphur dioxide present either in gaseous streams or in solutions (1), (2).

In this work an investigation is reported on the use of an electrochemical method to determine the concentration of sulphur dioxide in gaseous mixtures containing oxygen, nitrogen and up to 10% sulphur dioxide by volume.

The Sulphur Dioxide Measurement Device

The sulphur dioxide probe consists principally of an electrode that measures the partial pressure of sulphur dioxide in solution. The concentration of sulphur dioxide is detected by measuring its effect on the pH of an acidified sulphite or bisulphite internal filling solution which is separated from the sample by a gas-permeable hydrofobic membrane. The other device employed in the system is an expanded scale pH meter.

When the probe is in contact with the sulphur dioxide solutions the gas diffuses through the gas-permeable membrane until the partial pressure in the internal filling solution equals that in the sample solution. Consequently the pH of the former varies with the concentration of sulphur dioxide in the sample and these changes are sensed by the glass electrode/ reference electrode system provided.

The response of the probe is reported to be linearly related to the logarithm of the sulphur dioxide concentration in the range 5×10^{-2} $\underline{M}$ to 5×10^{-5} $\underline{M}$ (2). It has also been found to be almost independent of gradual variations in the range 273-313 K (same author).

(a) Adaptation for on-stream gas analysis

The probe must be immersed in liquid to prevent the electrode end from drying out of filling solution. Consequently its direct use in the gas stream is not possible.
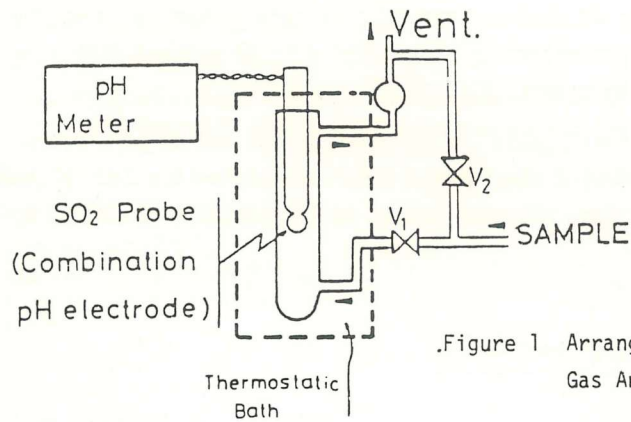

Figure 1 Arrangement for On-stream Gas Analysis

Figure 1 shows the arrangement used in this work. The gas to be analysed was passed into water contained in a narrow cylinder in which the probe was immersed. It was assumed that the concentration of sulphur dioxide would rapidly attain saturation level. This concentration is related to the partial pressure of the sulphur dioxide in the gas stream enabling a relationship to be obtained of this latter variable with the pH meter reading.

It is clear that the partial pressure of SO_2 in the gas in equilibrium with a given concentration in the solution will increase with the temperature (3). In other words the higher the temperature the wider the partial pressure range for a same range of SO_2 concentration in solution.

In this work the system was kept in a thermostatic bath at 309 K which is near the higher limit of the working temperature range recommended by the probe manufacturers (298 - 313 K).

(b) Study of the probe range and response

The limiting value of 5×10^{-2} $\underline{M}$ for linear response corresponds at 309 K to a partial pressure of SO_2 of around 25 mm Hg in the gas phase (i.e. a concentration of 3.2 mole percent SO_2 at atmospheric pressure). Tests were carried out to see if this range of SO_2 concentration could be widened. The technique used was that eventually developed to calibrate the instrument - a procedure which had to be repeated frequently.

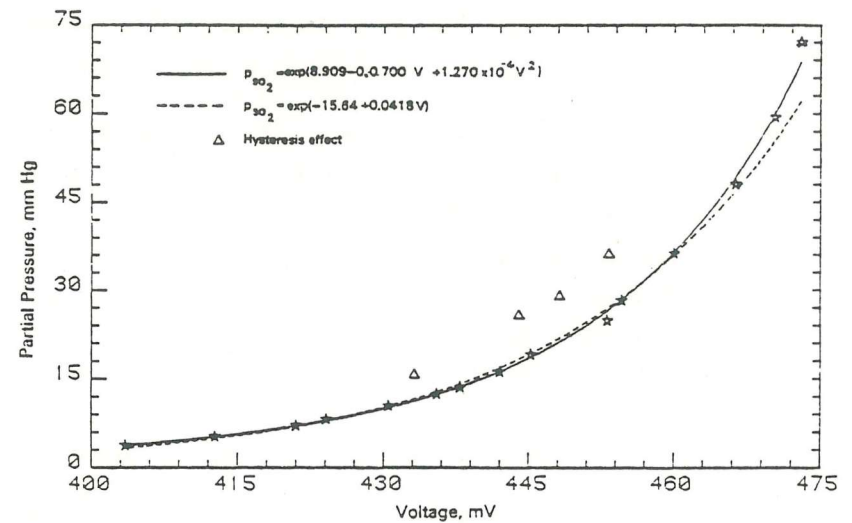The results of a typical test are presented in figure 2.

Figure 2 Response of Sulphur Dioxide Probe (showing also hysteresis effects)

The following conclusions can be reported:

(i) In the range of 3.8 to 25 mm Hg the following relationship holds -

$$p_{SO_2} = \exp(-14.18 + 0.03839\ V) \qquad (1)$$

where V is the pH meter reading in mV

and p_{SO_2} is the partial pressure of sulphur dioxide in mm Hg.
The relative error of the fitting is less than 1.5%.

(ii) In the range of 3.8 to 72 mm Hg (i.e. up to 9.5% of SO_2 by volume)

A relationship of the form of equation 1 does not give a reasonable fit (dotted line in figure 2).

Instead, the following exponential-quadratic relationship holds -

$$p_{SO_2} = \exp(8.909 - 0.07000\ V + 1.270 \times 10^{-4}\ V^2) \qquad (2)$$

with a maximum percentage error of 4.8%.

(iii) No hysteresis effects were detected when the use of the probe was limited to streams with SO_2 concentrations below 6.33% by volume (i.e. $p_{SO_2} < 48.1$ mm Hg).

(iv) Hysteresis effects were observed after the probe had been subjected to conditions where the partial pressures of SO_2 were greater than 48.1 mm Hg.

As a consequence its use is limited to streams with less than 6.33% of SO_2 by volume ($p_{SO_2} < 48.1$ mm Hg). At 309 K this corresponds approximately to concentrations of 0.07 $\underline{M}$ SO_2 .

(v) The dynamic response was generally poor. Step changes of around 3% in the molar concentration of SO_2 in the gaseous stream gave response times between 5 and 8 minutes - depending on the sign of the step. Equilibrium is reached more quickly after an increase in the concentration of the species.

(vi) The probe potential frequently drifted during the 7-10 hours working period. This drift was of the order of 3-5 mV in magnitude which was somewhat greater than the value of 1 mV in 12 hours admitted by the manufacturers. This may possibly be due to the fact that the conditions of the application in this work are different from the "closed flask" environment for which the probe has been designed. To alleviate this problem the filling solution was changed more frequently than advised by the manufacturers and the probe was recalibrated every three hours.

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