TECHNICAL DEVELOPMENT

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DESIGN AND CONSTRUCTION OF A PORTABLE SULPHUR DIOXIDE MONITOR

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Abstract

An investigation has been carried out on the colorimetric determination of sulphur dioxide, employing a starch-iodine-iodide solution. The accuracy and interferences in the determination are assessed. A portable sulphur dioxide monitoring instrument is developed and constructed. Sulphur dioxide measurements have been carried out during a period of two months at several locations in Bangkok.

It is found that atmospheric sulphur dioxide concentrations ranged from 0.01 to 0.1 ppm in factory areas and from 0.02 to 0.09 ppm in heavy traffic areas.

Introduction

Sulphur dioxide is regarded as one of the prime air pollutants produced from man-made sources. The gas, mostly produced in metal smelting and fossil fuel combustion, is odourless, nonflammable and invisible. It can exist in air either as a gas or dissolved in water droplets. It can be tasted by most people at concentrations of about 0.3 ppm or greater. Sulphur dioxide rapidly oxidises in air to form sulphur trioxide which readily combines with water vapour to form sulphuric acid.

Evidence has been found which suggests that sulphur dioxide may cause a depression of DNA synthesis and chromosome abnormalities in human lymphocytes[1], as well as inhibition of established cell lines[2]. It has also been observed[3] that sulphur dioxide causes an anaphase lag in mammalian chromosomes. Damaging effects on plants and non-living materials are evident. Metal smelting from sulphur-bearing ores has released sufficient sulphur dioxide to destroy vegetation in the vicinity of large smelters. Sulphur dioxide can also cause metal corrosion, weakening of textiles, deterioration of works of art, and fading of dyed materials.

Reports on atmospheric sulphur dioxide analysis in Thailand have been scarce although a range of analytical methods is available. This may be due to the unavailability of expensive automatic monitoring instruments and thus the awkward fact that collected samples have to be taken to the laboratory for analysis.

Available methods commonly employed for sulphur dioxide analysis are conductimetric[4,5], titrimetric[6], colorimetric[7-9], turbidimetric[10,11] and iodimetric[12-15] methods. These can be used as manual laboratory procedures or incorporated into automatic monitoring instruments. Comprehensive reviews and experimental details of the methods are provided by Katz[16], Lodge and Pate[17] and Hochheiser[18].

Several types of sulphur dioxide analysers employing similar principles are available commercially. One type[19,20] consists of a diaphragm pump, a vacuum gauge, and a rheostat to control the pump speed. The gas sample is filtered to remove dust, mixed with a stream of isopropanol and filtered again to separate off the isopropanol and sulphur trioxide. The remaining gas is then passed into an iodine solution for colorimetric determination of sulphur dioxide. The cost of this apparatus, without the colorimeter, is somewhere in the vicinity of 20,000 baht.

A simpler, and less expensive, portable gas analyser is also available in which a measured volume of gas is drawn through a tube of purified silica gel impregnated with a reagent that undergoes a colour change in the presence of sulphur dioxide. The length of the discoloured zone is proportional to the amount of sulphur dioxide sampled. This type of apparatus has a lower limit of approximately 1 ppm.

In the present study a simple colorimetric determination of sulphur dioxide, employing a starch-iodine solution, was investigated. An inexpensive portable instrument for measuring atmospheric sulphur dioxide was designed and constructed in the hope that the availability of such an instrument will encourage a wider participation in pollution control. The portable instrument was tested for its reliability and sulphur dioxide measurements were made at various locations in Bangkok.

Methods

The iodimetric method is based on the reducing properties of sulphur dioxide. In this method the air sample is allowed to bubble through a blue starch-iodine solution. Sulphur dioxide consumes iodine according to the reaction

$$SO_2 + I_3^- + H_2O \longrightarrow SO_3 + 3I^- + 2H^+ \qquad (1)$$

and reduces the intensity of the blue colour of the starch-iodine complex. The colour intensity is then measured spectrophotometrically. Unfortunately erroneous results are normally obtained since iodine in the solution is inevitably lost by evaporation into the passing air stream although this may be minimised by using very dilute solutions of iodine and controlling the added amounts of starch and potassium iodine[15,21]. The presence of atmospheric hydrogen sulphide gives rise to positive interference while nitrogen dioxide and ozone interfere negatively.

In the present investigation the method used in measuring sulphur dioxide concentrations with a portable apparatus was based on that of Katz[15] with modifications involving the use of two absorber solutions in connection with the blank determinations. The air sample was drawn through both solutions at the same rate. However, before bubbling through one of the solutions, sulphur dioxide was made to react with a strong oxidising agent, so that the air which has passed into that absorber solution contained no sulphur dioxide. Thus, the use of two gas bubblers simultaneously eliminated, or at least minimised, problems concerning the loss of iodine from the starch-iodine solution and negative interference by nitrogen dioxide and ozone which may be present in the atmosphere. The difference between the colour intensities of the two starch-iodine solutions, measured in terms of the electrical resistance of a photocell therefore represented the effect due to sulphur dioxide alone.

Some preliminary experiments were carried out to check the reliability of reaction (1) under actual experimental conditions. Passage of known volumes of sulphur dioxide, prepared by the reaction between citric acid and sodium sulphite[22], through the starch-iodine solution followed by titration with thiosulphate showed that reaction (1) occurred quantitatively. That the sulphur dioxide was completely absorbed by the iodine solution was evident by the fact that no sulphur dioxide was found in a trap, containing a starch-iodine solution, connected downstream to the gas bubbler.

Hydrogen sulphide which is a reducing gas will interfere when it is present in sufficiently large quantities, but the sulphide content of the atmosphere is usually very low compared to that of sulphur dioxide. This assumption is justified by the observation that 30-minute suction of air through lead (II) acetate-treated strips of filter paper failed to produce black lead (II) sulphide.

Instrumentation

The apparatus is as shown in Figure 1. Basically, an air sample is drawn through the two gas bubblers, A and B, each of 50-cm^3 capacity and containing a stabilised starch-iodine solution, using a small battery-operated pump. The air flowrate is regulated by means of the appropriate needle valves and is measured with the two flowmeters. After a predetermined sampling period, each of the solutions is discharged into the receiving test tube, C, and the colour intensity determined in terms of the photocell resistance, using a mini-flashlight as a constant light source. The photocell was supplied by Khuru Sapha, Ministry of Education, for highschool experiments. The

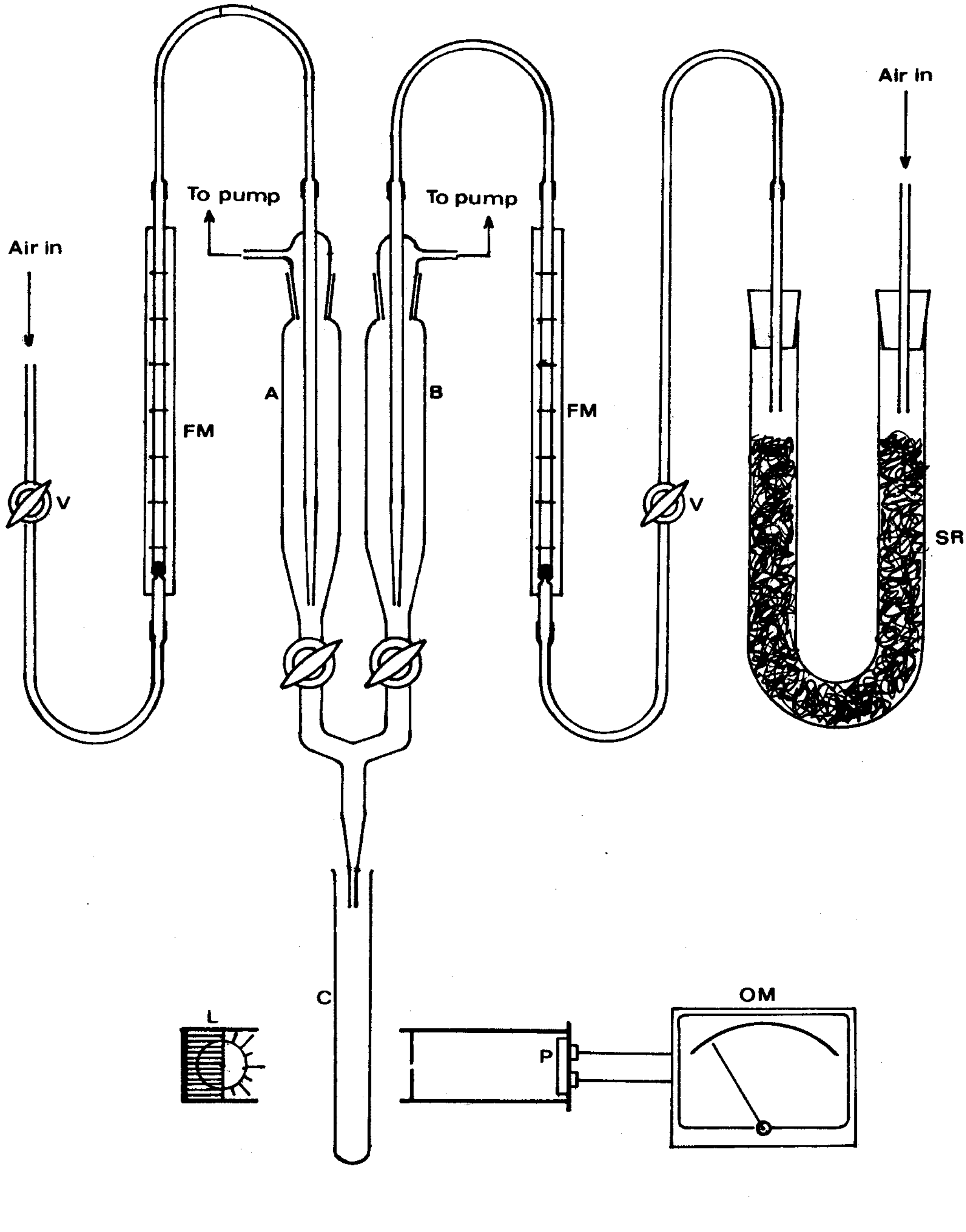

Figure 1. Diagrammatic representation of instrumental setup :

A,B	=	gas bubbler;	C	=	receiving tube;	FM	=	flowmeter;
L	=	light source;	P	=	photocell;	OM	=	ohmmeter;
SR	=	SO_2 remover;	V	=	needle valve.			

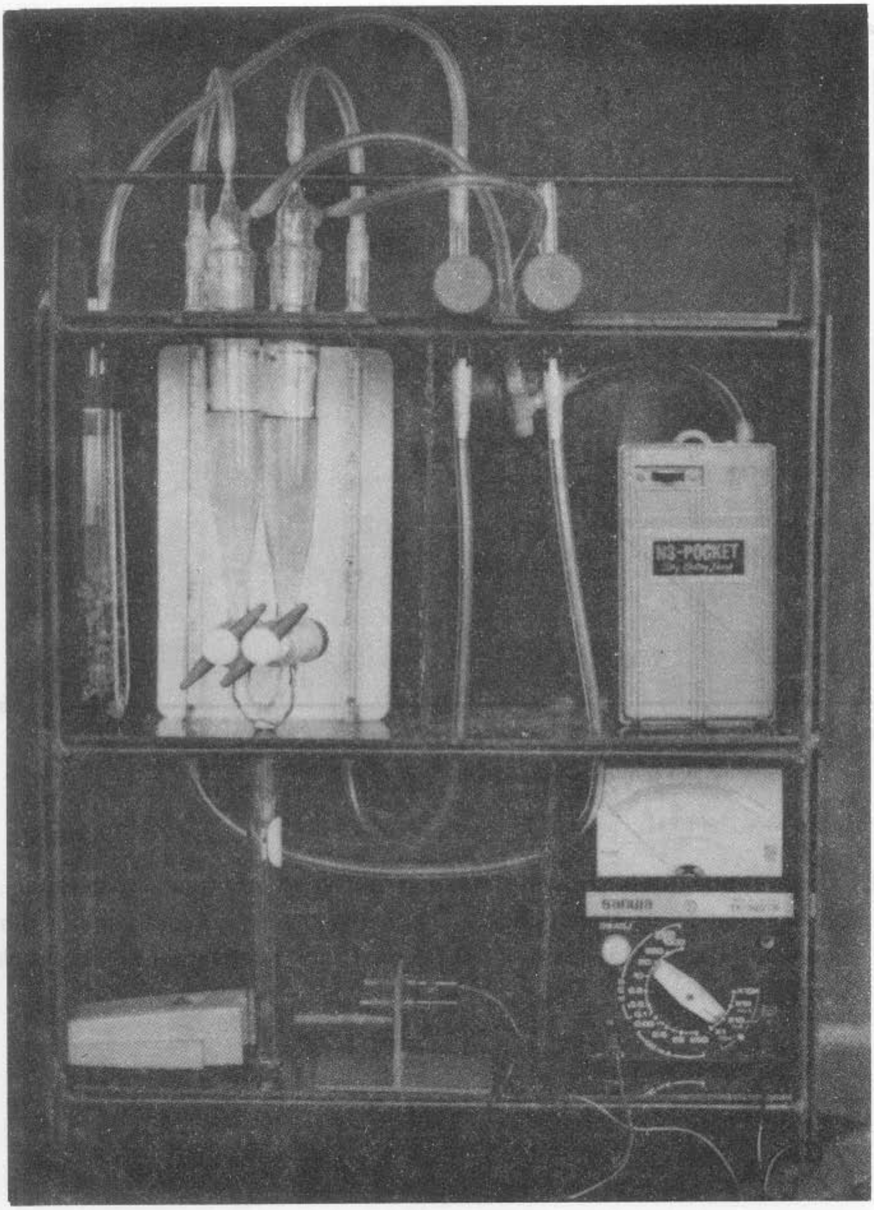

Figure 2. General view of the prototype instrument.

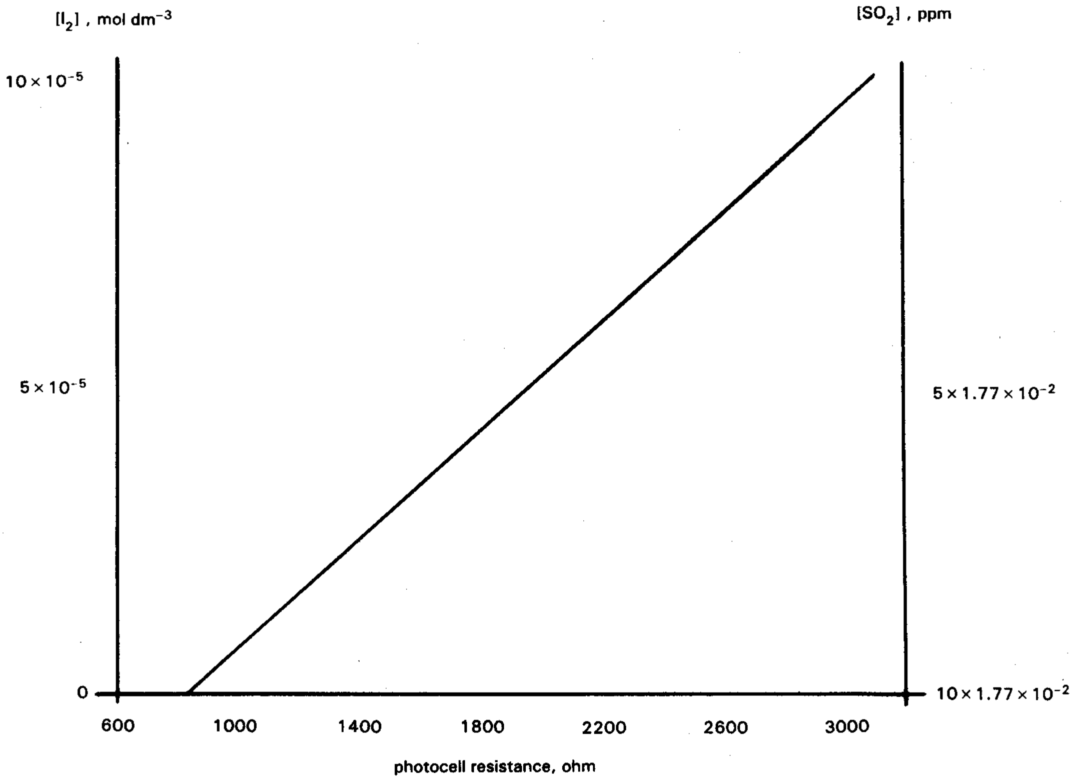

Figure 3. Calibration curve showing relation between photocell resistance and concentration of starch–iodine solution and atmospheric sulphur dioxide concentration. (Flow rate = 10.51 $dm^3\ min^{-1}$, absorber solution volume = 25 cm^3)

photocell resistance was measured using a Sanwa YX-360 TR multitester. A general view of the constructed prototype instrument is shown in Figure 2.

A calibration curve (Figure 3) is obtained by taking ohmmeter readings of the photocell resistance while varying the concentration of the starch-iodine solution and plotting $[I_2]$ vs resistance. A corresponding $[SO_2]$ vs resistance curve is obtained by converting $[I_2]$ into $[SO_2]$.

Operating Procedure

1. The U-tube was half-filled with small pieces (0.6 cm × 1.2 cm) of glass microfibre paper, which had previously been treated with a solution of chromium trioxide and sulphuric acid and dried at 80°-90°C for 1 hour.
2. The gas absorbers were filled with 25.0 cm^3 of ca. 1.0×10^{-4} mol dm^{-3} starch-iodine solution[22]. Exposure of the solution to strong light was prevented by wrapping round the absorbers with aluminium foil.
3. The air pump was switched on and the flow rate was adjusted to 10 dm^3 min^{-1} by using valves V. A 30-minute sampling period was allowed, after which the air-pump was switched off.
4. Each of the absorber solutions was discharged into the receiving tube. The light source was turned on and the ohmmeter reading taken.

Results and Discussion

The atmospheric sulphur dioxide concentration can be calculated from

$$[SO_2] = \frac{\triangle c \times V \times 2.24 \times 10^4}{r \times t} \text{ ppm}$$

where $\triangle c$ = concentration difference (mol dm^{-3}) between iodine solutions in the two bubblers after the sampling period
V = volume of absorber solution (cm^3)
r = air flowrate (dm^3 min^{-1})
t = sampling period (min)

In order to assess the reliability of the gas absorber, the incoming air stream was allowed to bubble through the starch-iodine solutions in both absorbers at the same flow rate for 30 minutes. It was found that no difference in colour intensity was detected.

After establishing the conditions necessary for sampling (e.g. sampling period, volume of absorber solution, flowrate) sulphur dioxide measurements were made at various locations in Bangkok. Results are shown in Table 1.

TABLE 1 SULPHUR DIOXIDE SAMPLING (AT 5 FEET ABOVE THE GROUND) IN BANGKOK BETWEEN MAY-JUNE 1980.

Place	Date and time of sampling	Atmospheric conditions during sampling	$[SO_2]$, ppm. (error)
a) Factory area			
Soi Kusolsilp (behind Ministry of Defense's Oil Refinery) Bang Chak	June 9 14.00–14.30 16.00–16.30	 Strong wind; Overcast Strong wind; Light drizzle	 0.01 (100%) n.d.
In front of M.O.D.'s Oil Refinery, Bang Chak	June 11 14.00–14.30	Sky clear; strong wind	0.10 (18%)
Thai Glassware Industry Ltd., Suksawad Rd., Rachaburana	June 16 14.00–14.30	Light overcast; moderate wind	n.d.
Thai Charoen Rice Mill, Suksawad Rd., Rachaburana	June 17 14.00–14.30	Strong wind; rain	n.d.
b) Heavy-traffic areas			
Siam City Bank, New Phetburi Br.	May 14 14.00–14.30	Sky clear; moderate wind; moderate traffic	0.03 (38%)
Pratunam Intersection	May 16 14.00–14.30	Sky Clear; moderate wind; heavy traffic; exhaust fume	0.07 (23%)
Central Dept. Store, Chidlom Br.	May 19 14.00–14.30	Sky clear; light wind; traffic jams; exhaust fume	0.06 (27%)
Phrakanong Theatre, Sukhumvit Rd.	May 20 14.00–14.30	Sky clear; light wind; heavy traffic, exhaust fume	0.04 (36%)
Sri Thong Phanich Shop, Yaowarat	May 22 14.00–14.30	Sky clear; light wind; traffic jams; dense exhaust fume	0.09 (19%)
Worachak Market	May 23 14.00–14.30	Sky clear; light wind; traffic jams; exhaust fume	0.07 (23%)

TABLE 1 (Cont.)

Place	Date and time of sampling	Atmospheric conditions during sampling	$[SO_2]$, ppm. (error)
Book Booth No.5, the Main Ground	May 24 14.00–14.30	Sky clear; moderate wind; traffic jams; exhaust fume	0.06 (27%)
Central Dept. Store, Silom Br.	May 28 14.00–14.30	Sky clear; calm; moderate traffic; exhaust fume	0.07 (23%)
Wat Wiset Market (near Siriraj Hospital), Bangkok Noi	May 30 14.00–14.30	Sky clear; light wind; traffic jams; exhaust fume	0.07 (23%)
Sinthong Watches, Saphan Kwai	June 3 14.00–14.30	Sky clear; moderate wind moderate traffic	0.02 (52%)
c) Light-traffic areas			
Soi Sukhumvit 31	May 13 16.00–16.30	Sky clear; strong wind	0.02 (52%)
Buranawit School, Bang Plad	May 27 14.00–14.30	Sky clear; light wind	n.d.
Soi Rachapruek (Sena Nivet)	June 5 14.00–14.30	Sky clear; moderate wind	n.d.

n.d. = not detected

The instrument has a lower limit of detection of about 0.003 ppm, depending on the sampling period and the concentration of the iodine solution used, which means that the photocell can detect a concentration difference between the two iodine solutions if light transmission by these solutions gives rise to a difference of not less than approximately 50 ohms. However, an uncertainty of 3% on the ohmmeter readings implies that as the sulphur dioxide concentration decreases the experimental error increases exponentially. Thus, as shown in Table 1, a sulphur dioxide concentration of 0.10 ppm is associated with an error of 18% and for a concentration of 0.01 ppm, the error is approximately 100%.

Despite the above limitation, however, the constructed instrument can still be of practical use, considering the standard levels of sulphur dioxide set by the World Health Organisation (0.21 ppm)[23] and the National Environment Committee of Thailand (0.126 ppm). Concentrations much lower than these standards need not be of great concern.

Certainly, better results may be obtained by analysing the absorber solution colorimetrically, titrimetrically, or by using commercially available instruments, but the fact remains that higher costs are involved. The constructed instrument, minus the flowmeters and the cost of glassblowing, costed less than 1,000 baht. Work on improving the performance of this instrument is currently in progress.

Acknowledgements

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาวิธีหาความเข้มข้นของแก๊สซัลเฟอร์ไดออกไซด์ในอากาศ โดยการวัดการดูดกลืนแสงของสารละลายไอโอดีน-น้ำแป้ง แล้วออกแบบและสร้างเครื่องมือแบบกระเป๋าหิ้วสำหรับวัดความเข้มข้นของซัลเฟอร์ไดออกไซด์ในอากาศ ณ บริเวณต่าง ๆ ของกรุงเทพมหานคร ในช่วงเวลาประมาณ 2 เดือน

จากการศึกษาพบว่าในบริเวณใกล้โรงงาน ความเข้มข้นของซัลเฟอร์ไดออกไซด์มีค่าระหว่าง 0.01 ถึง 0.1 ส่วนในล้านส่วน และในบริเวณที่มีการจราจรหนาแน่น ความเข้มข้นที่วัดได้มีค่าระหว่าง 0.02 ถึง 0.09 ส่วนในล้านส่วน.