### CHAPTER I



### INTRODUCTION

Sulfur dioxide  $(SO_2)$  is one of the major air pollutants. It is widely used as an index of the level of air pollution. Sulfur dioxide arises mainly from the combustion of fuels. Solid and liquid fossil fuels contain sulfur, usually in the form of inorganic sulfides or sulfurcontaining organic compounds. Combustion of fuel forms about 25 to 30 parts of sulfur dioxide to 1 part of sulfur trioxide  $(SO_3)$ . Sulfur dioxide is also released from petroleum refinery, chemical industries, mines and volcanic eruptions etc. Sulfur dioxide emitted from various sources in Bangkok in 1978 was reported by World Health Organization as shown in Table 1.



Emission of sulfur dioxide as 1,000 tons per year (1) Table 1.

## 1.1 Properties and Applications of Sulfur dioxide

Sulfur dioxide is a nonflammable, nonexplosive colorless gas with a pungent irritating odor, melting at  $-75.46^{\circ}$ C and boiling at  $-10.02^{\circ}$ C. Sulfur dioxide has an angular structure, the bond angle (0-S-0) being 119°C and the sulfur-oxygen bond distances being 1.43 A. It is very soluble in water, giving sulfurous acid  $(H_2SO_3)$ . Sulfur dioxide can act as an oxidizing agent (for example toward hydrogen sulfite, hydrogen etc.) and as a reducing agent (for example toward permanganate ion, dichromate ion etc.).

Sulfur dioxide is used as a refrigerant gas because of its high heat of vaporization. It is used as a disinfectant and fumigant and as a bleaching agent for materials such as straw, wood and silk. The major industrial use depends on its catalytic oxidation to sulfur trioxide in the manufacture of sulfuric acid  $(H_2SO_4)$ .

The gas is manufactured by buring sulfur or roasting (oxidizing) metallic sulfide in air or oxygen, by the reaction between a sulfite, Na<sub>2</sub>SO<sub>3</sub> or acid sulfite, NaHSO<sub>3</sub> and a strong acid or by the reaction of metals such as copper with concentrated sulfuric acid at elevated temperatures.

In the atmosphere, sulfur dioxide is partly converted to sulfuric acid or to sulfur trioxide and its salts by catalytic or photochemical process. The degree of oxidation of sulfur dioxide is dependent on time, residence, the intensity and the duration of sunlight and amount of moisture The amounts of catalytic material such as hydrocarbons and nitrogen present. oxides and the amounts of sorptive and alkaline materials present, also affect the oxidation process.

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## 1.2 Effects of Sulfur dioxide

Sulfur dioxide is a hazard which causes many effects on health, materials, vegetation and visibility, etc. Many of these effects are produced by a combination of sulfur dioxide and particular matter. The combination of sulfur dioxide and particulates produces an effect that is greater than sum of the effects caused by these pollutant individually.

1.2.1 Effects on Health

The effects on health are related to irritation of the respiratory system. Such injury is temporary or permanent. The response is dependent on particle size, with the smallest particles showing the greatest irritant potency. Sulfuric acid and irritant particulate sulfates have a greater irritant potency at a given concentration than does sulfur dioxide alone. The potentiation by particulate matter of toxic responses to sulfur dioxide has been observed under conditions which would promote the conversion of sulfur dioxide to sulfuric acid. The degree of potentiation is related to the concentration of particulate matter. The response of bronchoconstriction in man may be assessed in terms of a slight increase in airway resistance. Normal individuals, exposed to sulfur dioxide via the mouth, exhibit small changes in airway resistance, which are often insufficient to produce any respiratory The effects are even smaller when the subject breaths through symptoms. his nose.

Most people can taste sulfur dioxide at concentrations from 0.3 ppm to 1 ppm (about 0.9  $mg/m^3$ ) in air. At concentrations above 3 ppm (about 8.6 mg/m<sup>3</sup>), the gas has a pungent, irritating odor. Combined

effects of experimental exposures to sulfur dioxide and particulate are shown in Table 2. Short term exposure to sulfur dioxide produces symptoms, illnesses or diseases in otherwise healthy people Episodes of acute elevation of oxides of sulfur and other pollutant concentrations which have been associated with a larger number of deaths than expect are shown in Table 3.



Table 2. Combined effects of sulfur dioxide and particulates

 $\hat{\mathbf{v}}$ 

 $\hat{\mathbf{r}}$ 

 $\bullet$ 

 $\sim 10^6$ 



 $\hat{\omega}$ 

## Table 2. Continued



## Table 3. Sulfur dioxide episodes



maximum 24-hour average concentration

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maximum hourly concentration  $\star\star$ 

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1.2.2 Effects on Materials

The combination of particulates and sulfur oxides pollution is an important pollution in a wide range of damage to materials. It is apparent that corrosion rates of various metals are higher in urban and industrial atmospheres with relatively high levels of both particulate and sulfur oxides than they are in rural and other areas of low pollution. High humidity and temperature also play an important synergistic part in this corrosion reaction.

Sulfur oxides pollution attacks a wide variety of building materials such as limestone, marble, roofing slat and motar as well as statuary and other work of art, causing discoloration and deterioration. Certain textile fibers such as cotton, rayon and nylon are harmed by atmospheric sulfur oxides. Dyed fabrics may be faded in atmosphere containing sulfur oxides and other pollutants. Upham (15) found that at a mean sulfur dioxide level of 345  $\mu q/m^3$  (0.12 ppm) accompanied by high particulate levels, the corrosion rate for steel panels is increased by 50 percent.

1.2.3 Effects on Vegetation

Sulfur dioxide causes acute or chronic leaf injury to plants. Acute injury produced by high concentrations for relatively short periods, usually results in injured tissue drying to an ivory color; it sometimes results in a darkening of the tissue to a reddish-brown. Chronic injury, which results from lower concentrations over a number of days or weeks, leads to pigmentation of leaf tissue, or leads to a gradual yellowing, or chlorosis, in which the chlorophyll-making mechanism is impeded. Both acute and chronic injury may be accompanied by the suppression of growth and yield.

At a concentration of about 85  $\mu$ g/m<sup>3</sup> (0.03 ppm) of sulfur dioxide (annual mean), chronic plant injury and excessive leaf drop occur(16). After exposure to about 860  $\mu g/m^3$  (0.3 ppm) of sulfur dioxide for 8 hours, some species of trees and shrubs show injury (17). At concentration of about 145  $\mu$ g/m<sup>3</sup> to 715  $\mu$ g/m<sup>3</sup> (0.05 ppm to 0.25 ppm), sulfur dioxide react with either ozone or nitrogen dioxide in short term exposures (e.g., 4 hours) to produce moderate to severe injury to sensitive plants (18).

1.2.4 Effects on Visibility

Visibility is reduced by two effects which gas molecules and particles have on visible radiation : absorption and scattering of light. In addition to the reduction of visibility, air pollution affects urban climates with respect to increase fog formation and reduce solar radiation. With high concentration of sulfur dioxide, the formation of sulfuric acid by oxidation of sulfur dioxide on the surface of particles in a humid environment leads to the formation of small droplets of fog which are very effective as light scatterers. The exhaust from a coal-burning power generating station exhibits a characteristic dense plume which has a bluish tinge as a result of light scattering from the small particles of condensed vapor. Bushtueva (19) estimated that at a concentration of 285  $\mu$ g/m<sup>3</sup> of sulfur dioxide, with comparable concentration of particulate matter and relative humidity of 50 percent, visibility in New York City was reduced to about 5 miles.

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# 1.3 Analytical researchs on the determination of sulfur dioxide

Ellis (Katz. 1950:20) described the method for determination of sulfur dioxide; lodine, potassium iodate and starch solution were employed as the absorbent.

Smith and Friis (Katz. 1950:20) applied 0.1 N sodium hydroxide as a absorbent for sulfur dioxide. After absorption, the solution was titrated with 0.001 N iodine solution using starch solution as indicator. A comparision was made with a blank determination.

Thomas (21) suggested hydrogen peroxide as an absorbent for sulfur dioxide. The reaction produced sulfate and hydrogen ions and several methods were available for the determination of either of these ions.

Wilsdon and Mc. Connell(22) found reaction between sulfur dioxide and lead dioxide to form solid, stable lead sulfate (PbSO<sub>4</sub>).

To produce sensitive highly specific test, Steigmann (23) modified the Schiff reaction for bisulfite and used fuchsin and sulfurous acid to determine the concentration of formaldehyde by measuring the intensity of the color produced. Grant(24) adapted a chromogenic reaction of sulfur dioxide with fuchsin and formaldehyde in acid to quantitative colorimetric determination of 0 to 10 micrograms of sulfur dioxide in solution. Methods had been devised for direct application to alkaline extracts of animal tissues employing mercuric chloride to remove sulfhydryl interference. For determination in fruit, preliminary distillation was used to remove interfering substances.

Kozlyaeva (Urone and Boggs, 1951:25) applied the modification method of Steigmann to determine sulfur dioxide in air and found that hydrogen sulfide and carbon disulfide did not interfere, whereas the nitrogen oxides did.

The sulfur dioxide was absorbed in distilled water, and after an absorption period of 1 hour, the sampling solution was mixed with the color reagent. As little as 0.2 ppm of sulfur dioxide could be determined colorimetrically by means of a spectrophotometer using a cell with a 100-mm. light path and a capacity of 5  $cm^3$ 

Kitagwa (Patterson, 1952: 26) had done many unpublished research on gels for determination of the following gases and vapors: acetylene, ammonia, benzene, nitrogen dioxide and sulfur dioxide. Two sulfur dioxidesensitive gels were applied. One made of silica gel granules and potassium dichromate, it was yellow and turned blue when exposed to sulfur dioxide in the concentration range 0.1 to 15 % (by volume). The other, also based on silica gel granules, contained potassium iodate and turned from white to brown with sulfur dioxide in the range 0.005 to 0.2 %.

Atkin(27) used alkaline glycerol as sulfur dioxide absorbing The color response obtained by combining sulfur dioxide with solution. fuchsin-formaldehyde reagent in an acid medium followed Beer's law upto a concentration of 1 mg of sulfur dioxide in 500  $\text{cm}^3$  of solution at 25<sup>0</sup> to  $30^{\circ}$ C.

Katz (20) found that the dilute solution of starch-iodine was suitable for the continuous determination of low concentration of sulfur dioxide in smelter areas where hydrogen sulfide was not likely to occur.

Urone and Boggs (25) used a solution of 5 % glycerol in 0.1 N sodium hydroxide as the absorbing solution in the spectrophotometric determination of sulfur dioxide in air. These alcoholic alkali solutions

had a tendency to froth and foam because of their lowered surface tension, therefore very low sampling rates must be used.

Floyd and Byers (Tioh, 1976:28) determined sulfur dioxide by polarographic method and used a solution of 2% glycerol in 0.05 M sodium hydroxide as the absorbing solution.

Patterson and Mellon (26) described several granular gels which changed color when exposed to 150 cm<sup>3</sup> air samples containing 10 ppm of sulfur dioxide. The gel was placed in a glass tube and the air sample was drawn through the tube. Three methods of quantitative estimation may be used : The colors which appeared on the various gels may be matched with standard color cards ; the length of a colored column may be measured ; or the sample volume necessary to produce a desired color or length of colored column may be observed. These gels provided a simple pocket-sized method for estimating physiologically dangerous concentrations of sulfur dioxide in the atmosphere.

West and Gacke (29) described a Schiff reaction procedure for determinating sulfur dioxide. He utilized sodium tetrachlormercurate (II) (TCM) as absorbent and pararosaniline instead of fuchsin (a impure mixture of pararosaniline and rosaniline) which established the basis for the method in determining ambient sulfur dioxide. The sulfur dioxide reacted with the mercury complex to form the dichlorosulfitomercurate (II) complex.

Jacobs and Greenburg (30) determined sulfur dioxide in atmosphere by using hydrogen peroxide as absorbent. Sulfur dioxide was oxidized to sulfuric acid and was titrated with alkali solution.

Vogel(31) described an interesting qualitative test for sulfurous acid species in which a sample solution (or gas) was mixed with a test reagent prepared by mixing 50  $cm^3$  of 0.1 N hydrochloric acid, 15  $\text{cm}^3$  of 1 N barium chloride and 5  $\text{cm}^3$  of 0.1 N potassium permanganate. Addition of sulfur dioxide to the reagent resulted in transient formation of barium sulfite which was oxidized by the permanganate to give a precipitate of white barium sulfate.

Lyubimov (32) reported on the development of a continuous monitoring instrument in which sulfur dioxide was absorbed in a solution of barium chloride. Light transmission through the resulting turbid solution was continuously recorded and was directly proportional to the sulfur dioxide concentration.

Edwards (Schroeter, 1966:33) recommended the use of 40% benzyl cellosolve supported on diatomaceous earth for the gas chromatographic seperation of sulfur dioxide. Beuerman and Meloan(34) employed a 20 ft 30 percent dinonylphthalate column operating at  $92^{\circ}$ C to determine sulfur dioxide. Helium was used as the carrier gas and detection was accomplished with thermistors. Bond et al (Schroeter, 1966:33) employed gas chromatography for the determination of sulfur dioxide and sulfur trioxide in gas mixture containing 0.2 - 0.4 percent dioxide and 0.3 percent trioxide.

Stephens and Lindstrom (35) determined sulfur dioxide by passing samples of the gas through a solution of ferric ion and 1,10-phenanthro-It reduced the ferric ion to ferrous ion which reacted with 1,10line. phenanthroline to form the orange tris (1,10-phenanthroline) iron (II) complex. The color formed immediately in the absorbing solution and was stable for several days.

Hicky and Hendrickson (36) developed Wilsdon and Mc. Connell's method (lead dioxide candle) for determining sulfur dioxide. He found that hydrogen sulfide interfered this method, because of its Huey (37) used lead dioxide plate instead of sulfate formation. Lead dioxide plate is cheaper and higher lead dioxide candle. efficiency than lead dioxide candle.

Urone et al  $(38)$  determined sulfur dioxide by conductometry. Barendrecht and Martens (39) described a completely automatic, coulometric apparatus for determining sulfur dioxide in gases with concentrations ranging from 0.1 to 100 percent by volume.

Scaringelli et al (40) improved pararosaniline methods which yielded greater sensitivity, greater reproducibility and adherence to Beer's law throughout greater working range than the West and Gaeke method. The pararosaniline dye was specially purified and standardized to reduce variability problems. Phosphoric acid was used in the final color development to control pH, to liberate sulfur dioxide from its mercury complex and to form complex with heavy metals. Barringer and Mc. Neill (Syty 1973:41) applied the principles of molecular correlation spectrophoto metry to the determination of sulfur dioxide in air based on the absorption spectrum in the range of 290-310 nm. Williams and Hager (Syty 1973:41) applied spectrophotometry to determine sulfur dioxide based on the absorption in the range of 200-230 nm. The instrument involved in an absorption cell having a 7.72-m folded light path and was sensitive to concentrations as low as a few ppb of sulfur dioxide in air.

Axelrod et al(42) combined in the Schiff reaction with fluorimetry to produce a more reliable and sensitive sulfur dioxide test. The formaldehyde-bisulfite complex reacted with a fluorescent molecule to form a nonfluorescent or a weakly fluorescent species. The fluorescent molecule had only one primary amine site and could be obtained in relatively pure form.

Syty (41) described a rapid and specific spectrophotometric determination of sulfur dioxide which required minimal sample treatment and appeared to offer considerable freedom from interference. Sulfur dioxide, trapped by an absorbing solution, was released by treatment with acid. It was then carried by a stream of carrier gas to a flowthrough absorption cell, and UV absorption of the gas stream was measured at 215 nm.

Lambert et al (43) recommended 4-nitro-1, 2-diaminobenzene instead of pararosaniline in the West-Gaeke method. They used nearly decolorized 4-nitro-1,2-diaminobenzene to be converted to a colored dye by reaction with released from a tetrachloromercurate (II) absorbing hydrogensulfite, solution, and formaldehyde. The reaction was versatile, having been used for the determination of formaldehyde as well as sulfur dioxide and serving as the basis for the indirect determination of ozone and sulfur aerosol.

Fein and Bailey (44) analysed sulfur dioxide from routine monitoring in southern California by conductimetric and pararosaniline methods, 24-h average to estimate method uncertainties. Random measurement error ranged to 0.02 and 0.006 ppm for the two methods, respectively. Total conductimetric method uncertainties ranged to 0.06 ppm.

Hence, this method was not satisfactory for determining compliance with very low ambient air quality standards.

Fernandez et al  $(45)$  applied precipitation of barium sulfate and formation of a blue complex between unreacted barium and Sulphonaza III. The absorbance was inversely proportional to sulfate content and the working range for the method was from 3 to 30 µg (as  $so_a^{2^-}$ ) per 5 cm<sup>3</sup> of sample  $(0.6 \times 10^{-5}$  to 6 x 10<sup>-5</sup> M). The procedure was intended mainly for the determination of sulfur dioxide in ambient air after absorption in dilute hydrogen peroxide.

Dusgupta et al (46) used formaldehyde (7 mM) buffered at pH~4 to stabilize atmospheric sulfur dioxide as hydroxymethanesulfonic acid. Sulfite, liberated from this compound by base, was added to acidic pararosaniline for color development by the Schiff reaction, and absorbance was measured at 580 nm. The method was comparable to the West-Gaeke method in absorption and recovery efficiency, sensitivity, and precision. In 1981, Dusgupta (47) used 1-Napthylammonium chloride instead of pararosaniline hydrochloride for a fluorometric version (excitation 342 nm, emission 442 nm) of the Schiff reaction used for the determination of sulfur dioxide.

Vinjamoori and Ling  $(48)$  used triethanolamine (TEA) impregnated on molecular sieve 13X as solid sorbent for sampling collection of sulfur dioxide and nitrogen dioxide in the 1-10 ppm range. Sulfur dioxide and nitrogen dioxide were stripped from the sorbent with a standard eluant mixture (0.003 M NaHCO<sub>3</sub> /0.0024 M Na<sub>2</sub>CO<sub>3</sub>) and determined by ion chromatography as sulfate and nitrite after oxidation of sulfite with hydrogen peroxide.

Suleiman and Guilbault (49) described a piezoelectric crystal detector utilizing a mercury displacement reaction for the detection and determination of sulfur dioxide. The mercury vapor, produced by bubbling the sulfur dioxide through a mercurous nitrate solution, was detected by a gold-coated piezoelectric crystal due to the formation of a mercury amalgam. This detector exhibited good sensitivity and selectivity and could be used in the ppb and ppm concentration ranges of sulfur dioxide.

Irgum and Lindgren (50) used enthanedial to stabilize sulfur dioxide after initial hydrolysis. Reaction took place on a partly regenerated poly (acrylic acid) weak cation exchange gel that was used as buffering carrier for the stabilizer solution. This resulted in high acid/base buffer capacity without release of anions to the sample solution, which permited use of both colorimetric and ion chromatographic determinations.

Margeson et al(51) developed a manual 24-h integrated method for determining sulfur dioxide in emission from electric utility plants. Samples were collected in alkaline potassium permanganate solution contained in restricted-orifice impinger. Sulfur dioxide was oxidized to  $so_4^{2-}$  and  $s_2o_6^{2-}$ . Samples were analysed by ion chromatography. The method showed 100 % collection efficiency for all the pollutants at a sample flow rate of 35 cm<sup>3</sup>/min and was found to be unbiased relative to independent monitoring systems. At a flow rate of 75 cm<sup>3</sup>/min., the collection efficiency was still 100 percent for sulfur dioxide.

## 1.4 Air Quality Standards

Sulfur dioxide is associated with the activities of man. It exists wherever there are large cities and industrial area and is a danger to the health of every town deweller. It affects, not only human health and comfort but also animal and plant lives, building, metals and fabrics, etc. To prevent effects of air pollution, some governments prescribe legal standards for ambient air quality. In the United States for example they are called air quality standards, which there are two types: one is primary standards which are based on the protection of health, and the other is secondary standards, are based on the protection of public welfare including protection against known or anticipated effects of air pollution on property, materials, climate, economic values and personal comfort. Air quality standards of sulfur dioxide which have been adopted by the United States in 1971 are shown in Table 4.

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Table 4. Air quality standards, 1971 (52)

a<sub>Not to be exceeded more than once a year.</sub>

In Thailand, ambient air quality standard of sulfur dioxide which is established by the National Environment Board(53) is not higher than 0.30  $mg/m^3$  (0.104 ppm) - 24 hour average and not higher than 0.10 mg/m<sup>3</sup> (0.035 ppm) - annual average (by Pararosaniline method).

## 1.5 Objective of the Study

The technique which is most frequently used to measure sulfur dioxide is Pararosaniline method  $(54)$ . Pararosaniline method provides good efficiency and specificity for low concentration of sulfur dioxide but the chemicals used are expensive, not easy to find locally and tetrachloromercurate salt which is sulfur dioxide absorbing reagent is So there were many researchs on the determination of sulfur toxic. dioxide in order to find a new technique.

In this study, an attempt will be made to find a simple, low cost and efficient method. The absorbing reagent used must be not toxic and must form a stable compound with sulfur dioxide.

There are many absorbing reagents which have been used, however, the absorbing reagents which react with sulfur dioxide to produce sulfite and sulfonate compound are

1.5.1 0.1 N sodium hydroxide solution (20)

1.5.2 2% glycerol in 0.05 N sodium hydroxide solution (28)

1.5.3 Buffered formaldehyde solution (7mM HCHO and 1mM KHP) (46)

The sulfite compound and sulfonic acid are more promise to determine in low concentration than other sulfur compounds. Thus, these absorbing reagents will be used in this study. Sulfite and sulfonate compound have been determined by several methods. However, the simplest and economic methods are selected for this study. There are

1.5.4 Iodine method (55)

Excess standard solution of potassium iodate-iodide (0.025 N KIO<sub>3</sub>-0.1 N KI) is added to the sulfite compound in acid condition,

Iodine which is liberated oxidises sulfite compound and the remained iodine is titrated with standard solution of sodium thiosulfate or by spectrophotometer.

1.5.5 Alkalimetric Method (56)

The sulfite solution is titrated with standard sulfuric acid, methyl orange is used as indicator.

1.5.6 Aniline method (57)

The sulfite compound reacts with aniline solution and formaldehyde solution give the new compound which its spectrum is in ultraviolet region.