CHAPTER IV

RESULTS AND DISCUSSION

The results of this study were depicted into 3 parts as following

1. Absorbing reagents

2. Analysis methods

3. Determination of sulfur dioxide in inert gas and ambient air

4.1 Absorbing reagents

According to TCM, absorbing reagent in pararosaniline method, is toxic and expensive, many absorbing reagents instead of TCM solution have been tried in this study and the results are

4.1.1 0.1 N sodium hydroxide solution

This solution was used because the chemical was cheap and easy to find. There were many researchs which used 0.1 N sodium hydroxide solution as absorbent. This solution absorbed sulfur dioxide, given sulfite. The degradation rates of sulfite in this solution and in water were studied by using iodine method as shown in Table 5.

Table 5. Degradation rates of sulfite in 0.1 N NaOH and in water

Absorbing reagent	Time, Days	SO_2 found $(\mu g/cm^3)$	% Loss
Deionized water	0	30.2	−
	1	24.2	20
	2	13.6	45
0.1 N NaOH	0	30.2	−
	1	21.1	30
	2	6.0	80

From Table 5, the sulfite solution was unstable even in the deionized water. The presence of a base increased the instability. Thus, this absorbing reagent should be used for a short period of sampling and the analysis has to perform immediately after sampling. It is not suitable for sampling air in 24 hours.

4.1.2 2% glycerol in 0.05 N sodium hydroxide solution

According to Haller(25) the oxidation of sulfite proceeded only in the presence of certain catalysts, chiefly traces of salts of copper and iron.   It was suggested that the use of a "negative catalyst" to form a nonionizable compound with these salts would prevent the oxidation of the sulfite. Atkin (27) used a solution of 5% glycerol and 10% sodium hydroxide in his scrubbers and the oxidation was reduced successfully. The 2% glycerol in 0.05 N sodium hydroxide solution as absorbent was also successful (28). This solution was found to be almost 100% absorption efficiency. Therefore, in this study, 2% glycerol in 0.05 N sodium hydroxide solution was tried.

In order to study the stability of sulfite in this solution, standard sodium sulfite was added into 0.2% glycerol in 0.05 N sodium hydroxide solution and the concentration of sulfite in this solution was determined by iodine method at the period of time as in 4.1.1. The results of these determinations are shown in Table 6.

Table 6. Degradation rate of sulfite in 2% glycerol in 0.05 N NaOH

Absorbing reagent	Time, days	SO_2 found $(\mu g/cm^3)$	% Loss
2% glycerol in 0.05 N NaOH	0	30.2	-
	1	29.8	1.3
	2	29.4	2.6

From Table 5 and 6, the instability of sulfite solution decreases in the 2% glycerol in 0.05 N sodium hydroxide solution. Because of the good absorption efficiency and the increase of sulfite stabilization, this absorbing reagent is promising for sulfur dioxide sampling. However, this absorbing reagent has a tendency to froth and foam, corresponding to its lowered surface tension. Therefore low sampling rates must be used.

4.1.3 Buffered formaldehyde solution

Dasgupta et al [46] reported that the buffered formaldehyde solution pH 4-5, which stabilized sulfur dioxide as hydroxymethanesulfonic acid, provided the absorption efficiency for sulfur dioxide nearly 100% at the flow rate of gas as 0.4 liter/minute and the degradation rate was no more than 1%/30 days for the sample stored at 25°C. In this study the degradation rate of hydroxymethanesulfonic acid in buffered formaldehyde solution (pH 4.3) was determined by iodine method

as shown in Table 7.

Table 7. Degradation rate of hydroxymethanesulfonic acid in buffered

formaldehyde solution.

Absorbing reagent	Time, Days	SO_2 found $(\mu g/cm^3)$	% Loss
Buffered formaldehyde solution	0	30.2	–
	1	30.1	0.4
	2	29.9	0.8
	10	29.8	1.2
	15	29.7	1.5
	30	29.6	2.0

For Table 7 and experiment of Dusgupta et al., the

buffered formaldehyde is the efficient absorbing reagent for sulfur

dioxide and it forms a stable compound with sulfur dioxide.

4.2 Analysis method

The methods selected for determination of sulfite in this study

are

4.2.1 Iodine method

Iodine method has been a well-known method to determine

sulfite compound because of its high efficiency and simplicity. In

this study, the sulfite in three absorbing reagents was determined by

iodine method. The results of this study are shown in Table 8, 9, 10

and Figure 9.

Table 8. The determination of sulfur dioxide by Iodine method using
·0.1 N NaOH as absorbent.

Standard sulfite concentration ($\mu g/cm^3$)	Standard SO_2 ($\mu g/cm^3$)	SO_2 found iodine titration ($\mu g/cm^3$)	mean ± mean deviation	a % Error
11.32	5.75	(1) 5.36	5.05 ± 0.20	12.1
		(2) 4.94		
		(3) 4.86		
9.12	4.63	(1) 4.72	4.06 ± 0.44	12.3
		(2) 3.54		
		(3) 3.92		
8.21	4.17	(1) 3.59	3.36 ± 0.21	19.5
		(2) 3.04		
		(3) 3.44		
6.91	3.51	(1) 3.21	2.96 ± 0.18	15.7
		(2) 2.72		
		(3) 2.94		
5.71	2.90	(1) 1.98	2.18 ± 0.18	24.7
		(2) 2.45		
		(3) 2.12		
4.92	2.50	(1) 1.50	1.32 ± 0.12	47.2
		(2) 1.27		
		(3) 1.19		

[a] %Error = $\dfrac{\text{standard } SO_2 - \text{mean}}{\text{standard } SO_2} \times 100$

Table 9. The determination of sulfur dioxide by Iodine method using 2% glycerol in 0.05 N NaOH as absorbent.

Standard sulfite concentration ($\mu g/cm^3$)	Standard SO_2 ($\mu g/cm^3$)	SO_2 found iodine titration ($\mu g/cm^3$)	mean $\pm$ mean deviation	% Error [a]
10.16	5.16	(1) 5.06	5.55 ±0.31	-7.6
		(2) 5.66		
		(3) 5.94		
8.98	4.56	(1) 3.86	4.23 ±0.25	7.2
		(2) 4.39		
		(3) 4.44		
7.52	3.82	(1) 3.40	3.34 ±0.17	12.5
		(2) 3.11		
		(3) 3.52		
5.53	2.81	(1) 2.54	2.49 ±0.18	11.5
		(2) 2.22		
		(3) 2.70		
4.88	2.48	(1) 2.08	2.04 ±0.10	17.6
		(2) 1.89		
		(3) 2.16		
3.68	1.87	(1) 1.59	1.54 ±0.11	17.6
		(2) 1.38		
		(3) 1.66		
2.93	1.49	(1) 1.05	0.90 ±0.11	40.0
		(2) 0.91		
		(3) 0.74		

[a] %Error = $\dfrac{\text{standard } SO_2 - \text{mean}}{\text{standard } SO_2} \times 100$

Table 10. The determination of sulfur dioxide by Iodine method using buffered formaldehyde solution as absorbent.

Standard sulfite concentration ($\mu g/cm^3$)	Standard SO_2 ($\mu g/cm^2$)	SO_2 found iodine titration ($\mu g/cm^3$)	mean± mean deviation	a % Error
9.57	4.86	(1) 4.65	4.39 ± 0.18	9.7
		(2) 4.20		
		(3) 4.31		
7.30	3.71	(1) 3.30	3.26 ± 0.15	12.1
		(2) 3.44		
		(3) 3.04		
5.87	2.98	(1) 2.87	2.68 ± 0.13	10.1
		(2) 2.52		
		(3) 2.65		
4.64	2.36	(1) 2.15	1.97 ± 0.12	16.4
		(2) 1.82		
		(3) 1.95		
4.02	2.04	(1) 1.76	1.58 ± 0.12	22.5
		(2) 1.54		
		(3) 1.45		
3.68	1.87	(1) 1.20	0.97 ± 0.15	48.1
		(2) 0.93		
		(3) 0.78		

[a] %Error = $\dfrac{\text{Standard } SO_2 - \text{mean}}{\text{standard } SO_2} \times 100$

Figure 9 % Error vs Standard SO_2, $\mu g/cm^3$

The error (%) for determination of sulfur dioxide in 2% glycerol in 0.05 N NaOH is lower than the other absorbents but the deviations in using buffered formaldehyde is lower than the other absorbents. Thus in iodine method, buffered formaldehyde solution or 2% glycerol in 0.05 N NaOH should be used as absorbents. In higher concentration of sulfur dioxide, the errors are lower than the lower concentration.

The detection limits for sulfur dioxide in 0.1 N NaOH, 2% glycerol in 0.05 N NaOH and buffered formaldehyde solution are 3.0, 1.8 and 2.0 $\mu g/cm^3$ respectively. Because of high error tiration, the detection limits for sulfur dioxide found are too high, thus a large volume of air is required. However, the precision of these three analysis methods are not satisfied for determination of sulfur dioxide at low range concentration. This method should be used to determine sulfur dioxide in areas which there are rather high concentration of sulfur dioxide.

4.2.2 Alkalimetric method

This method is simplicity, low cost and the chemicals can be bought easily. Alkalimetric method was used for determining sulfite compound but never be used for determination of sulfur dioxide in air. Thus in this study, the modification of this method was attempted. Methyl orange indicator in glycerol or formaldehyde gives yellow color as the sulfite does so it interferes the titration of the sulfite. Therefore, the absorbing reagent that used in this method was 0.1 N sodium hydroxide solution. The results of the determination of sulfur dioxide by this method is shown in Table 11.

From Table 11, the error were as high as 11 to 40%. The detection limit of this method for determination of sulfur dioxide was 75 $\mu g/cm^3$ SO_2. It is still very high concentration so this method is

not satisfied to determine sulfur dioxide in ambient air.

Table 11. The determination of sulfur dioxide by Alkalimetric method

Standard sulfite concentration ($\mu g/cm^3$)	Standard SO_2 ($\mu g/cm^3$)	SO_2 found acid titration ($\mu g/cm^3$)	mean $\pm$ mean deviation	% Error [a]
271.29	137.8	(1) 117.0	113.5 ± 2.3	11.2
		(2) 112.4		
		(3) 111.1		
229.95	116.8	(1) 103.7	102.0 ± 2.0	12.7
		(2) 102.8		
		(3) 99.4		
209.28	106.3	(1) 88.5	85.4 ± 2.1	10.9
		(2) 83.1		
		(3) 84.5		
188.60	95.8	(1) 77.4	74.3 ± 2.1	12.9
		(2) 72.4		
		(3) 73.1		
158.09	80.3	(1) 67.9	67.6 ± 0.7	15.8
		(2) 68.4		
		(3) 66.5		
146.86	74.6	(1) 56.4	54.3 ± 2.0	27.2
		(2) 51.3		
		(3) 55.2		
138.40	70.3	(1) 44.2	42.3 ± 1.3	40.0
		(2) 41.7		
		(3) 40.9		

[a] % Error = $\dfrac{\text{standard } SO_2 - \text{mean}}{\text{standard } SO_2} \times 100$

4.2.3 Aniline method

Aniline, the simplest aromatic amine, is easy to find locally and is cheaper than pararosaniline. Aniline reacts with formaldehyde and sulfite to give a new compound(57) which gives a spectrum in ultraviolet region. The 0.1 N sodium hydroxide absorbing reagent was not used in this method because the sulfite in this solution was very unstable as shown in Table 5.

4.2.3.1 Using 2% glycerol in 0.05 N NaOH

The proportionality of sulfur dioxide concentration and absorbance was studied. As seen from Figure 10 and Appendix 1, two linear curves were obtained, one was concentration of 6.30 $\mu g/cm^3$ and 0.75 $\mu g/cm^3$, the other was between 1.25-0 $\mu g/cm^3$. The slope of the lower concentration range was more than of higher concentration range. However it can be concluded that the absorbance is dependent directly on concentration of sulfur dioxide.

Reproducibility was studied as shown in Table 12.

Table 12. Reproducibility of aniline method using 2% glycerol in 0.05 N NaOH as absorbent.

No.	Absorbance, 242 nm.
1	0.097
2	0.080
3	0.101

SO_2 used was 3.0 $\mu g/cm^3$

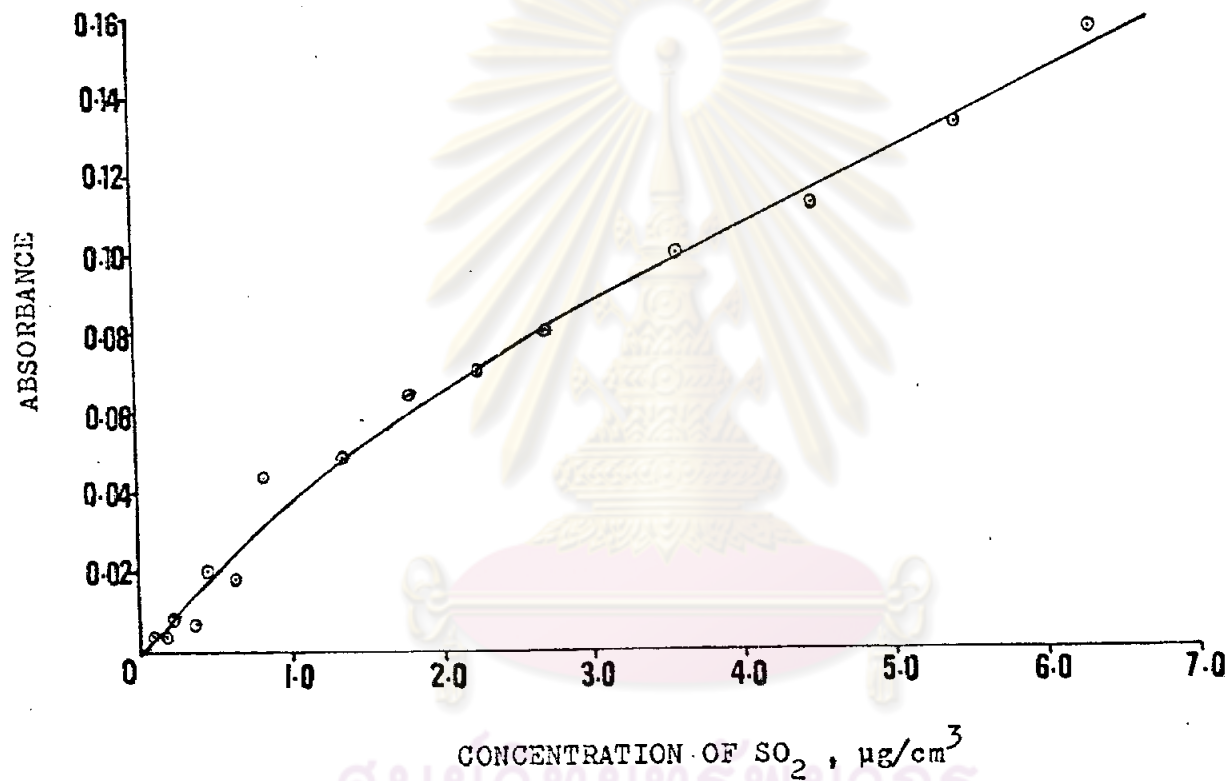From Table 12, the reproducibility is ±0.008 (mean deviation)   and ± 0.024 (at 95% confidence level)

Figure 10 Dependence of Absorbance on concentration of sulfur dioxide by aniline method using 2% glycerol in 0.05 N NaOH as absorbent.

4.2.3.2 Using buffered formaldehyde solution

The proportionality of sulfur dioxide concentration and absorbance was studied. As seen from Figure 11 and Appendix 2, the curves are linear in the range of 0.25–1.62 µg/cm^3 and the range 1.70–6.12 µg/cm^3. Below 0.25 µg/cm^3 the absorbances of the solutions were nearly the same. Thus the detection limit for this linear curve is 0.25 µg/cm^3 SO$_2$.

Reproducibility was studied as shown in Table 13.

Table 13. Reproducibility of aniline method using buffered formaldehyde solution as absorbent.

No.	Absorbance, 242 nm	
	1.0 µg/cm^3 SO$_2$	3.0 µg/cm^3 SO$_2$
	a	b
1	0.032	0.150
2	0.042	0.139
3	0.032	0.142
4	0.045	0.137
5	0.039	0.152
6	0.040	0.145
7	0.030	0.130

[a]Reproducibility: ±0.006 (standard deviation)

: ±0.006 (at 95% confidence level)

[b]Reproducibility: ±0.008 (standard deviation)

: ±0.008 (at 95% confidence level)

From Table 13, The relative standard deviation is 16% at 1 µg/cm^3 SO$_2$ and 5.6% at 3.0 µg/cm^3 SO$_2$.
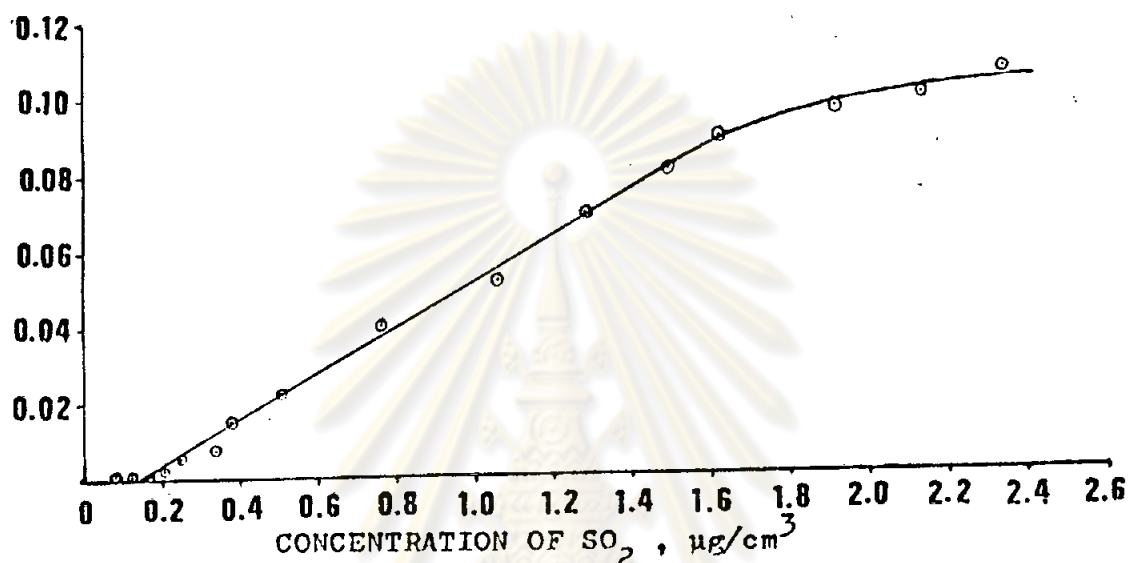
Figure 11 a   Dependence of absorbance on concentration of sulfur dioxide
by aniline method using buffered formaldehyde solution as
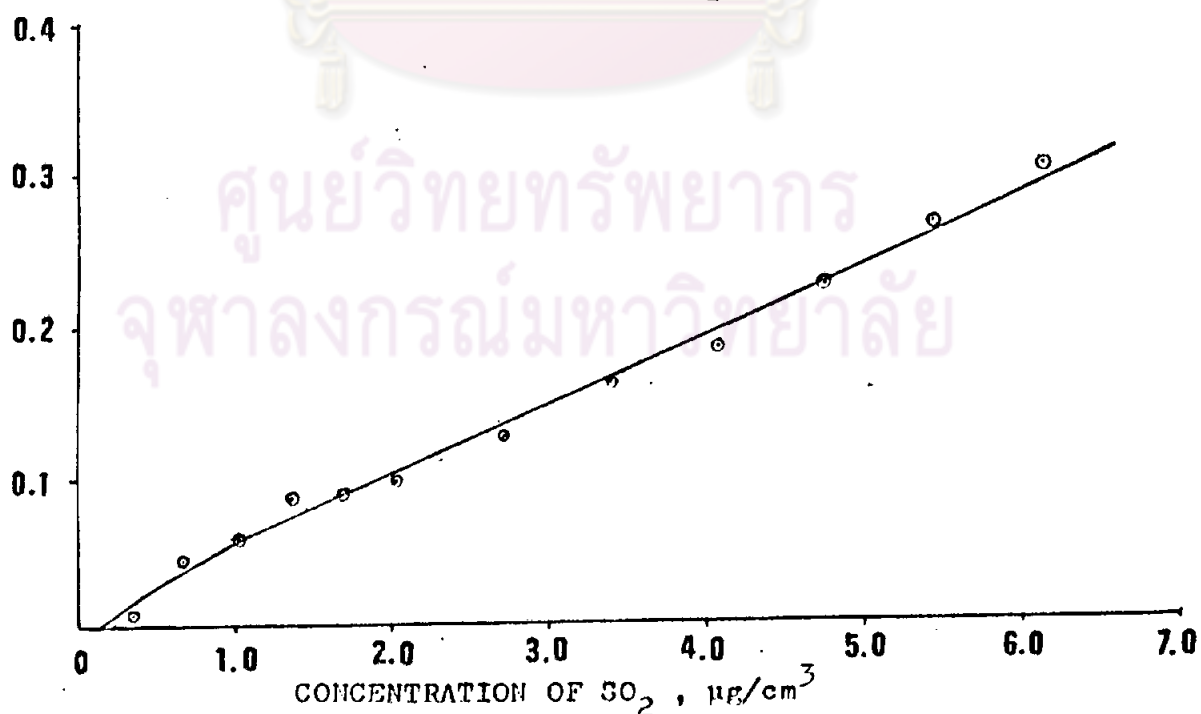absorbent at 0.1-2.4 ug/cm^3 SO$_2$.

Figure 11 b   Dependence of absorbance on concentration of sulfur dioxide
by aniline method using buffered formaldehyde solution as
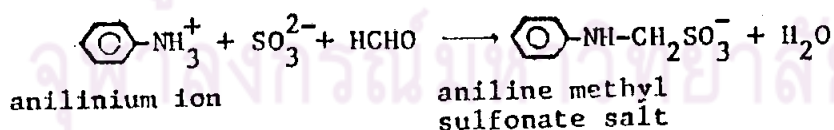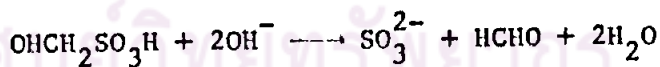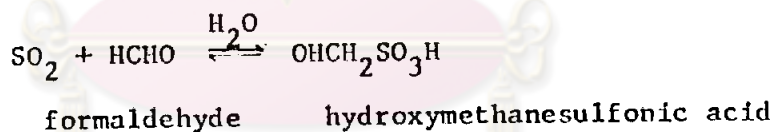absorbent at 0.3-6.2 µg/cm^3 SO$_2$.

By aniline method, the use of 2% glycerol in 0.05 N NaOH as absorbent provided the detection limit for sulfur dioxide and the deviation higher than that from the buffered formaldehyde solution. Thus, buffered formaldehyde solution was used as absorbent for the determination of sulfur dioxide in air.

The aniline method gives higher sensitivity and precision than the titration method so in this study, the aniline method is used for determination of sulfur dioxide in air.

4.2.4 Modified aniline method

In this method, sulfur dioxide is absorbed with the buffered formaldehyde solution to form hydroxymethanesulfonic acid. Hydroxymethanesulfonic acid is stable and oxidized at low rate. Sulfite, liberated from this compound by adding base, is determined by aniline method.

4.2.4.1 Reactions

$$SO_2 + HCHO \underset{H_2O}{\rightleftharpoons} OHCH_2SO_3H$$

formaldehyde   hydroxymethanesulfonic acid

$$OHCH_2SO_3H + 2OH^- \longrightarrow SO_3^{2-} + HCHO + 2H_2O$$

$$\langle O \rangle - NH_3^+ + SO_3^{2-} + HCHO \longrightarrow \langle O \rangle - NH-CH_2SO_3^- + H_2O$$

anilinium ion   aniline methyl
                                               sulfonate salt

4.2.4.2 Spectra

Aniline methyl sulfonate gave spectrum in ultra-violet region so the spectrum of the mixture solution was run in range 190-320 nm. For examining any interference of the spectrum, the spectra of reagents used were also recorded as illustrated in Figure 12. The maximum absorption peak (λ_{max}) of the product of the mixture solution
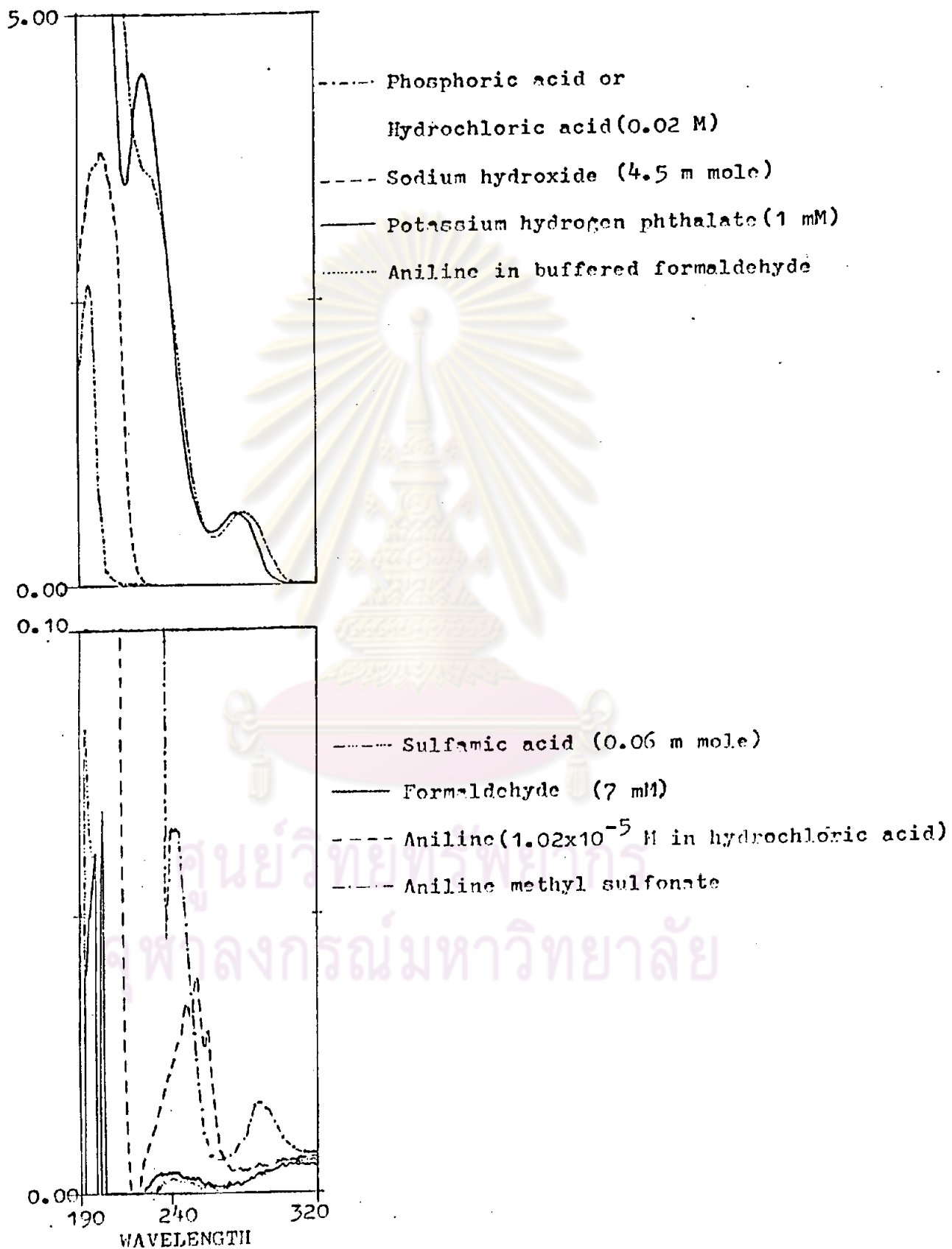
Figure 12   Spectra of reagents and the product
(aniline methyl sulfonate)

showed at 242 nm and λ_{max} of reagents showed at other wavelengths (Table 14), this meant that no maximum absorption peaks of reagents interfered the maximum absorption peak of the product. Since the concentration of aniline in this solution was about 20 times higher than that of sulfur dioxide, consequently, it was about 20 times higher than the product, the absorption peak of aniline is buffered formaldehyde (λ_{max} = 224) would raise up the base line of the spectrum of the product if water was used for reference (see Figure 13). Therefore, a reagent blank had to be used for reference in this method.

Absorption spectrum of the product at various pH was also studied as shown in Figure 14 and Table 15.

Table 14 λ_{max} of reagents and the product

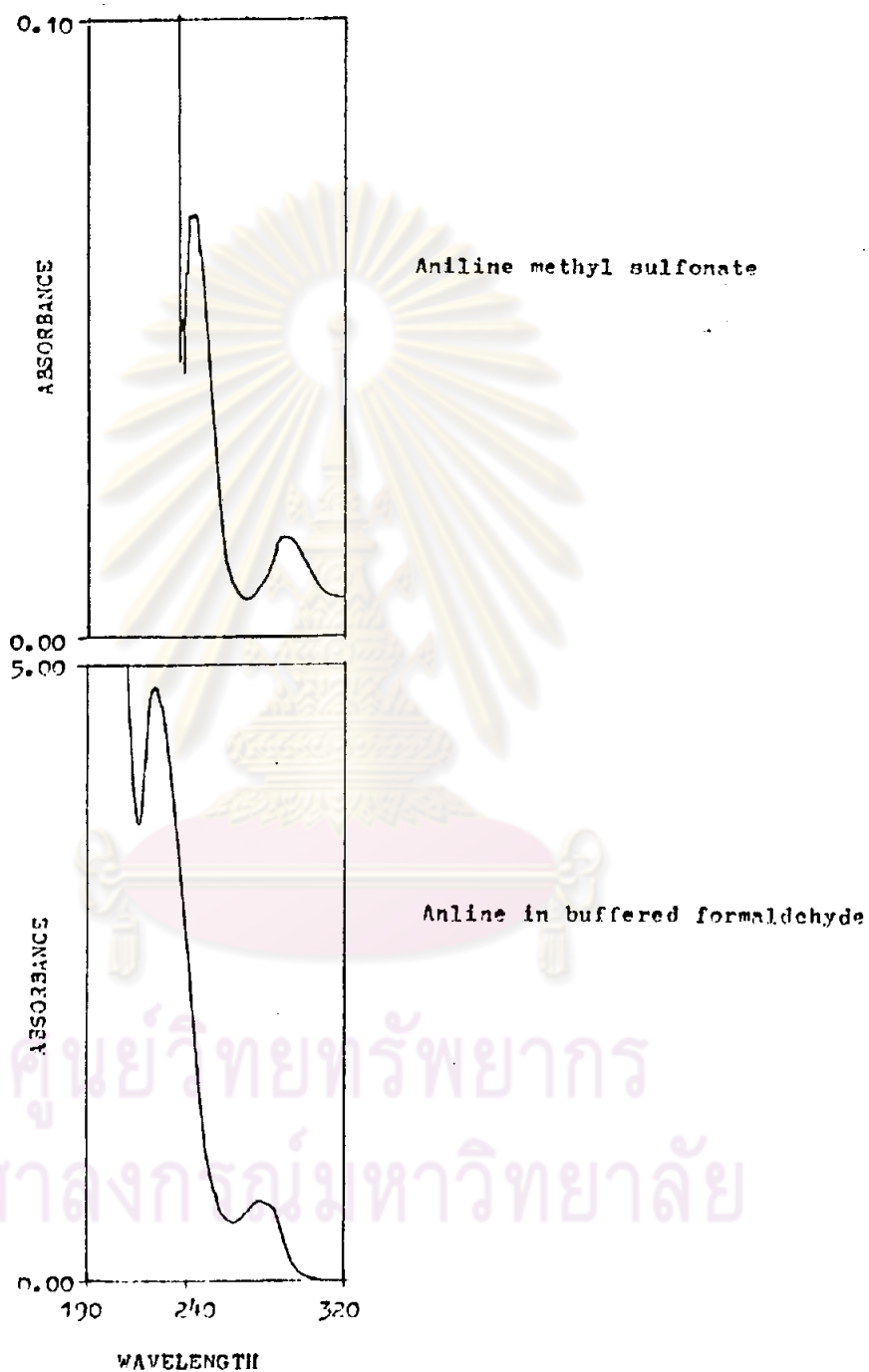| Reagents	λ_{max}, nm
Aniline	252
Formaldehyde	202
Hydrochloric acid	197
Phosphoric acid	197
Potassium hydrogen phthalate	224
Sodium hydroxide	204
Sulfamic acid	·202·
Aniline in buffered formaldehyde	224
Aniline methyl sulfonate	242

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Figure 13 Comparision of spectra between aniline methyl sulfonate and
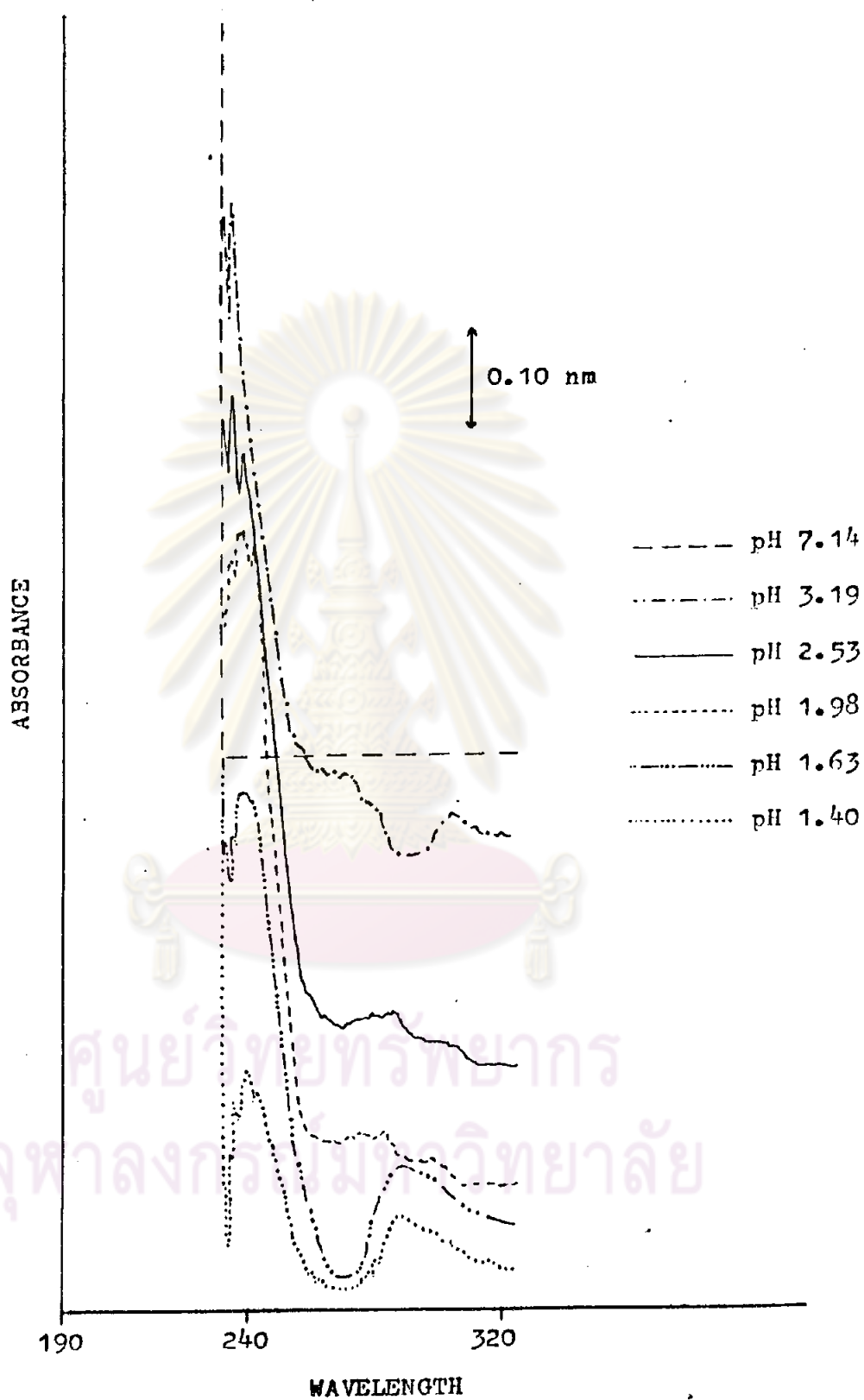aniline in buffered formaldehyde.

Figure 14 Absorption spectra at various pH of solutions

Table 15. λ_{max} of aniline methyl sulfonate at various pH

pH	λ_{max}
1.40	242
1.63	242
1.98	242
2.53	238
3.19	238
7.14	236

From Figure 14 and Table 15, these spectra showed a small hysochromic shift with pH. The sharp peak with an maximum absorbance at 242 nm at the lower pH value (pH 1.40) shifted to 236 nm at higher pH value (pH = 7.14).

At 238 nm, the peak of the product was difficult to separate from the reagent blank. Thus, the product was measured at 242 nm.

Optimum acidity for the maximum absorbance of the product at 242 nm was studied in detail by adding sodium hydroxide solution because sulfite in this method was liberated by sodium hydroxide solution. The results are illustrated in Figure 15 and Table 16.
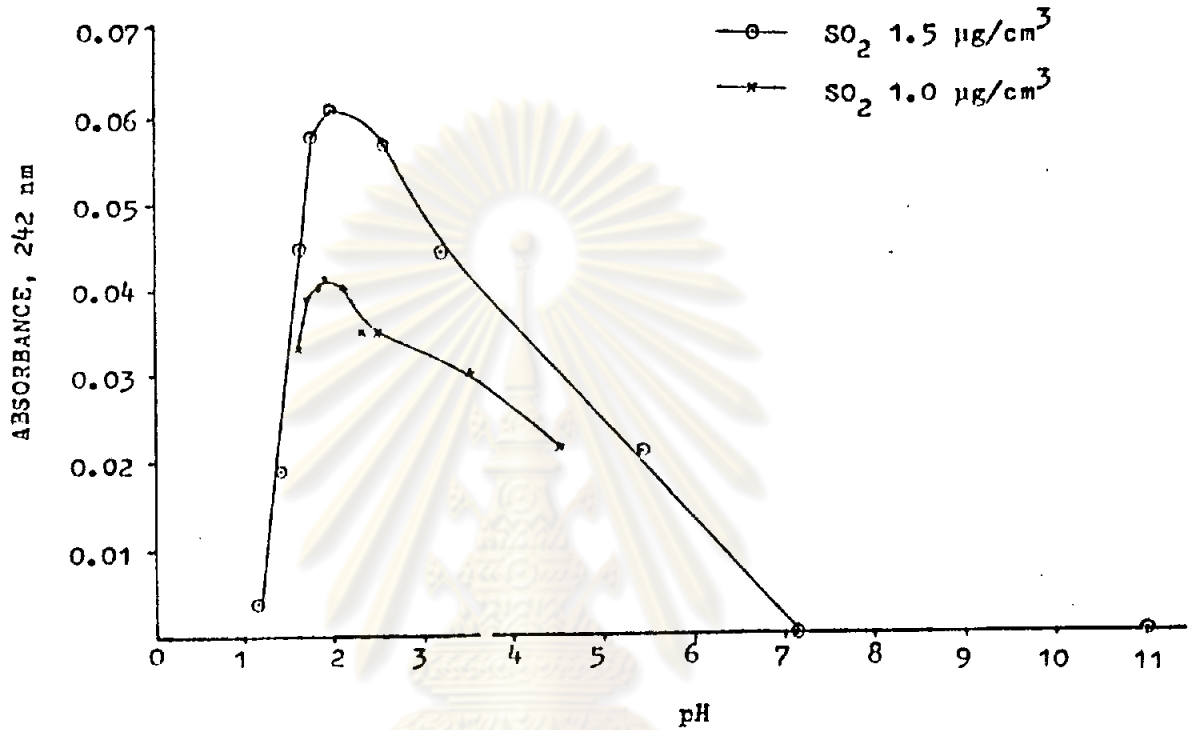
Figure 15 Absorbance of the product vs pH

Table 16 pH of the solution after adding various amount of the base

SO_2 used $\mu g/cm^3$	Sodium hydroxide added m mole	pH	Absorbance (242 nm)
1.5	1.35	1.18	0.004
	2.25	1.40	0.019
	3.60	1.65	0.045
	4.36	1.78	0.058
	4.50	1.98	0.061
	4.95	2.53	0.053
	5.40	3.19	0.044
	5.85	5.42	0.021
	6.07	7.14	0.000
	6.75	11.06	0.000
1.0	3.60	1.64	0.033
	4.36	1.72	0.039
	4.45	1.86	0.040
	4.50	1.90	0.041
	4.72	2.15	0.040
	4.82	2.35	0.035
	4.95	2.49	0.035
	5.40	3.51	0.030
	5.62	4.78	0.021

This indicated that pH was a critical factor in the analysis. The maximum absorbance reached with 4.36-4.72 m moles of sodium hydroxide leading to a final pH of about 1.7-2.2. Thus, in the present study, the pH of solution was controlled at 1.7-2.2 that 1 cm^3

of 4.5 M NaOH (4.5 m mole NaOH) was added to the solution for liberating sulfur dioxide from the absorbing reagent.

4.2.4.3 Concentratoin of aniline solution

Aniline is a significant reagent in formation of the product so the amount of aniline is important. From the reactions for formation of aniline methyl sulfonate, 1 mole anilinium hydrochloride equivalents to 1 mole sulfur dioxide that is 1.56×10^{-6} mole of aniline equivalents to 2 $\mu g/cm^3$ sulfur dioxide. In this study, concentration of sulfur dioxide range 0-7 $\mu g/cm^3$ were studied, thus aniline must higher than 5.46×10^{-6} mole. The 1.02×10^{-5} mole aniline was used for this study. For higher concentration of SO_2, the amount of aniline used must be increased.

4.2.4.4 Time

The lifetime of the product in the solution was studied by measuring the absorbance at λ_{max} 242 nm of the mixture solution after standing between 0-50 minutes. The results are shown in Appendix 3 and Figure 16.
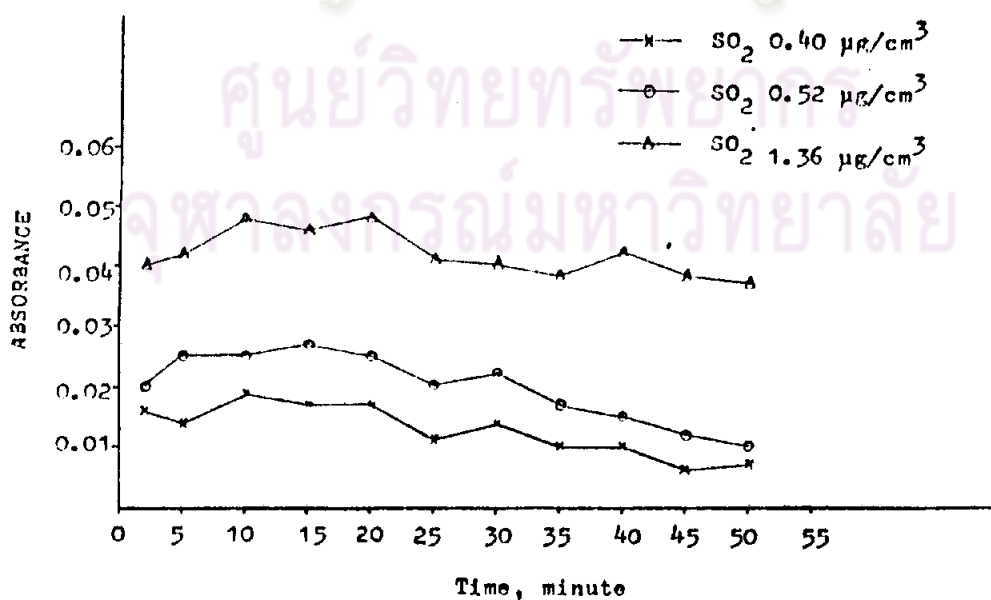

Figure 16 Absorbance of the compound vs time

From Figure 16, the maximum absorbance reached in 10-20 minutes. Thus, the optimum time to determine the product is in 10-20 minutes.

4.2.4.5 Interference

Significant interferences of sulfur dioxide determination are heavy metals and oxides of nitrogen.

4.2.4.5.1 Heavy metals [Cu (II), Pb (II), Mn (II)]

The effects of Cu (II), Pb (II) and Mn (II), all of which were known to catalyze the aerobic oxidation of S (IV) species, were investigated. Copper (II) nitrate, Lead (II) nitrate and Manganese (II) nitrate were used as interferences. Effects of interferences of heavy metals on the absorption of aniline methyl sulfonate at 242 nm (λ_{max}) are shown in Table 17, 18 and 19.

Table 17 Effect of Copper (II) on the absorption of aniline methyl sulfonate at 242 nm.

Copper (II), µg	Absorbance
0	0.052
1	0.052
5	0.051
9	0.050
10	0.048
11	0.041
15	0.030

SO_2 used was 1.6 µg/cm^3

Table 18 Effect of Lead (II) on the absorption of aniline methyl

sulfonate at 242 nm.

Lead (II), µg	Absorbance
0	0.052
1	0.051
5	0.053
10	0.054
11	0.042
12	0.030
15	0.027

SO_2 used was 1.6 µg/cm^3

Table 19 Effect of Manganese (II) on the absorption of aniline methyl

sulfonate at 242 nm.

Manganese (II), µg	Absorbance
0	0.052
1	0.053
2	0.051
3	0.046
4	0.035
5	0.028

SO_2 used was 1.6 µg/cm^3

From Table 17, 18 and 19, no significant inter-
ferences were found when the concentration of copper (II) and lead (II)
were less than 10 µg, but for manganese (II) when the concentration was

higher than 2 µg, it interfered significantly.

4.2.4.5.2 Oxides of nitrogen

Oxides of nitrogen are significant inter-ferences as shown in Table 10. Standard sodium nitrite ($NaNO_2$) was used for examination of this effect. The Effect of nitrogen oxides on sulfur dioxide determination by the modified aniline method was eliminated by adding sulfamic acid (46,63)

The efficiency of sulfamic acid in eliminating nitrogen oxides is also shown in Table 20 and Figure 17.

Table 20 Efficiency of sulfamic acid in eliminating nitrogen oxides

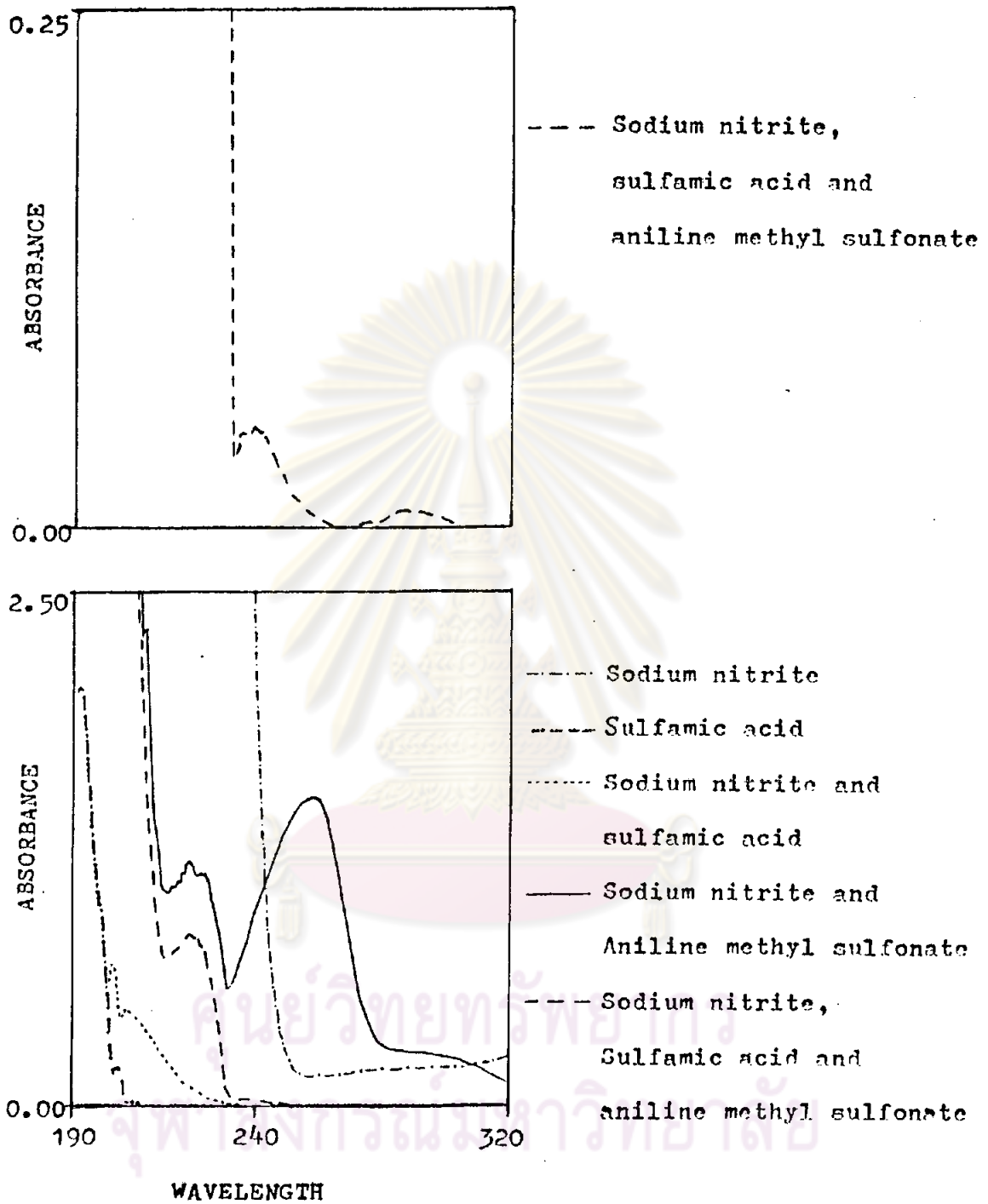| NO_2, µg/cm^3	Sulfamic acid, m mole	Absorbance, 242 nm
0	0.00	0.060
5	0.00	0.109
10	0.00	0.285
0	0.06	0.056
0	0.09	0.045
0	0.12	0.032
5	0.06	0.057
10	0.06	0.059
11	0.06	0.078
15	0.06	0.143
20	0.06	0.306

SO_2 used was 1.4 µg/cm^3

Figure 17   Action of sulfamic acid on nitrite

From Table 20 and Figure 17, sulfamic acid

0.06 m mole can be used to eliminate 0.01 m mole NO_2 (10 $\mu g/cm^3$ NO_2).

Sulfamic acid decomposes nitrite, releasing nitrogen gas. In higher

concentration of nitrogen oxides, sulfamic acid must be used more.

However, excess sulfamic acid reduced the absorption at 242 nm.

According to Pate et al(63), the oxidation of sulfamic acid may be

occured. This oxidation product of sulfamic acid would decrease the

aniline methyl sulfonate.

4.3 Determination of sulfur dioxide in inert gas and ambient air

Determination of sulfur dioxide in inert gas and ambient air

were attempted by both the modified aniline method and the pararosani-

line method.

The accuracy of the modified aniline method for determination

of sulfur dioxide was studied by using standard sulfur dioxide gas in

inert air (oxygen free nitrogen) and the results are shown in Table 21.

From Table 21, the concentration of sulfur dioxide found by

pararosaniline method was 3% negative deviation from the concentration

of standard sulfur dioxide but by modified aniline method it was 5%

positive deviation. Thus accuracy of pararasaniline is better than this

method. However, this modified aniline method could provide better

accuracy if the high sensitivity of the instrument was used and the

skillful technician performed it. The determination of sulfur dioxide

in inert gas at very low concentration could not be performed because of

the limit of the Dynacalibrator.

Table 21 Determination of sulfur dioxide in inert gas

No.	Time of sampling[a] (minutes)	Volume of air sampled at STP (liter)	Concentration of SO_2 found, $\mu g/m^3$ (ppm)			Relative Deviation (%)	
			Dynacalibrator	Pararosaniline method	Modified method	Pararosaniline method	Modified method
1	120	63.31	612.56 (0.234)	596.92 (0.228)	645.80 (0.247)	-2.5	+5.4
2	240	126.62	280.10 (0.107)	270.84 (0.103)	293.76 (0.112)	-3.3	+4.9
3	240	126.62	206.81 (0.079)	200.31 (0.076)	215.97 (0.082)	-3.1	+4.4
					average	-3.0	+4.9

[a]Flow rate 0.4 liter/minute

Determination of sulfur dioxide in amtient air are shown in Table 22.

From Table 22, pararosaniline method can be used to determination sulfur dioxide in ambient air from 5.65 µg/ m^3 but the modified aniline method can be determined from 24.56 µg/ m^3. Since the lower concentration provides absorbance out of the limit of the method, thus this method is less sensitive than pararosaniline method.

Comparison modified mothod with pararosaniline method. It is found that

1. There is consistent trend for modified method to yield values slightly higher than pararosaniline method with the relative deviation 8%.

2. The modified aniline method leads to faster development of product, maximum tensity is reached in about 10 minutes and no significant change occurs until 15 minutes. In contrast the pararosaniline method reaches maximum color intensity in about 30 minutes, continues undiminished to about 60 minutes.

3. Cost of the chemicals which are difference in these two method are shown as follows.

Pararosaniline method

Mercuric chloride	1,700 baht/500 grams
Pararosaniline hydrochloride	240 baht/gram
Potassium chloride	245 baht/kilogram

Modified aniline method

Aniline solution	550 baht/liter
Potassium hydrogen phthalate	440 baht/250 grams
Sodium hydroxide	170 baht/kilogram

Table 22 Determination of sulfur dioxide in ambient air at Mae Moh

Basin

Location	Date	Volume of air sampled at STP (liter)	Concentration of SO_2 found, $\mu g/m^3$	
			Pararosaniline[a] method	Modified method
Ban Hua Fai	6-1-86	419.8	n	n
	12-1-86	398.6	8.57	n
	11-2-86	400.6	n	n
Pump house at power plant units 4-7	6-1-86	408.1	n	n
	12-1-86	388.9	5.65	n
	11-2-86	382.9	11.56	n
Old power plant housing	6-1-86	425.7	n	n
	12-1-86	422.0	207.04	219.42
	11-2-86	411.2	n	n
Huai Khing dam	6-1-86	416.3	n	n
	12-1-86	407.7	19.81	24.56
	11-2-86	374.0	5.40	n

n non-detectable

[a]Source from Electricity Generating Authority of Thailand

In preparation reagents in one experiment, pararosaniline method is about 60 baht higher than modified method.

This modified aniline method appears to be less sensitive than pararosaniline, but this method is also specific for sulfur dioxide. Thus, this method can be used to determine sulfur dioxide in the area of high sulfur dioxide concentration because it's low cost and the chemicals can be find locally.

Concentrations of SO_2 in the range of 25 to 900 $\mu g/m^3$ can be measured with the prescribed absorbing solution volume and sample flow rates. Concentrations below 25 $\mu g/m^3$ can be measured by sampling larger volumes of air, but if this is done, the absorption efficiency of the collection system must be checked.