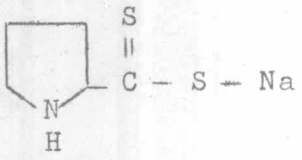
CHAPTER 3

DETERMINATION OF LEAD (II) BY INFRARED SPECTROPHOTOMETRIC TECHNIQUE

A method for qualitative and quantitative infrared spectroscopic analysis of metal-tetramethylenedithiocarbamate mixtures without preceding separation had been proposed (12, 13). Trace amount of lead (II) after complexation with Na-TMDTC and recrystallization in $CHCl_3$ was determined in KBr at 305 cm^{-1} which is the metal-S vibrational band (13).

The structural formula of Na-TMDTC is shown below,



tetramethylenedithiocarbamate sodium salt

(pyrrolidinedithiocarbamate sodium salt)

Owing to the wave number limitation of the equipment used in this study (4000 - 667 cm^{-1}), the metal-S vibrational band cannot be obtained. Thus, trace lead as $Pb(TMDTC)_2$ was quantitatively determined in KBr at 693 cm^{-1} which is the C-S vibrational band.

Since $Pb(TMDTC)_2$ was synthesized for this determination, the composition of the synthesized compound was studied.

Both techniques show that the preparation mentioned in 2.3.1 resulted only one stable compound with a molar ratio of Pb(II) to Na-TMDTC of 1:2. This is evident that the synthesized compound has a molecular formular as $Pb(TMDTC)_2$.

3.2 Physical properties of synthesized $Pb(TMDTC)_2$

The crystal of $Pb(TMDTC)_2$ after recrystallization in $CHCl_3$ has a white needle-shape. Its color changes to yellow at 264°C and the crystal decomposes at 286.5°C, leaving a black residue.

3.3 Infrared spectrophotometric study of $Pb(TMDTC)_2$

In infrared spectrophotometric analysis, the $Pb(TMDTC)_2$ in KBr shows a strong peak of C = N vibration and a weak peak of C-S vibration (see Figure 5). The C-S peak was a symmetrical peak but the C=N peak was unsymmetry and broadening when the concentration of $Pb(TMDTC)_2$ increased (see Figure 5). Corresponding to the C=N peak was reported for qualitative analysis of $Pb(TMDTC)_2$ in KBr (12) at 1462 cm^{-1} and C-S peak (693 cm^{-1}) was symmetry, the quantitative analysis of $Pb(TMDTC)_2$ in this study was examined at 1462 cm^{-1} and 693 cm^{-1}.

Since the amount of KBr in a pellet affected the infrared spectrum, the optimum amount of KBr for making a pellet of $Pb(TMDTC)_2$ was studied. A series of 0.50 - 3.00 mg $Pb(TMDTC)_2$ in a 70.00 mg KBr pellet, in a 100.00 mg KBr pellet, and in a 225.00 mg KBr pellet were investigated.

3.1 Composition of synthesized Pb(II)-TMDTC

The simplest spectrophotometric technique which has been used for study of complex formation equilibria is the molar ratio method (14). Therefore, the composition of synthesized Pb(II)-TMDTC compound is studied by plotting molar ratio of either Pb(II) to TMDTC or TMDTC to Pb(II) against its absorbance.

3.1.1 Ultraviolet spectrophotometric technique

Corresponding to the maximum absorbance of aqueous Na-TMDTC solution at 276.0 nm and 253.0 nm (see Figure 2) and no absorbance of aqueous Pb(II) solution in UV range, the absorbance of a series of solution as mentioned in 2.3.3.1 was measured at both maximum wavelengths. The data obtained are listed in Table 1 and the composition of this compound determined by the graphical method, as shown in Figure 3, is 2:1 for $[TMDTC^{-}]:[Pb^{+2}]$.

3.1.2 Atomic absorption spectrophotometric technique

At the wavelength of 217.0 nm where the maximum absorption peak of aqueous Pb(II) solution appears, there is no absorption of the aqueous Na-TMDTC solution. Thus, the molar ratio of Pb(II) to Na-TMDTC in the synthesized compound is performed at 217.0 nm. The data of this study is illustrated in Table 2 and the graphical determination of molar ratio of Pb(II) to Na-TMDTC (see Figure 4) results a 1:2 ratio.

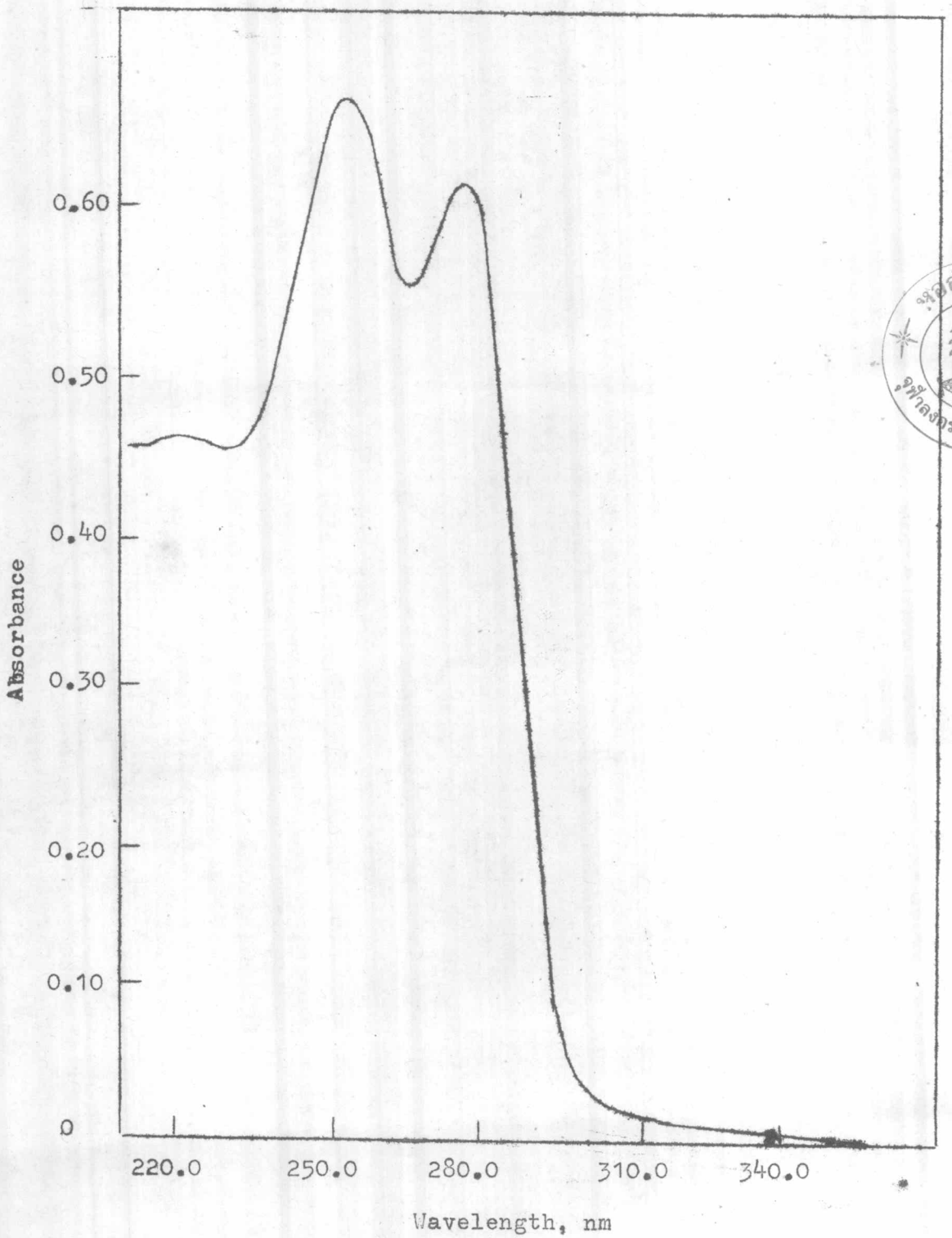


Figure 2 Ultraviolet spectrum of 4.00×10^{-5} M Na-TMDTC

Table 1 Composition study of the synthesized Pb(II)-TMDTC by ultraviolet spectrophotometric technique.

molar ratio, $[Pb^{+2}]$: [Na-TMDTC]	absorbance	
	276.0 nm	253.0 nm
0	0.245	0.172
0.1	0.205	0.133
0.2	0.155	0.102
0.3	0.110	0.065
0.4	0.052	0.028
0.5	0	0
0.6	0	0
0.7	0	0
0.8	0	0

Table 2 Composition study of the synthesized Pb(II)-TMDTC by atomic absorption spectrophotometric technique.

molar ratio, [Na-TMDTC] : $[Pb^{+2}]$	absorbance at 217.0 nm
0.4	0.16
0.8	0.14
1.2	0.10
1.6	0.05
2.0	0
2.4	0
2.8	0

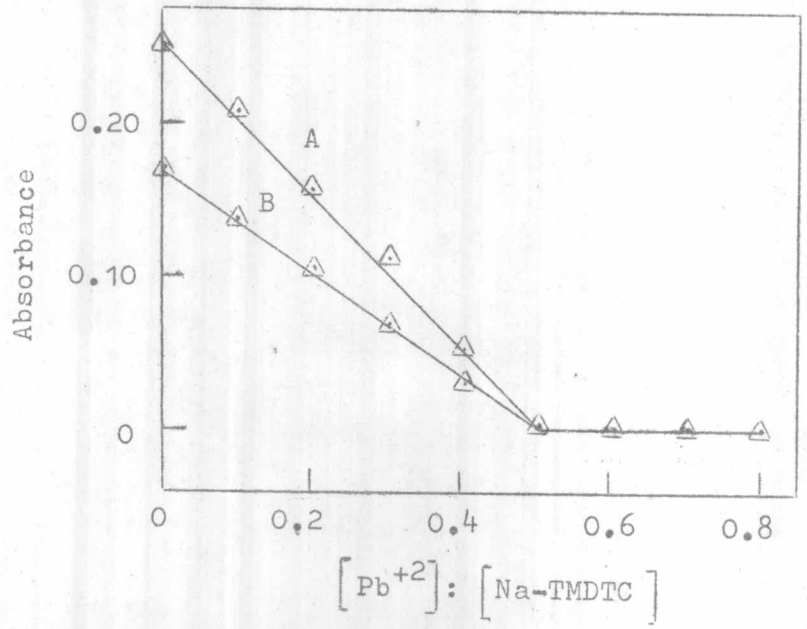


Figure 3 Molar ratio plot for solutions containing 4.00×10^{-5} M Na-TMDTC and various concentrations of Pb(II) ion in aqueous solution. The absorbances were measured at A) 276.0 nm and B) 253.0 nm.

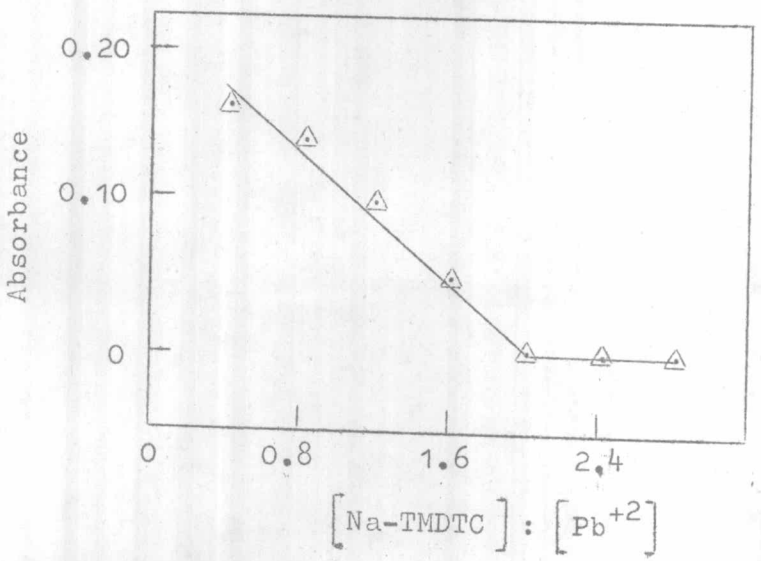


Figure 4 Molar ratio plot for solutions containing 40 $\mu g/cm^3$ lead (II) and various concentrations of Na-TMDTC.

The infrared absorption peaks of C=N vibration and C-S vibration of the pellet contained 70.00 mg KBr and 100.00 mg KBr showed non-linearities of absorbance to amounts of $Pb(TMDTC)_2$. As observed, the thinner of a pellet obtained the lost of pellet edge resulted. This should not affect the absorbance of $Pb(TMDTC)_2$ measured since the even thickness of pellet was used for all IR analysis.

From the IR spectra of 0.25-6.00 mg $Pb(TMDTC)_2$ in 225.00 mg KBr pellets, when the amount of $Pb(TMDTC)_2$ increased, the broadening of C=N peak resulted. In addition, the absorbance of $Pb(TMDTC)_2$ at this peak, both peak height and peak area measured, was not proportional to the amount of $Pb(TMDTC)_2$. Thus, the C=N peak cannot be used for quantitative analysis of lead in $Pb(TMDTC)_2$. The absorbance of C-S peak is proportional directly to the amount of $Pb(TMDTC)_2$ in the range of 0.25-4.00 mg $Pb(TMDTC)_2$ and a constant value is obtained as the amount of $Pb(TMDTC)_2$ is greater than 4.00 mg $Pb(TMDTC)_2$ (see Table 3 and Figure 6). This means that 0.25-4.00 mg $Pb(TMDTC)_2$ can be determined by IR C-S vibrational peak at 693 cm^{-1}. The smaller amount of $Pb(TMDTC)_2$, less than 0.25 mg $Pb(TMDTC)_2$, had been tried and the absorbance of C-S peak was too small to measured accurately. Therefore, the detection limit of this technique is 0.25-4.00 mg $Pb(TMDTC)_2$ or 0.10-1.66 mg Pb(II). This sensitivity obtained is lower than the one reported by reference 13, 10 µg Pb(II) at the metal-S peak. However, it is a precised method for determining Pb(II) as $Pb(TMDTC)_2$ at the C-S vibrational peak, 693 cm^{-1}.

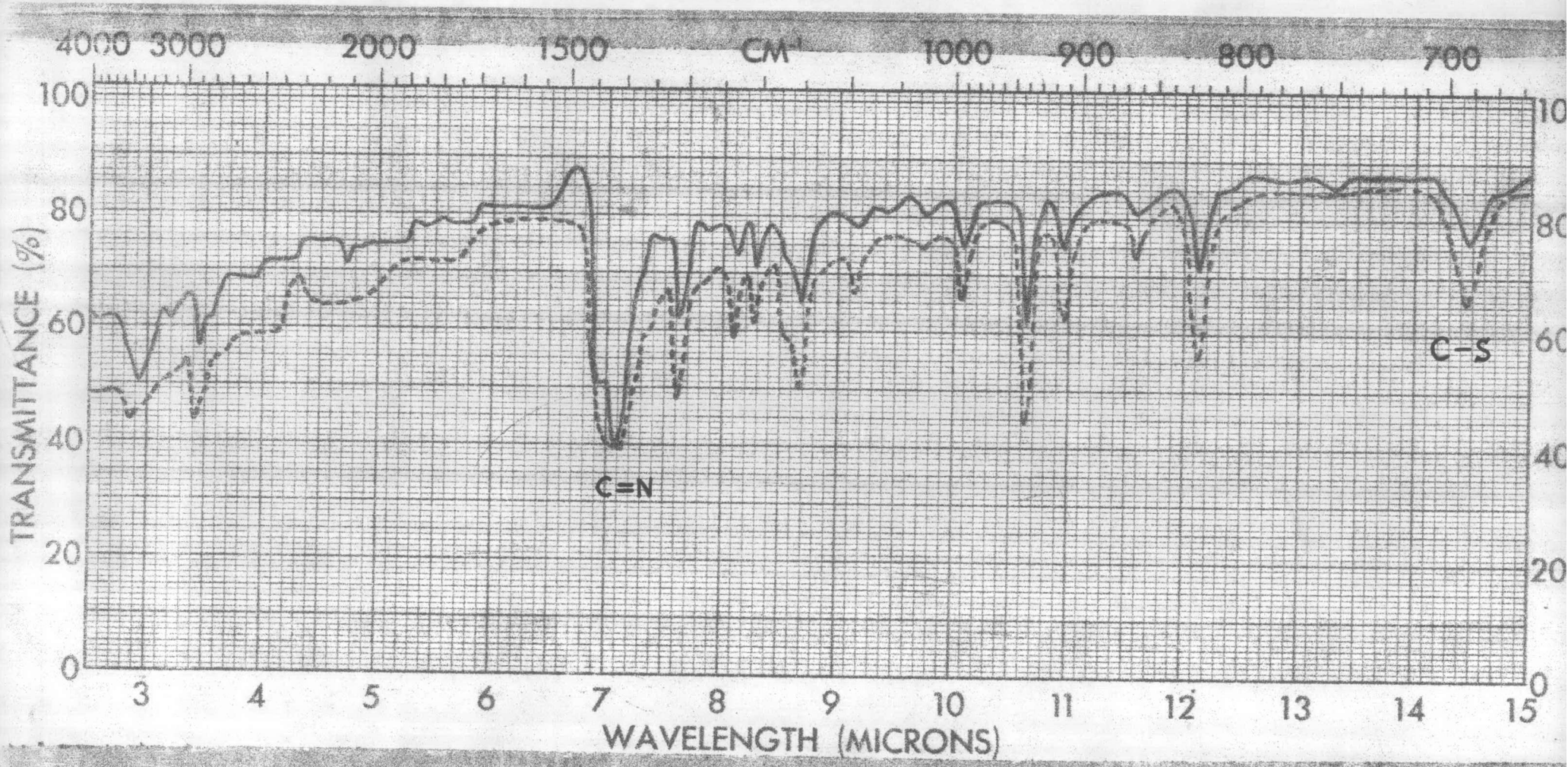


Figure 5 IR spectra of $Pb(TMDTC)_2$ in 225.00 mg KBr

—— for 1.00 mg $Pb(TMDTC)_2$

--- for 2.00 mg $Pb(TMDTC)_2$

Table 3 IR absorbance of various concentration of $Pb(TMDTC)_2$

$Pb(TMDTC)_2$, mg	Absorbance[a] at 693 cm^{-1}	No. of trials
0.25	0.030 ± 0	2
0.50	0.043 ± 0.003	2
0.75	0.055 ± 0	2
1.00	0.068 ± 0.005	4
1.60	0.101 ± 0.004	2
2.00	0.122 ± 0.002	3
2.50	0.135	1
3.00	0.168 ± 0.003	2
4.00	0.215 ± 0.005	2
5.00	0.220 ± 0.010	2
6.00	0.220	1

[a] with mean deviation

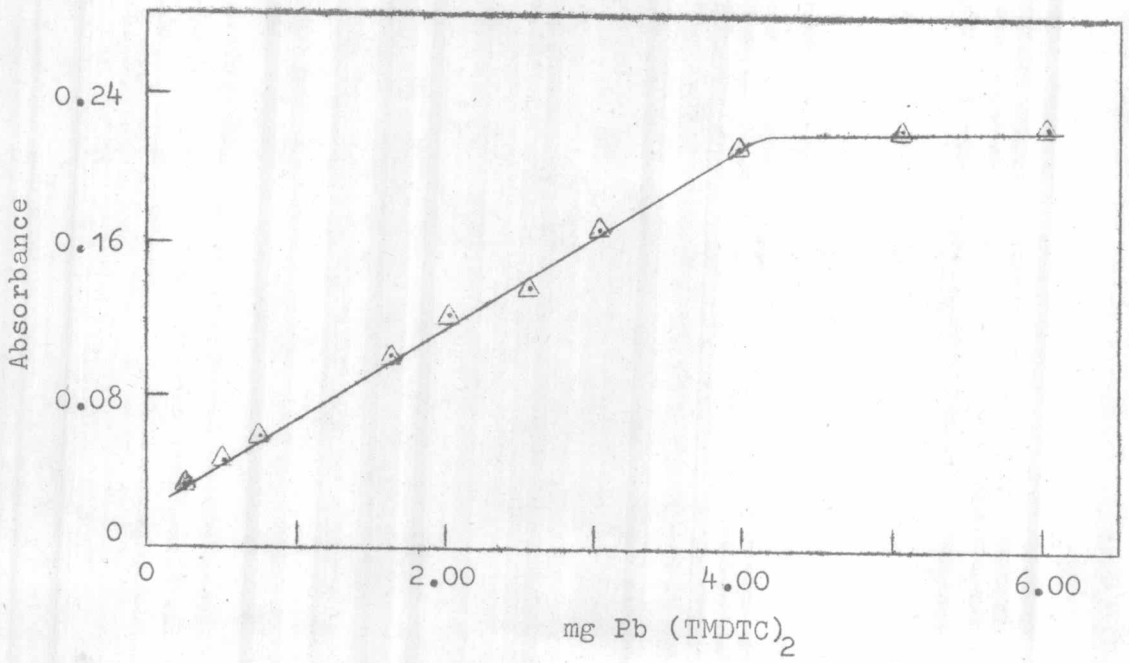


Figure 6 Quantitative study of $Pb(TMDTC)_2$ at 693 cm^{-1}, C-S stretching vibrational band.