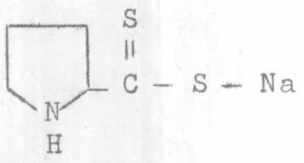
CHAPTER 3

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.

of 0.071 cm^2 was used as a working electrode (9, 10).

The pH measurements were obtained with a pH meter (Radiometer Copenhagen type PHM 28).

2.3 Procedure

2.3.1 $Pb(TMDTC)_2$ (lead-tetramethylenedithiocarbamate)

A 100.0 cm^3 of 8.00 X 10^{-2}M Na-TMDTC solution was slowly added to a 100.0 cm^3 of 3.00 X 10^{-2}M $Pb(NO_3)_2$ solution. The white precipitate of $Pb(TMDTC)_2$ was formed. The precipitate was filtered and recrystallized in chloroform. The needle shaped crystals obtained was dried at 110°C and stored in the desiccator.

2.3.2 Study of ligand number in Pb (II)-TMDTC

2.3.2.1 Ultraviolet spectrophotometric technique

A series of solutions which contained equal concentrations of Na-TMDTC (4.00 X 10^{-5}M) but different concentrations of lead (II) (4.00 X 10^{-6}M - 3.20 X 10^{-5}M) was prepared. The precipitate of Pb(II)-TMDTC was filtered out of each solution and the absorbance of this solution was measured at the wavelength 276.0nm and 253.0 nm where the Na-TMDTC solution absorbed.

2.3.2.2 Atomic absorption spectrophotometric technique

A series of solutions containing equal concentrations of lead (II) (40 $\mu g/cm^3$) and different concentrations of Na-TMDTC (16 $\mu g/cm^3$ - 112 $\mu g/cm^3$) was prepared. The precipitate of Pb(II)-TMDTC

was filtered out of each solution and the transmittance of this solution was then measured at the wavelength 217.0 nm where lead ion absorbed.

2.3.3 Infrared spectrophotometric studies

A 0.25 - 4.00 mg of Pb $(TMDTC)_2$ was weighed out and transferred to a clean dry motar. The dried KBr (225.00 mg) was gradually added, each addition should be about equal to the amount of total material in the motar. After each addition the mixture of KBr and Pb $(TMDTC)_2$ was ground thoroughly by using the pestle. The purpose of this grinding operation was to achieve thorough, homogeneous mixing of the sample and the KBr. The mixture was then transferred to a standard die (13 mm) and was spread evenly. The die was assembled, transferred to the press, and evacuated. A pressure of 15,000 lbs/inch^2 was applied to press the powder into a pellet. After releasing the pressure, the die was disassembled, and the pellet was removed and transferred to a pellet holder. The pellet holder was placed on the IR spectrophotometer and the spectrum was scanned from 4000 cm^{-1} to 667 cm^{-1}.

2.3.4 Anodic stripping voltammetry

2.3.4.1 Standard solutions

2.3.4.1.1 lead (II) solution

A 1.00 X 10^{-3} M Pb $(NO_3)_2$ solution was prepared by dissolving 0.03312 g of Pb $(NO_3)_2$ in 0.10 M HNO_3. The volume of this solution was made up to 100.0 cm^3 with 0.10 M HNO_3.

A series of standard solutions containing 2.00 X 10^{-7} - 1.50 X 10^{-6}M $Pb(NO_3)_2$ was also prepared by successive dilution of 1.00 X 10^{-3}M $Pb(NO_3)_2$ solution with 0.10 M HNO_3.

2.3.4.1.2 mercuric nitrate

A 0.01623 g of $Hg(NO_3)_2$ was dissolved in 0.10 M HNO_3 and the volume of the solution was made up to 500.0 cm^3 with 0.10 M HNO_3. This solution is 1.00 X 10^{-4}M $Hg(NO_3)_2$.

2.3.4.1.3 test solution

Test solution was prepared by mixing the appropriate concentration of $Pb(NO_3)_2$ standard solution in 1.00 X 10^{-5}M $Hg(NO_3)_2$ and 0.10 M in KNO_3 solution.

2.3.4.2 Voltammetric and stripping analysis

To obtain the deposition potential of Pb(II) solution, a cathodic voltammogram of Pb(II) solution must be recorded and the peak potential was measured.

Before the test solution was placed in the cell for either voltammetric or stripping analysis, the test compartment was washed twice with thrice deionized water. Then a 15.0 cm^3 test solution was transferred to the cell, and N_2 gas was bubbled through the solution for 5 minutes. Adjust N_2 gas inlet tube to let N_2 flow gently above and across solution surface. The GCE was then inserted in the test compartment.

For deposition of Pb(Hg), the strirrer motor was turned on, a potential of -0.80V was set and the electrolysis was proceeded for 20 minutes.

In cathodic and anodic voltammetry, the desired potential range, current sensitivity, scan rate and polarity were set on the instrument and the voltammogram was scanned.

2.3.5 Preparation of Pb(II) solution from tooth paste

Lead (II) in tooth paste was ashed by modifying the method for determination of lead in evaporated milk (11). A 25.0 g tooth paste sample was weighed in a porcelain basin. The sample was dried overnight at 120°C and placed in a 250°C furnace. The temperature of this furnace was raised up slowly (50 increments) to 350°C and held until smoking ceased. The temperature was then increased to 500°C in ca. 75 increments. The sample was ashed at this temperature for 6 hours and was removed from the furnace. After cooling down to room temperature the residue was dissolved in 20 cm^3 1 N HNO_3, warmed on the hot plate 2 - 3 minutes to aid solution. The solution was filtered and the filtrate was concentrated to 10 cm^3. In stripping analysis, pH of the filtrate was adjusted to 1.5 with either HNO_3 or ammonia. If any precipitate occurred, it was filtered and the solution was diluted with 0.10 M HNO_3 to give the total volume of 25.0 cm^3 in 1.00 X 10^{-5}M $Hg(NO_3)_2$ and 0.10 M in KNO_3. In infrared spectrophotometric technique, the filtrate was neutralized with ammonia and the precipitate was filtered out of the solution. The 2% Na - TMDTC solution was added to the filtrate to form $Pb(TMDTC)_2$. The precipitate of $Pb(TMDTC)_2$ was filtered and lead (II) in the sample was determined as mentioned in 2.3.3.