COPY NO. 40

TECHNICAL MEMORANDUM 2023

PREPARATION OF ANALYTICALLY PURE MONOBASIC COPPER SALICYLATE

BY

DANIEL R. SATRIANA

OCTOBER 1971

PICATINNY ARSENAL
DOVER, NEW JERSEY

The findings in this report are not to be construed as an official Department of the Army position.

DISPOSITION

Destroy this report when no longer needed. Do not return it to the originator.

Technical Memorandum 2023

PREPARATION OF ANALYTICALLY PURE MONOBASIC COPPER SALICYLATE

By

Daniel R. Satriana

October 1971

Approved for public release: distribution unlimited.

DA Project: 1M262302A211
AMCMS Code: 5222.11.58500

Propellants Division
Feltman Research Laboratories
Picatinny Arsenal
Dover, New Jersey

The citation in this report of the trade names of commercially available products does not constitute official indorsement or approval of the use of such products.

TABLE OF CONTENTS

ABSTRACT

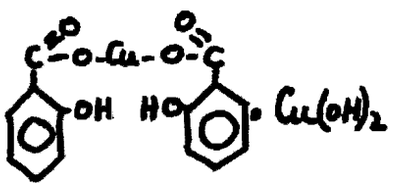
Preparation of analytically pure monobasic copper salicylate by two distinct synthetic routes and characterization of the products by infrared spectroscopy, X-ray diffraction and thermogravimetric analysis is described.

CONCLUSIONS

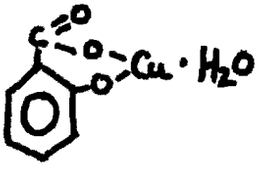
Analytically pure monobasic copper salicylate can be synthesized in excellent yield by reacting basic copper carbonate and salicylic acid in a 1 to 2.2 molar ratio. The pure monobasic salt can also be prepared by reacting copper hydroxide and salicylic acid in a 1 to 1 molar ratio. However, the yield, in this case, is comparatively low. Characterization of the product can be accomplished by infrared spectroscopy, X-ray diffraction, thermogravimetric analysis, and elemental analysis for copper, carbon and hydrogen.

RECOMMENDATIONS

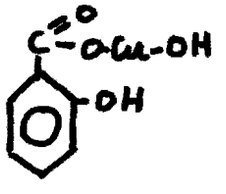
1. The following three structural formulas are possible forms of the monobasic copper salt:



I



II



III

Since the exact configuration of the salt has never been determined, it is recommended that further thermal and X-ray spectroscopic studies be conducted to resolve the presence of the hydrate form shown in formula II.

2. Evaluation of these salts in propellant formulations is also recommended.

3. Further investigation of the reaction of copper hydroxide and salicylic acid should be undertaken to improve the yield.

INTRODUCTION

A propellant composition containing a ballistic modifier composed of a mixture of dibasic lead beta resorcylate and monobasic copper salicylate exuded beta resorcylic acid when stored for extended periods of time. In addition to this exudation problem, inconsistent ballistics were encountered. Consequently, it was requested that methods be developed for preparing reproducibly pure salts of lead beta resorcylate and copper salicylate. As a result of this investigation, optimum conditions for synthesizing pure monobasic and dibasic lead beta resorcylate salts were developed[1]. In an effort to complete the objective, this report relates only to the synthesis and characterization of monobasic copper salicylate.

RESULTS AND DISCUSSION

Two types of copper salicylates have been reported in the literature; the monobasic and dibasic salts. Only two direct methods of preparation of the monobasic salt have been reported[2]; the treatment of hot solutions of salicylic acid with equimolar quantities of copper carbonate and the fusion of copper oxide with salicylic acid[3]. The commercial method of manufacture, however, has not been reported in the literature.

The British Explosive Research and Development Establishment has recently investigated the synthesis of monobasic copper salicylate[4]. The route to the basic salt explored was the reaction between copper sulfate, made basic by the addition of alkali, and a molar equivalent of sodium salicylate. Very careful control is required to give reproducible material, and the particular phase obtained depends not only on the temperature at which the reaction is carried out but also on the relative ratios of the reactants and their mixing.

In the initial stages of our investigation, only one approach was

1. Picatinny Arsenal Technical Memorandum 2021, dated October 1971
2. Babko, A. K., Shevchenko, L. L., Russ. J. Inorg. Chem., 9, 22(1964)
3. Italian Patent 611,678 (1960)
4. Fraser, R. T. M., et al, "The Preparation of Basic Copper Salicylate, ERDE Report 11 (1967).

considered; the reaction of basic copper carbonate and salicylic acid. Several experiments were conducted in an effort to determine optimum conditions. The various procedures tried and their products are compared in Table 1. This table also contrasts the commercial products of National Lead Company and Shepherd Product with the salts prepared in the laboratory at Picatinny. Excellent yield and purity can be obtained by reacting basic copper salicylate and salicylic acid in a 1 to 2.2 molar ratio. The reaction can be conducted in either water or ethyl alcohol, at room temperature or 50° to 60°C. Less foaming, however, occurs when aqueous ethanol is used in the reaction. This could be important in large scale preparation since processing operations may be hampered by excessive foaming.

Purity of the products was determined by analyzing the mixture for copper, carbon and hydrogen. These results indicate that analytically pure monobasic salicylate can be prepared by the method described.

The monobasic salt was also synthesized, from a completely different approach, by reacting copper hydroxide and salicylic acid in a 1 to 1 molar ratio. Although the yield was low (37.5%), purity based on the elemental analysis corresponded to the calculated values. Reaction conditions and experimental results are shown in Table 1 (Sample 71-1).

The various salts prepared in the laboratory were also characterized by X-ray diffraction and infrared spectroscopy. The spectra are shown in Figures 1-24.

Examination of the National Lead Company product shows that the major intensity peaks occur at the following 2θ angles; 9.2, 17.9, 22.4, and 29.4. In contrast, the major peaks for the Shepherd product occur at 5.9, 17.0, 17.9, 24.8 and 25.8. Comparison of the several spectra showed that most of the salts are similar to the National Lead Company product. Only Samples 75-1 and 76-1 resemble the Shepherd product.

Differences in the infrared spectra of the various salts are less evident. There is, however, in the region of characteristic OH group frequency (3600-3500 cm^{-1}), a broadening of the band toward the lower frequency in the samples resembling the National Lead Company product. This may be attributed to the phenomenon of hydrogen bonding.

The thermal behavior of the various basic copper salicylate salts that had been prepared in the laboratory were also studied. The samples were initially dried to constant weight at 50°-60°C. In general, there was an additional loss in weight of 0.1% to 0.3% upon further drying at 100°C. However, Samples 75-1 and 76-1 lost 3.8% and

5.5%, respectively; the Shepherd Product sample lost 5.1%. Also, a color change (green to brown) was observed in the three samples. Color reversion, however, accompanied a gain in weight after exposure to the atmosphere. It can probably be assumed that water is responsible for these color changes.

Thermogravimetric analysis of the various salts actually shows three regions in which loss in weight occurs. At first, as the temperature is raised at a rate of 20°C. per minute to 145°C, there is a gradual loss in weight of about 2%. This is followed by a further loss of 5-6% until 175°C. is reached. Exothermic decomposition finally takes place near 275°C. and is completed at 450°C. Total weight loss is 56%. Sample 79-1, representing a typical thermogravimetric profile of the samples resembling the National Lead Company product, is shown in Figure 25. Thermal decomposition curves for the commercial products are shown in Figures 26 and 27.

EXPERIMENTAL PROCEDURES

Preparation of Basic Copper Salicylate from Basic Copper Carbonate

The following procedures may be conducted in water or in mixed solvent.

Elevated Temperature (50-60°C.)

30.4g (0.22 mole) of salicylic acid is dissolved in 450 ml of 33% ethyl alcohol. The solution is heated to 50-60°C. and 23.9g (0.1 mole) of basic copper carbonate is added. The slurry is stirred for 5 hours while the temperature is maintained at 50-60°C. The solid is separated by filtration, washed several times with cold 33% ethyl alcohol solution, and finally dried in the oven at 50°C. The weight of the product is 41.0g. The elemental analysis values are shown in Table 1 (Sample 75-1).

At Room Temperature

A slurry of 23.9g (0.1 mole) of basic copper carbonate, 30.4g (0.22 mole) of salicylic acid, and 800 ml water is stirred for approximately 18 hours at room temperature. The solid is filtered; washed with water, alcohol, and acetone; then dried in the oven at 50°C. The weight of the product is 39.4g or 90.5% yield based on the amount of basic copper carbonate used in the reaction. The elemental analysis values are shown in Table 1 (Sample 79-1).

Preparation of Basic Copper Salicylate from Copper Hydroxide

A slurry of 9.75g (0.1 mole) of copper hydroxide, 13.8g (0.1 mole) of salicylic acid, and 400 ml of water was stirred at 60-65°C. for five hours. The solid was filtered, washed several times with water, then washed several times with acetone, and finally dried in the oven at 50°C. The product weight was 8.2g or 37.5% yield, based on the amount of copper hydroxide used in the reaction. The elemental analysis was: Found - Cu-28.65%, C-38.71%, H-2.75%; Calculated - Cu-29.19%, C-38.63%, H-2.78%.

Infrared Analysis

Infrared spectra were obtained by means of the KBr pellet technique with a Perkin-Elmer, Model 621, Grating Infrared Spectrophotometer. The pellets, containing approximately 0.5% sample, were pressed to 0.7 mm thickness.

X-Ray Analysis

The diffractograms were taken with a Norelco X-Ray Diffractometer, using copper radiation and a nickel filter. The samples were mounted in an aluminum holder and scanned at 0.5° per minute.

Thermogravimetric Analysis

Loss in weight was determined with a 950 DuPont Gravimetric Analyzer under the following conditions:

Sample Size: 7-8 mg
Heating Rate: 20°C/min.
Atmosphere: Air

TABLE 1

EFFECTS OF REACTION CONDITIONS ON THE SYNTHESIS OF BASIC COPPER SALICYLATE

Sample No.	Metal Component	Mole Ratio (MC/SAL)	Solvent Medium	Temp. (°C)	Time (Hrs)	Yield (%)	Analysis Cu (%)	Analysis C (%)	Analysis H (%)	Remarks
69-1	Basic $CuCO_3$	1/2.2	Water	50-60	2	89.0	31.15	35.85	2.66	I.R. and X-ray resembles Nat'l Lead Product Impure Monobasic Salt
70-1	Basic $CuCO_3$	1/2.2	50% Ethanol	50-60	4	82.3	33.55	32.75	2.62	I.R. and X-ray resembles Nat'l Lead Product Impure Monobasic Salt
71-1	$Cu(OH)_2$	1/1	Water	60-65	5	37.5	28.65	38.71	2.75	I.R. and X-ray resembles Nat'l Lead Product
72-1	$Cu(OH)_2$	1/2	Water	60-65	5	----	11.10	51.95	3.66	Impure Normal Copper Salicylate
74-1	Basic $CuCO_3$	1/3	33% Ethanol	50-60	5	86.3	28.94	38.08	2.67	I.R. and X-ray resembles Nat'l Lead Product
75-1	Basic $CuCO_3$	1/2.2	33% Ethanol	50-60	5	94.3	31.13	37.52	2.88	I.R. and X-ray resembles Shepherd Product
76-1	Basic $CuCO_3$	1/2.2	Water	Room	18	95.5	31.16	38.04	2.80	I.R. and X-ray resembles Shepherd Product
77-1	Basic $CuCO_3$	1/2.2	16.5% Ethanol	Room	18	95.4	29.66	37.27	2.77	I.R. and X-ray resembles Nat'l Lead Product

TABLE 1 (Con't)

EFFECTS OF REACTION CONDITIONS ON THE SYNTHESIS OF BASIC COPPER SALICYLATE

Sample No.	Metal Component	Mole Ratio (MC/SAL)	Solvent Medium	Temp. (°C)	Time (Hrs)	Yield (%)	Analysis Cu (%)	Analysis C (%)	Analysis H (%)	Remarks
78-1	Basic $CuCO_3$	1/2.8	Water	Room	18	77.5	28.90	38.56	2.78	I.R. and X-ray resembles Nat'l Lead Product
79-1	Basic $CuCO_3$	1/2.2	Water	Room	18	90.5	29.66	38.83	2.78	I.R. and X-ray resembles Nat'l Lead Product
National Lead (P-203-434-5-6)							29.42	37.51	2.71	Commercial Product
Shepherd (S-70)							28.98	37.42	2.63	Commercial Product
			Basic Copper Salicylate				29.19	38.63	2.78	Calculated
			Normal Copper Salicylate				18.81	49.78	2.98	Calculated

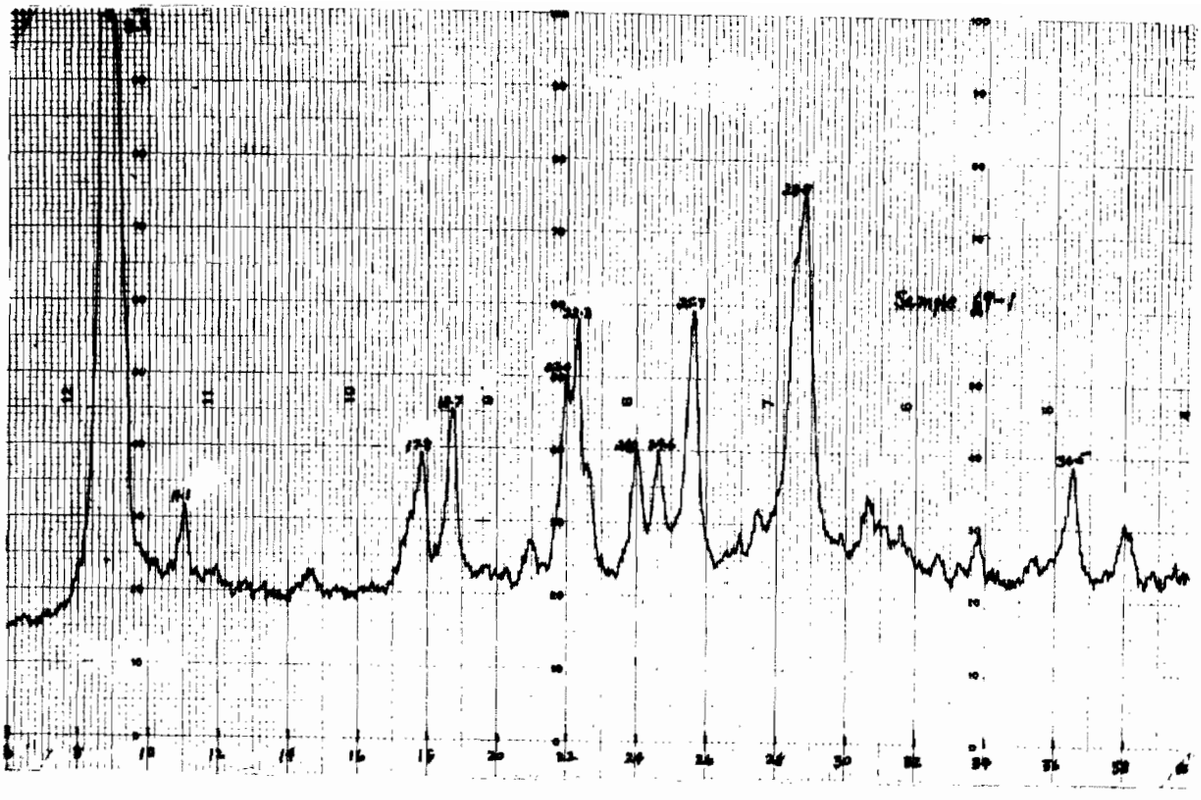


Figure 1 X-ray Diffraction Pattern of Sample 69-1

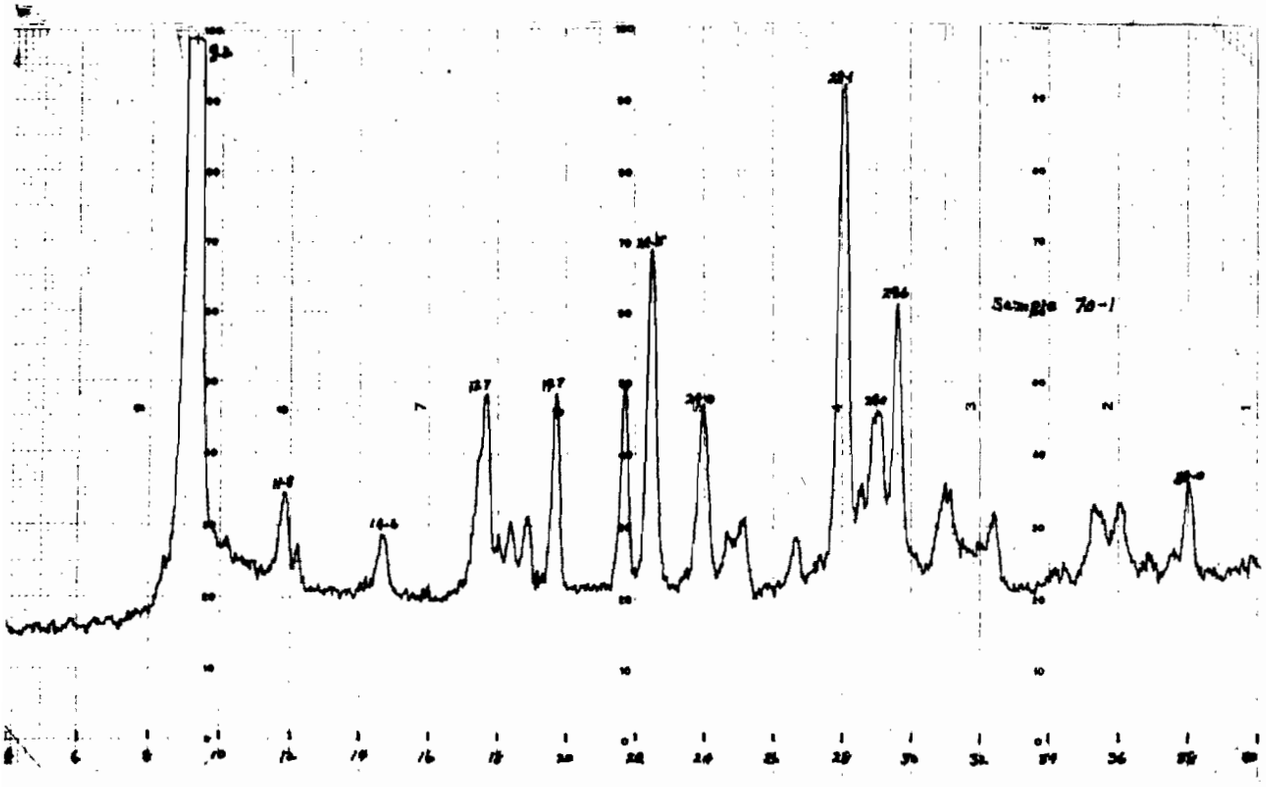


Figure 2 X-ray Diffraction Pattern of Sample 70-1

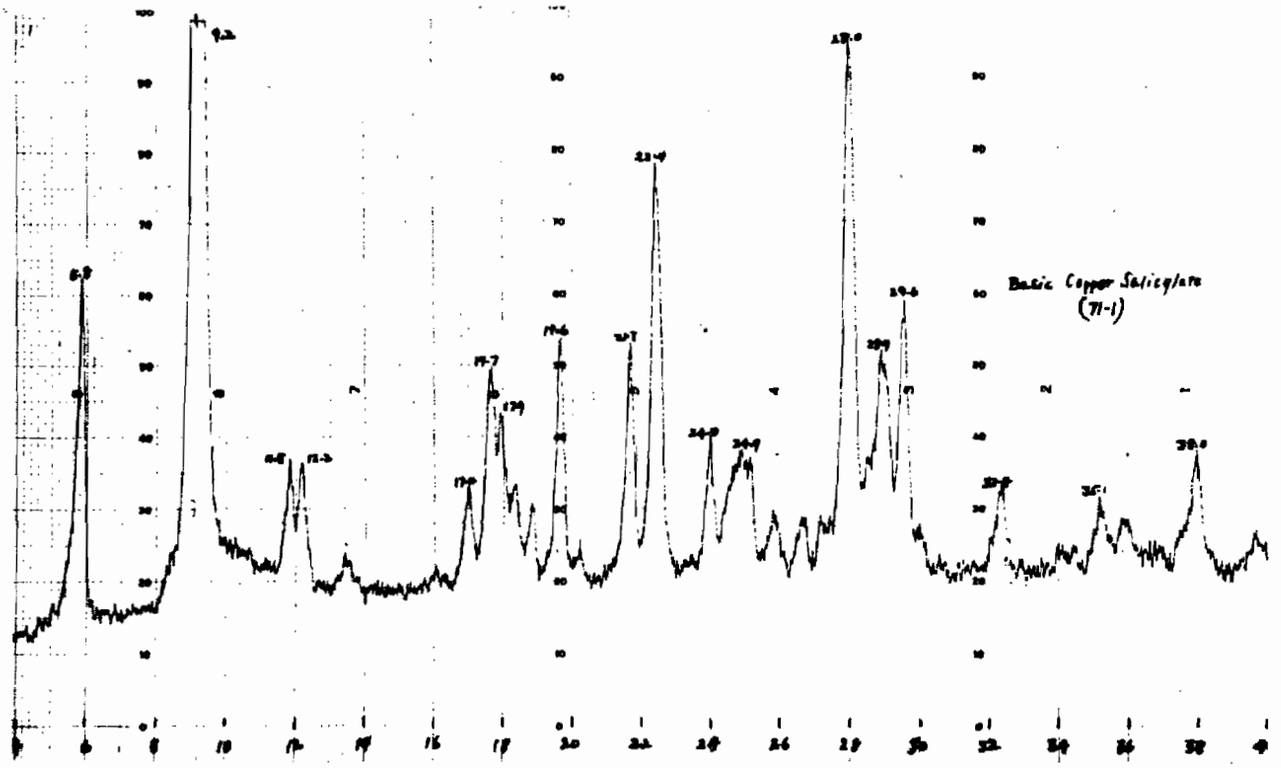


Figure 3 X-ray Diffraction Pattern of Sample 71-1

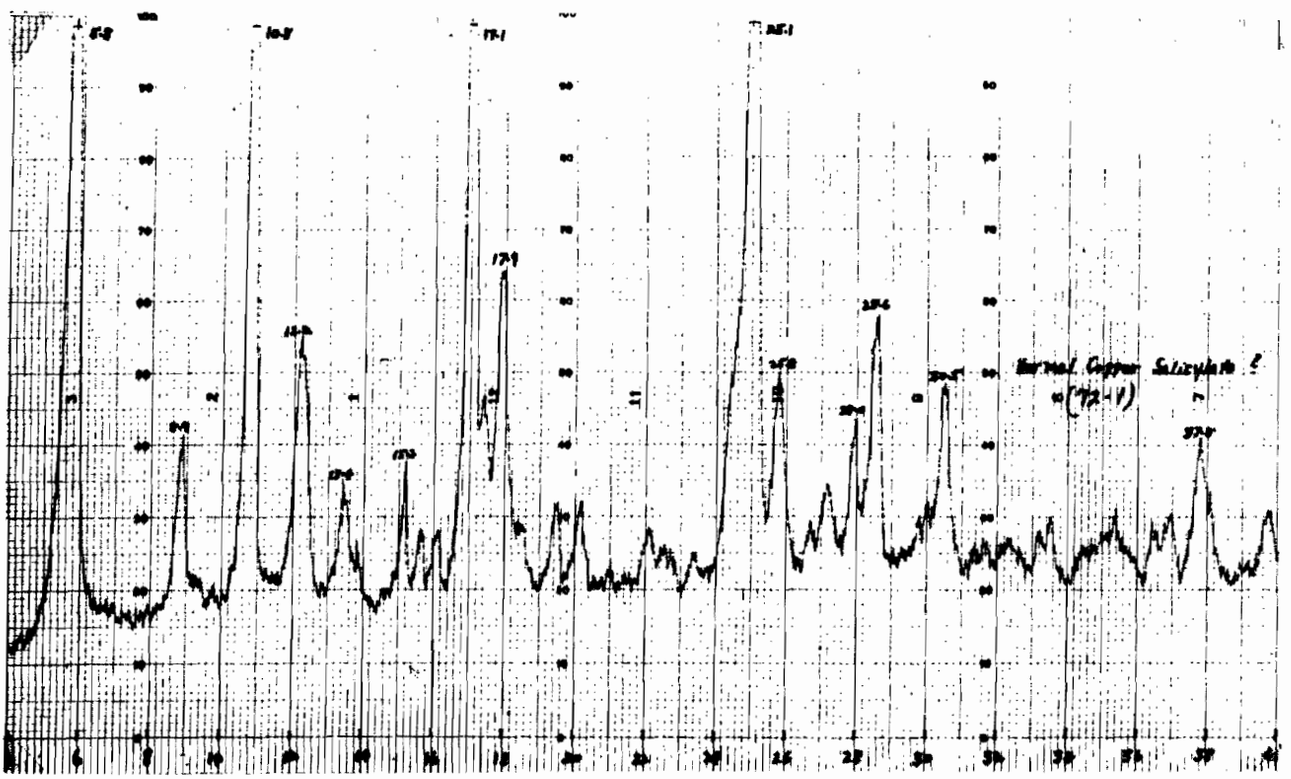


Figure 4 X-ray Diffraction Pattern of Sample 72-1

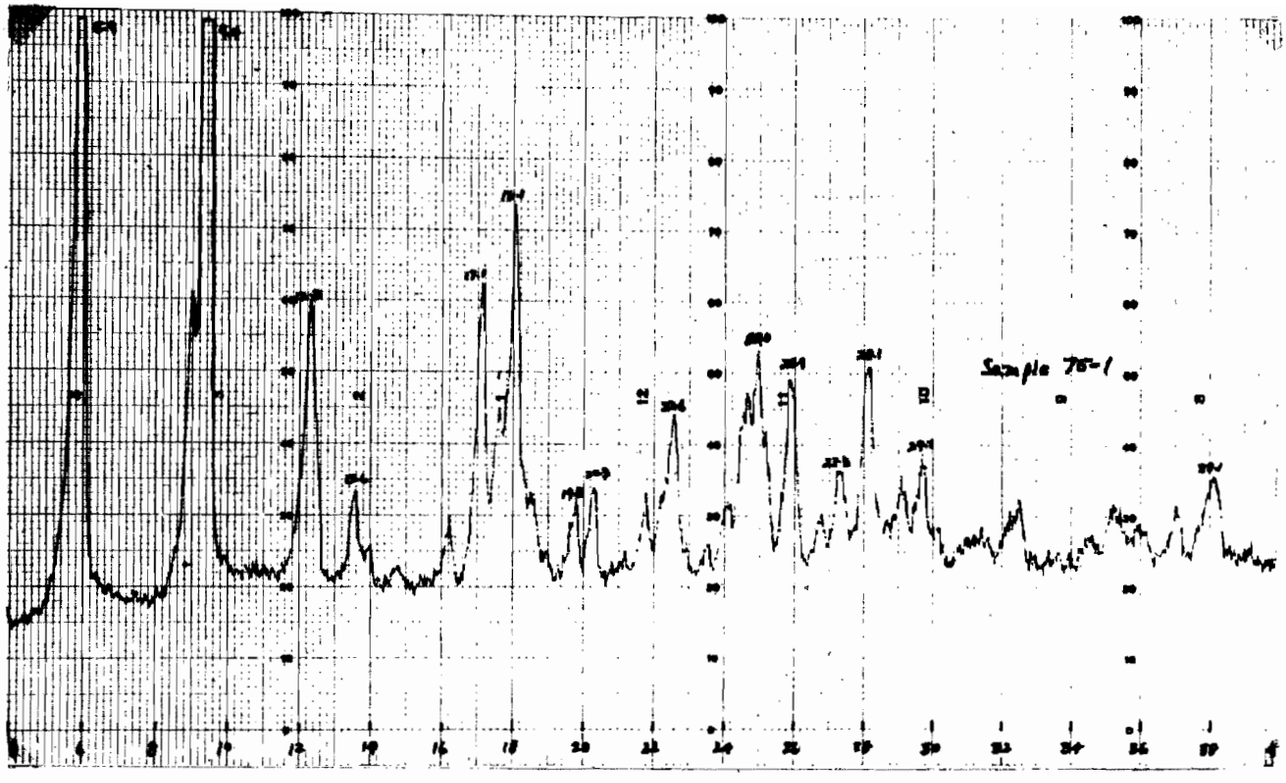


Figure 5 X-ray Diffraction Pattern of Sample 75-1

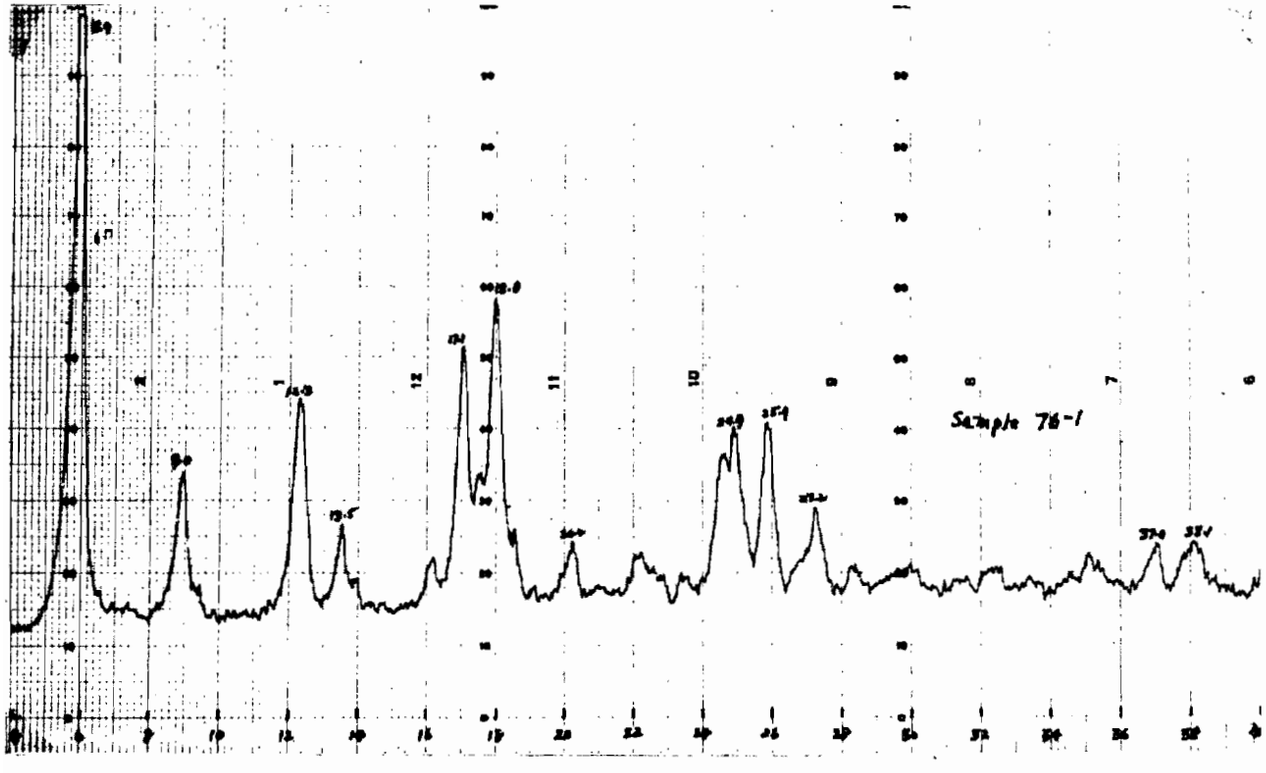


Figure 6 X-ray Diffraction Pattern of Sample 76-1

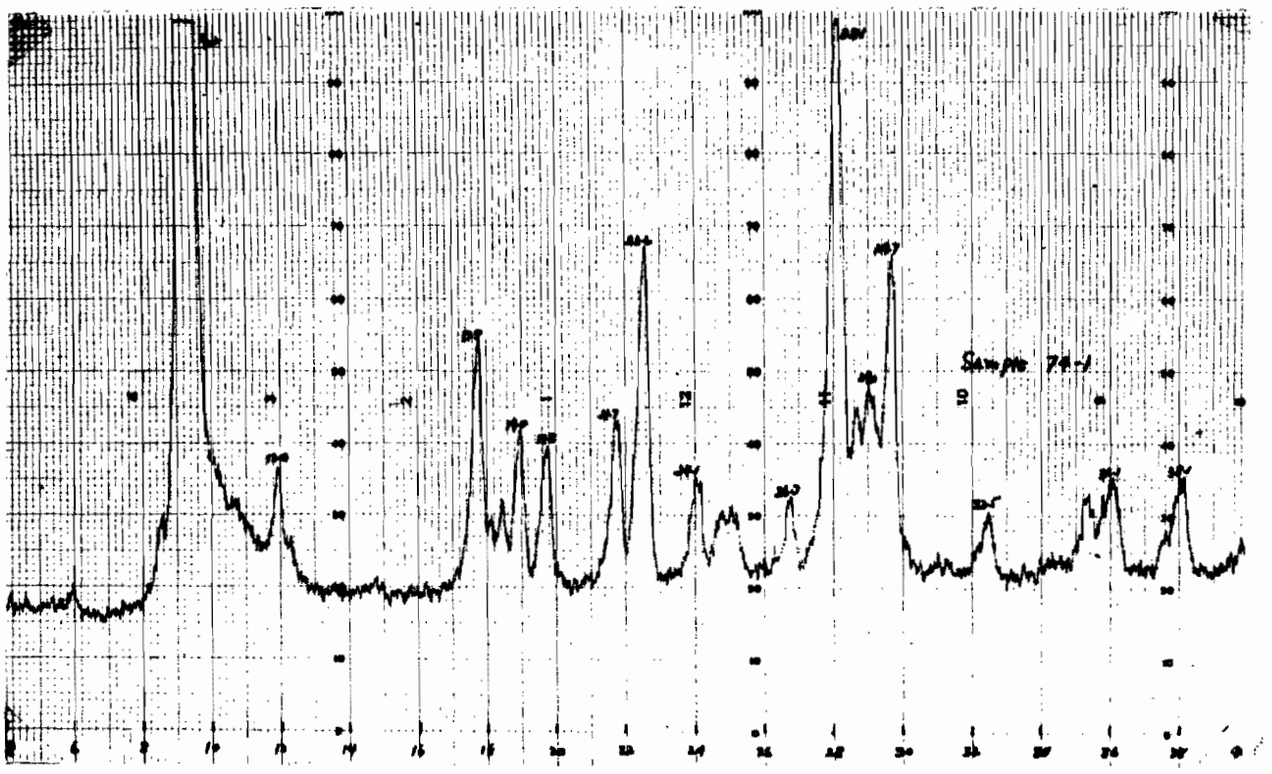


Figure 7 X-ray Diffraction Pattern of Sample 74-1

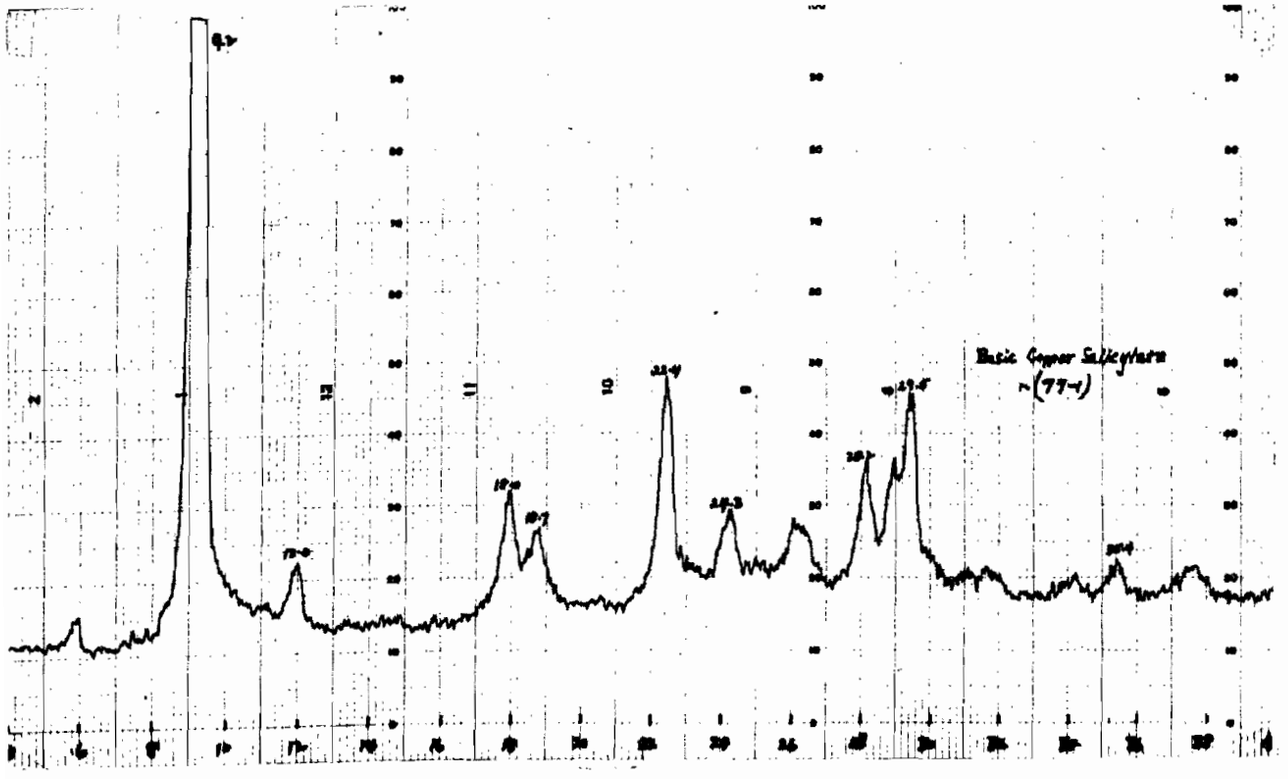


Figure 8 X-ray Diffraction Pattern of Sample 77-1

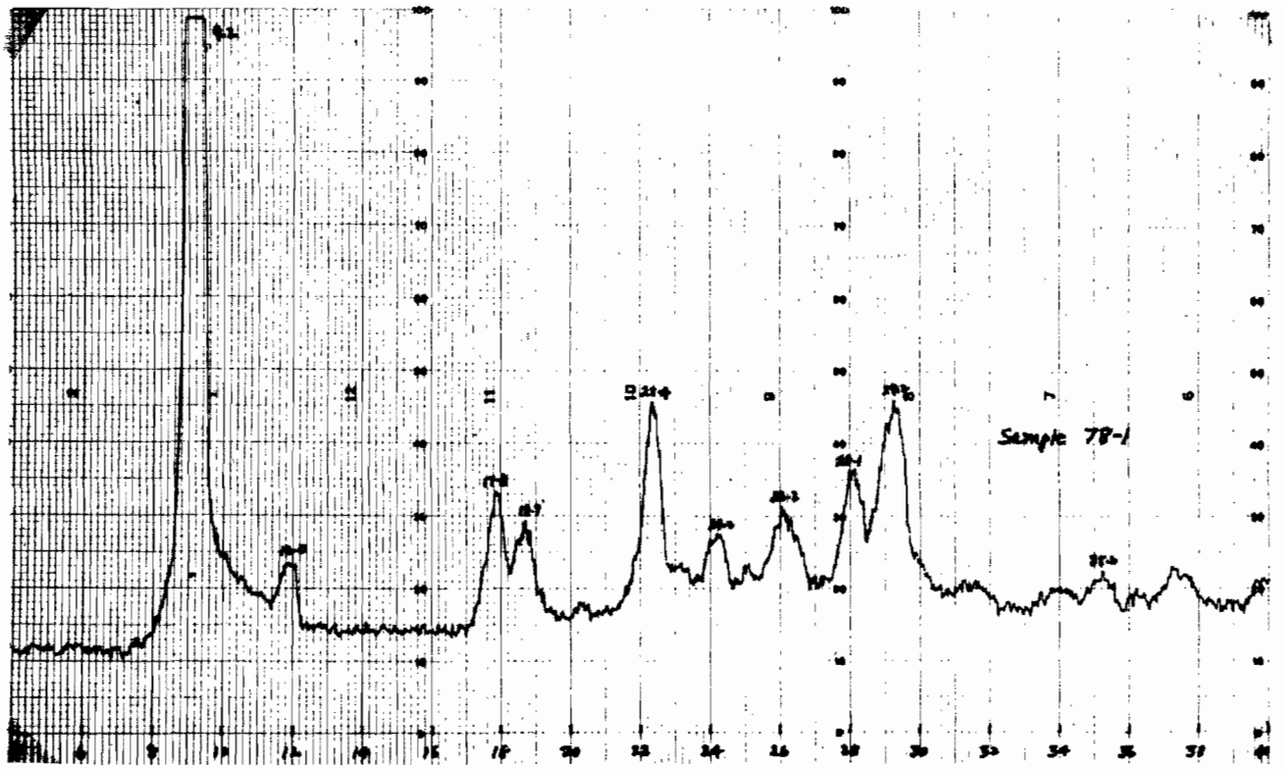


Figure 9 X-ray Diffraction Pattern of Sample 78-1

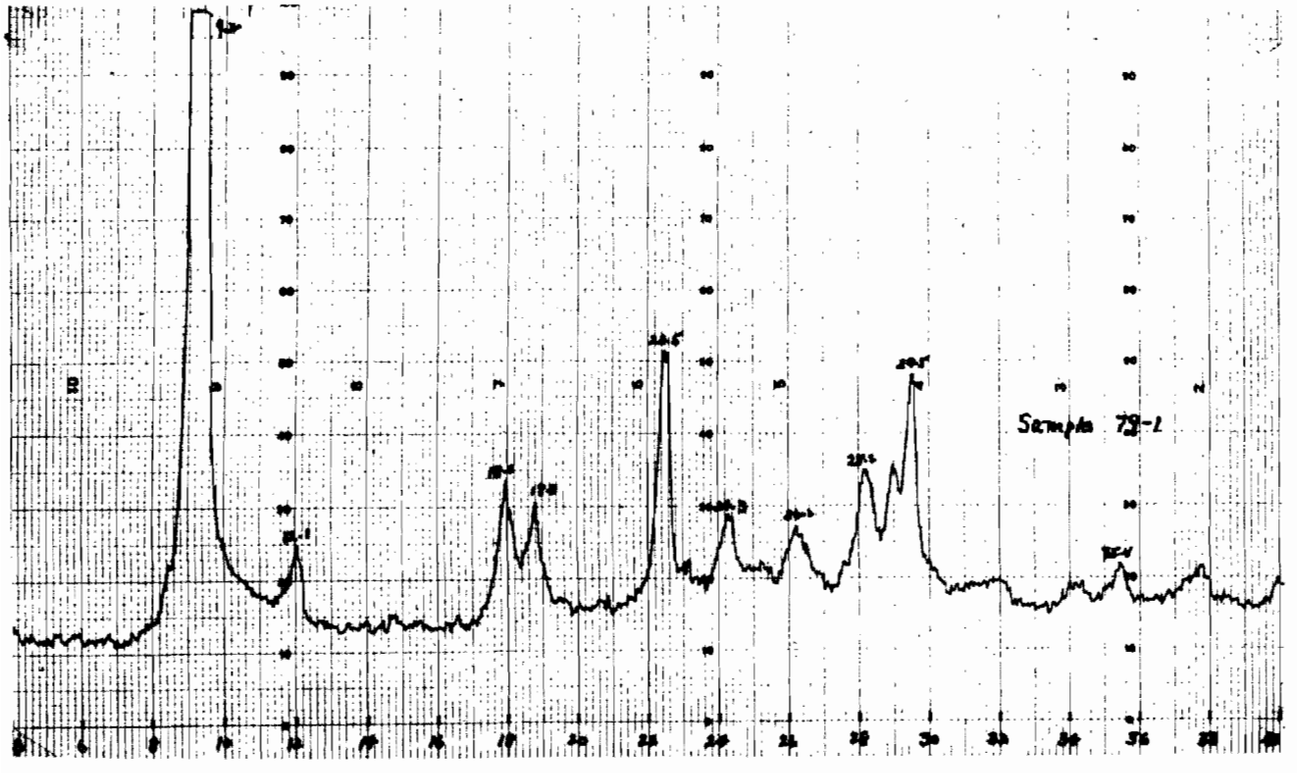


Figure 10 X-ray Diffraction Pattern of Sample 79-1

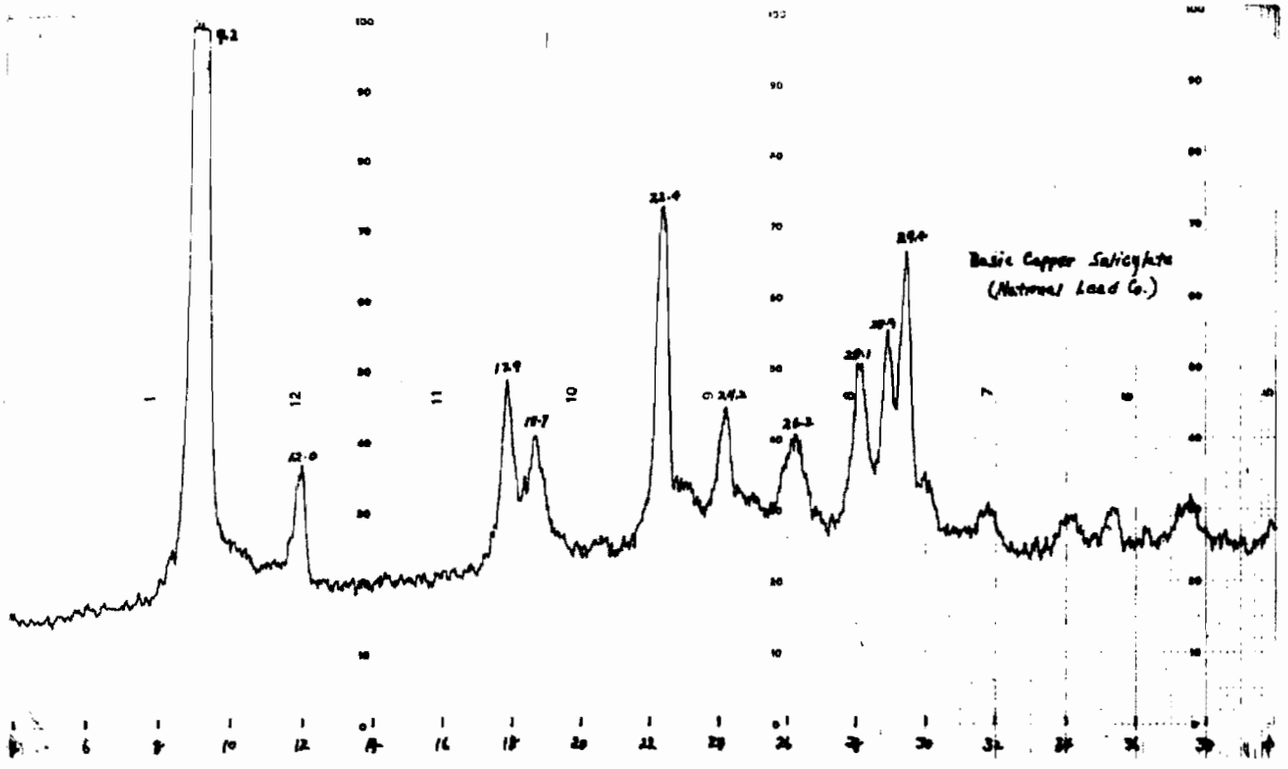


Figure 11 X-ray Diffraction Pattern of National Lead Co. Product

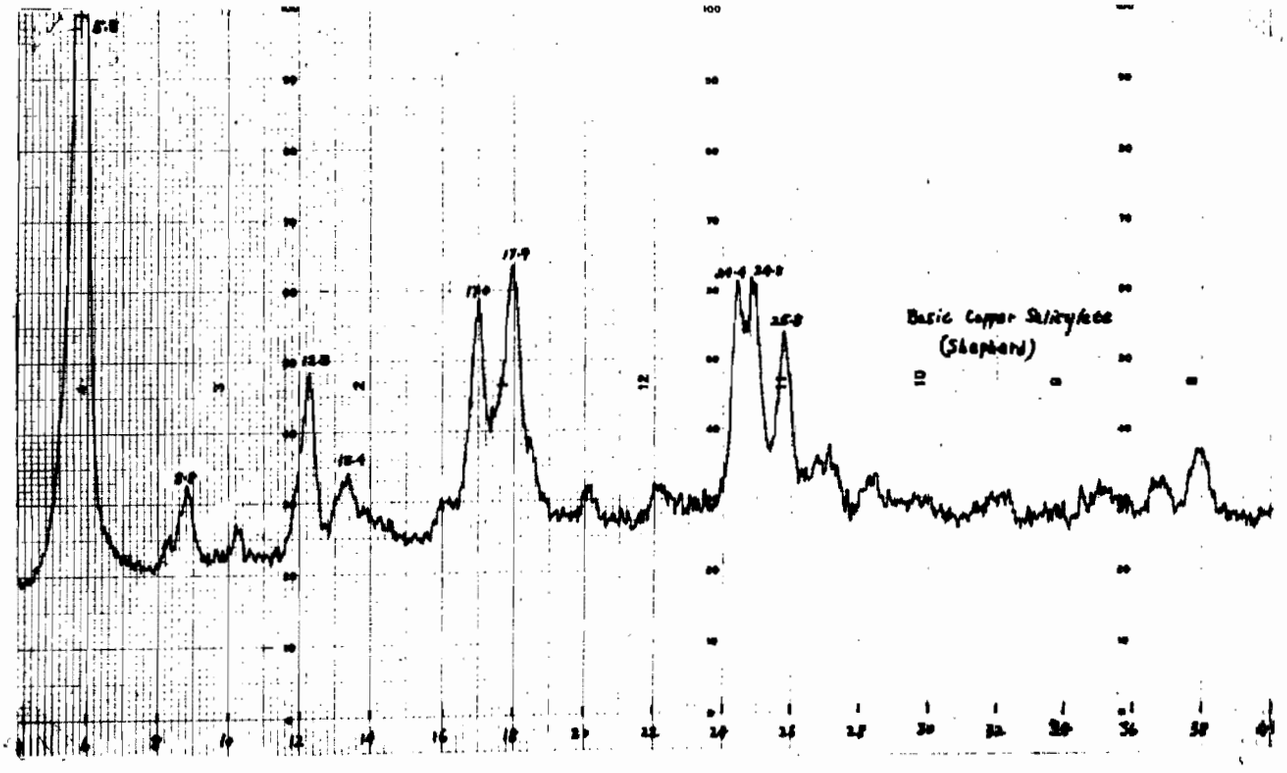


Figure 12 X-ray Diffraction Pattern of Shepherd Product

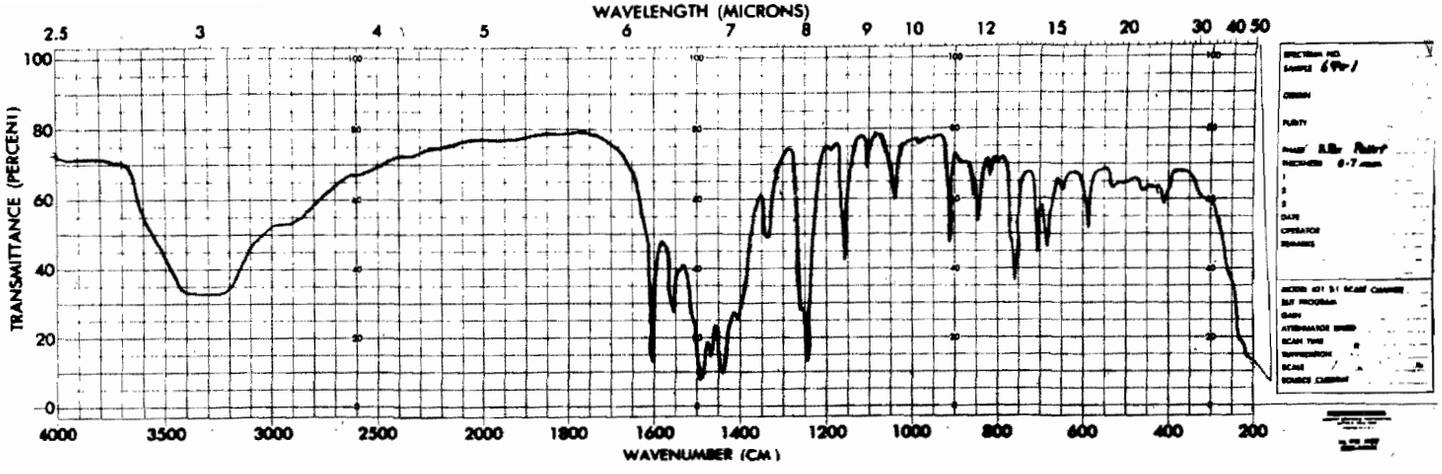


Figure13 Infrared Spectrum of Sample 69-1

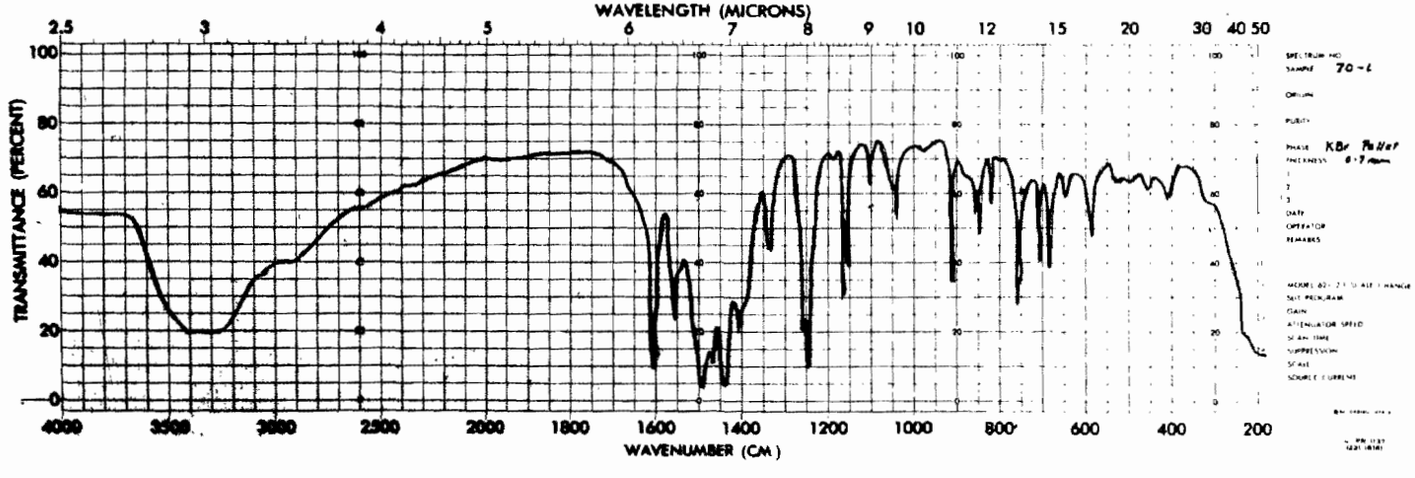


Figure14 Infrared Spectrum of Sample 70-1

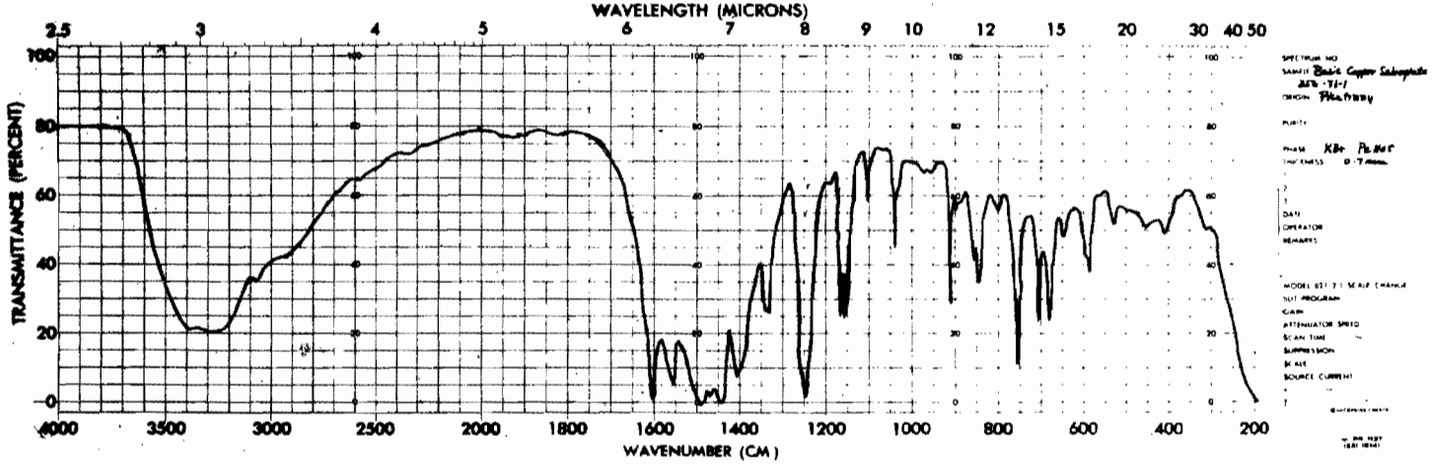


Figure 15 Infrared Spectrum of Sample 71-1

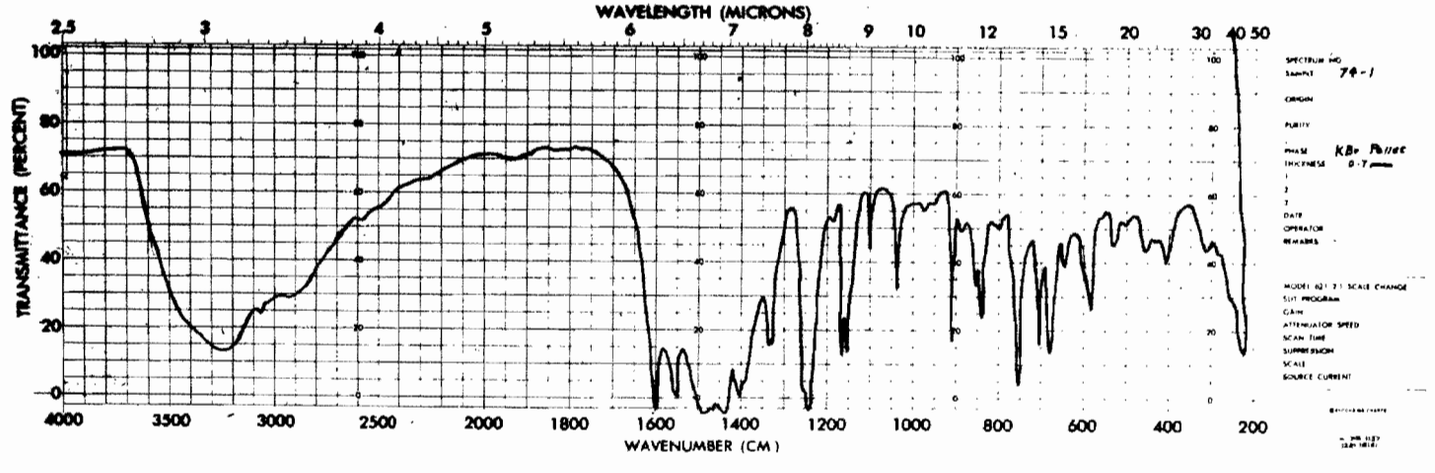


Figure 16 Infrared Spectrum of Sample 74-1

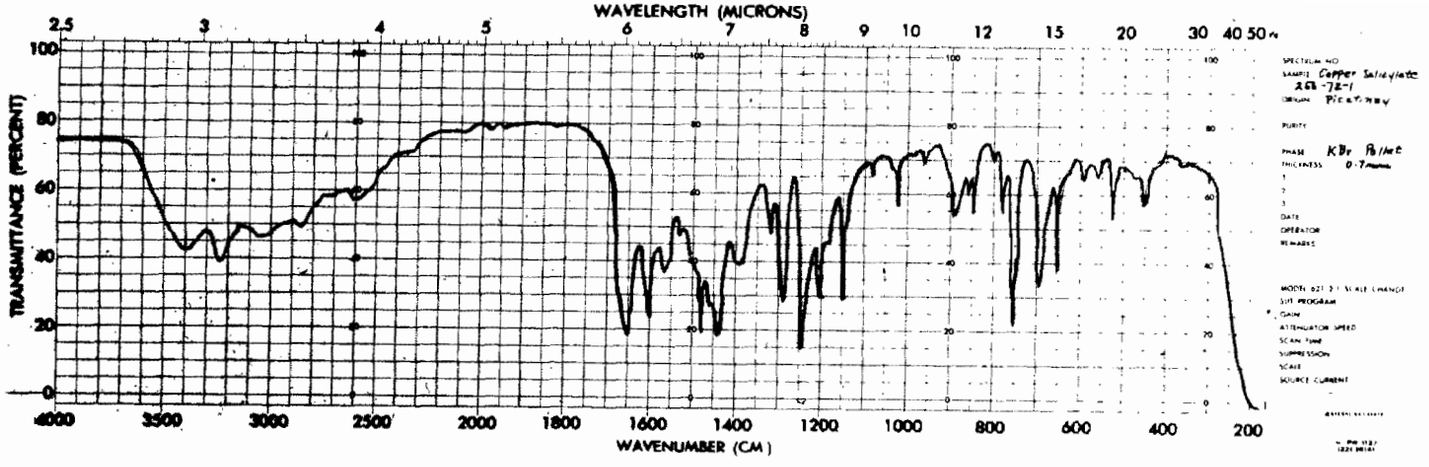


Figure 17 Infrared Spectrum of Sample 72-1

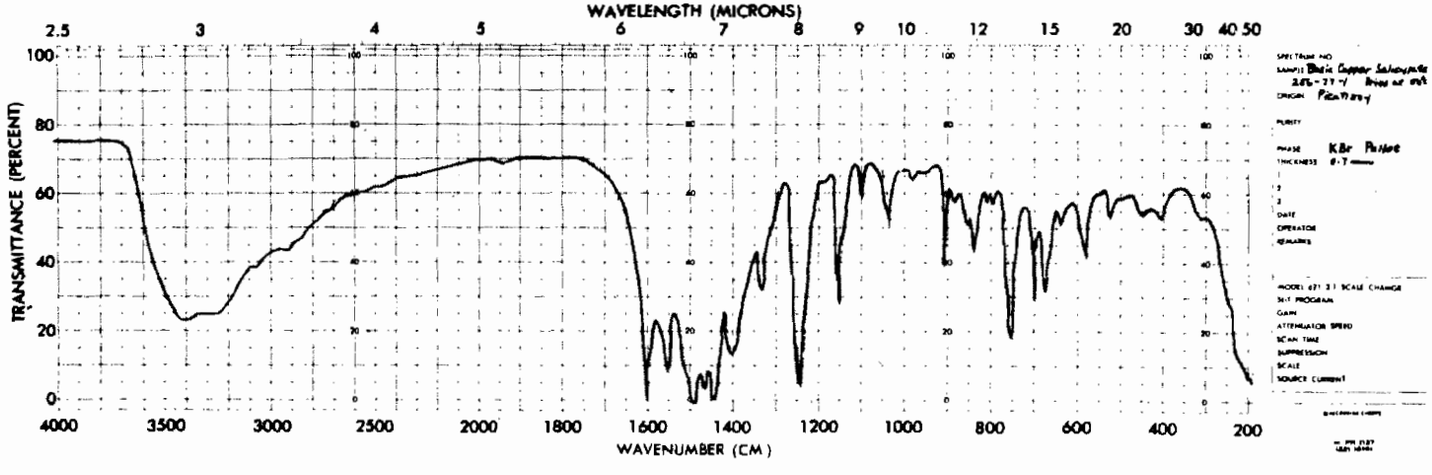


Figure 18 Infrared Spectrum of Sample 77-1

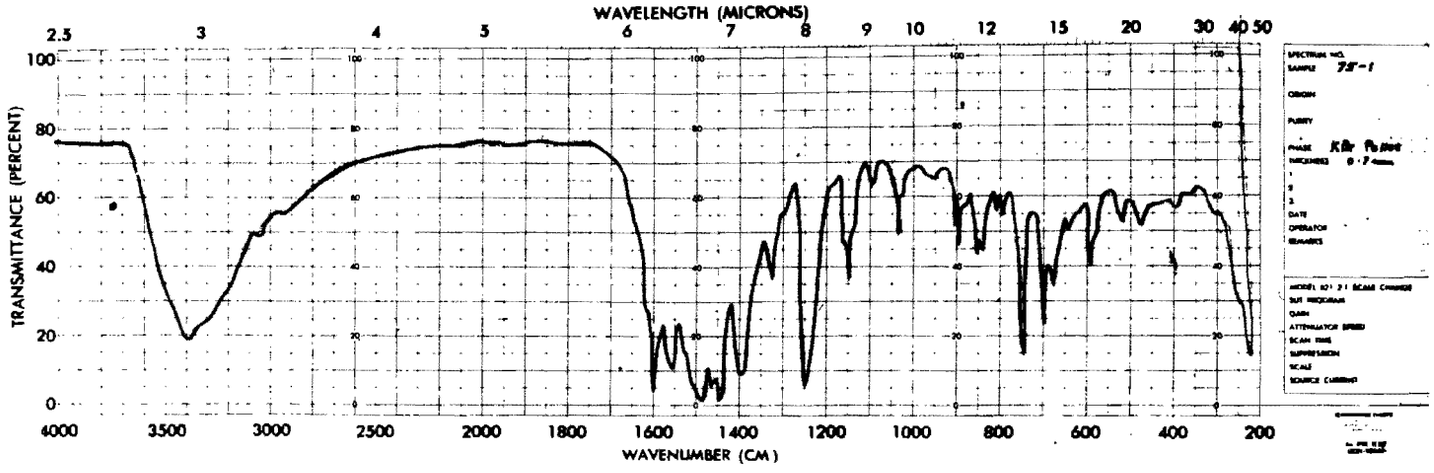


Figure 19 Infrared Spectrum of Sample 75-1

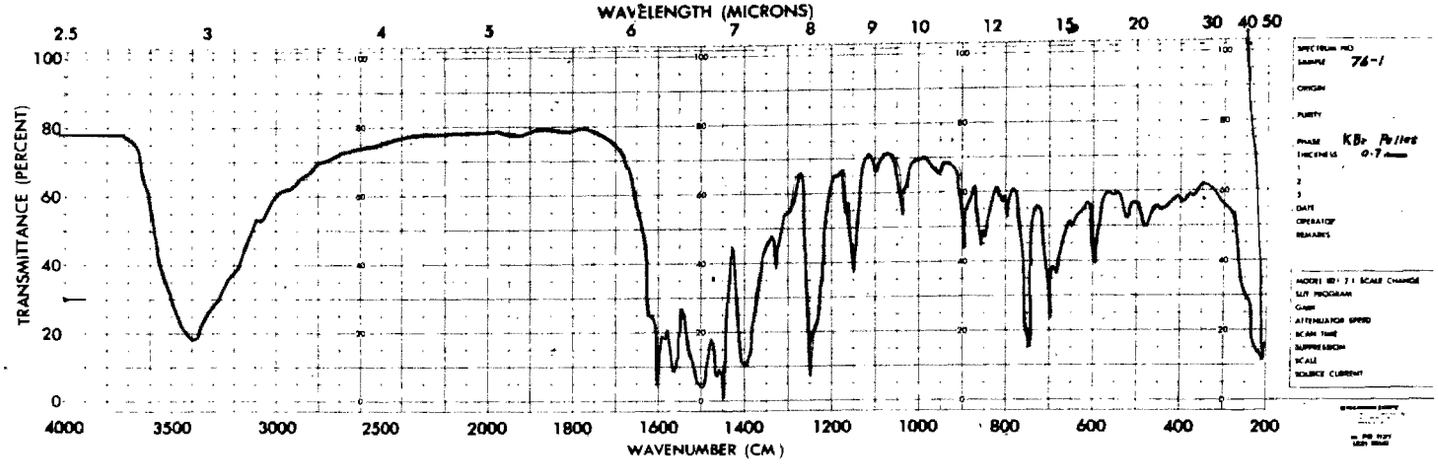


Figure 20 Infrared Spectrum of Sample 76-1

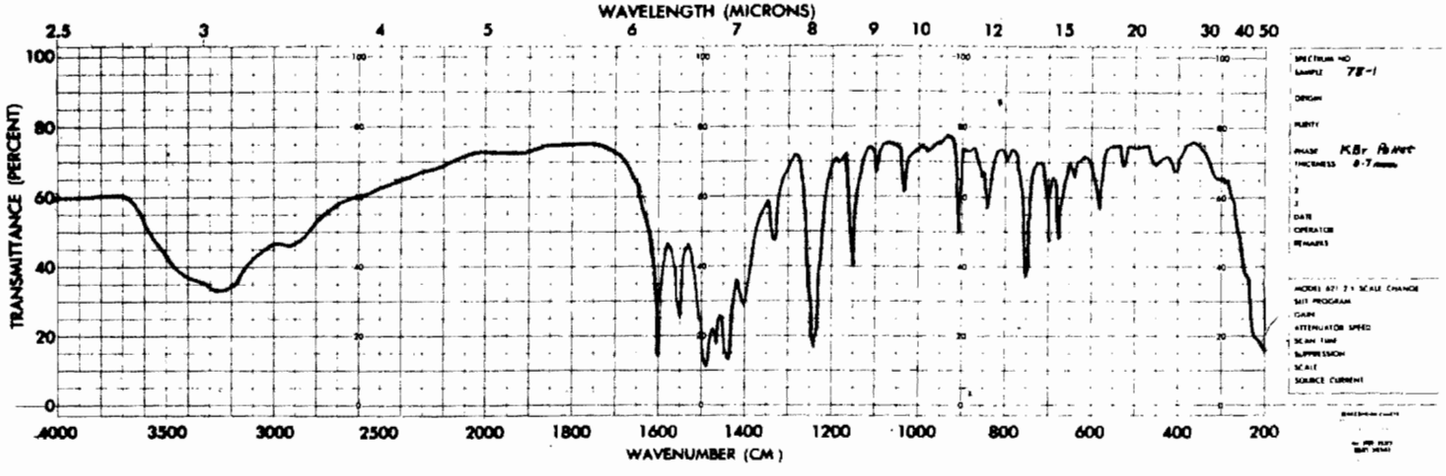


Figure 21 Infrared Spectrum of Sample 78-1

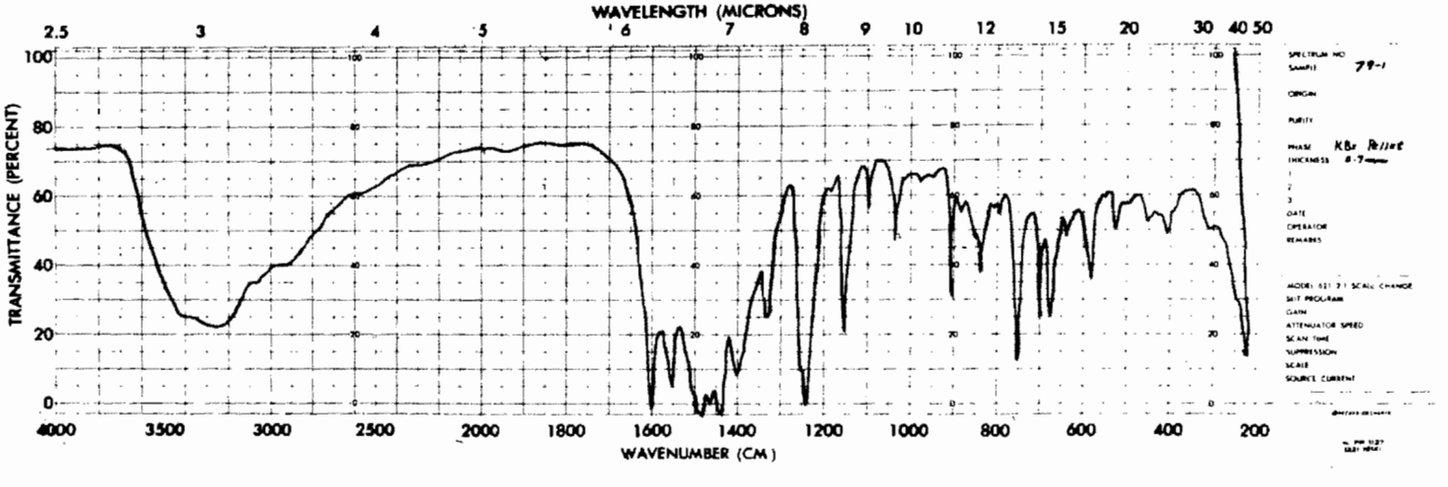


Figure 22 Infrared Spectrum of Sample 79-1

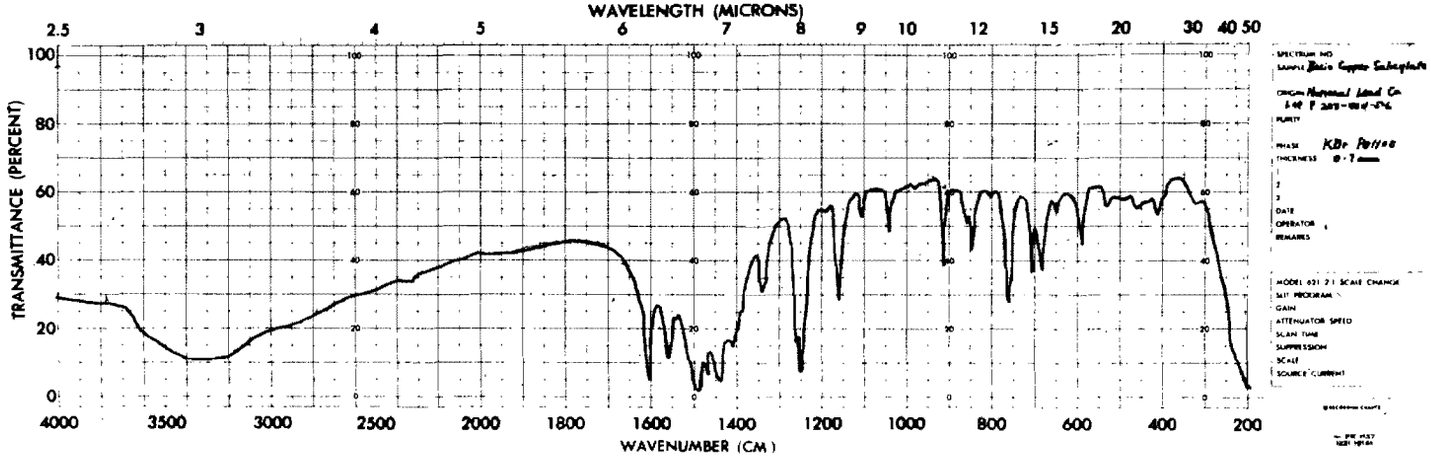


Figure 23 Infrared Spectrum of National Lead Co. Product

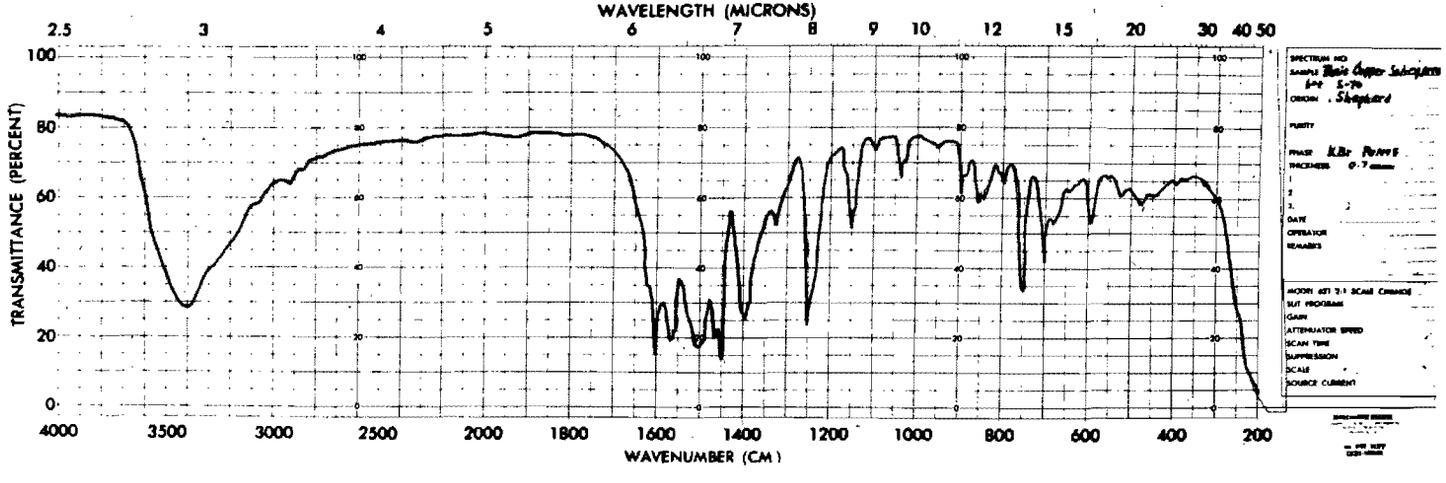


Figure 24 Infrared Spectrum of Shepherd Product

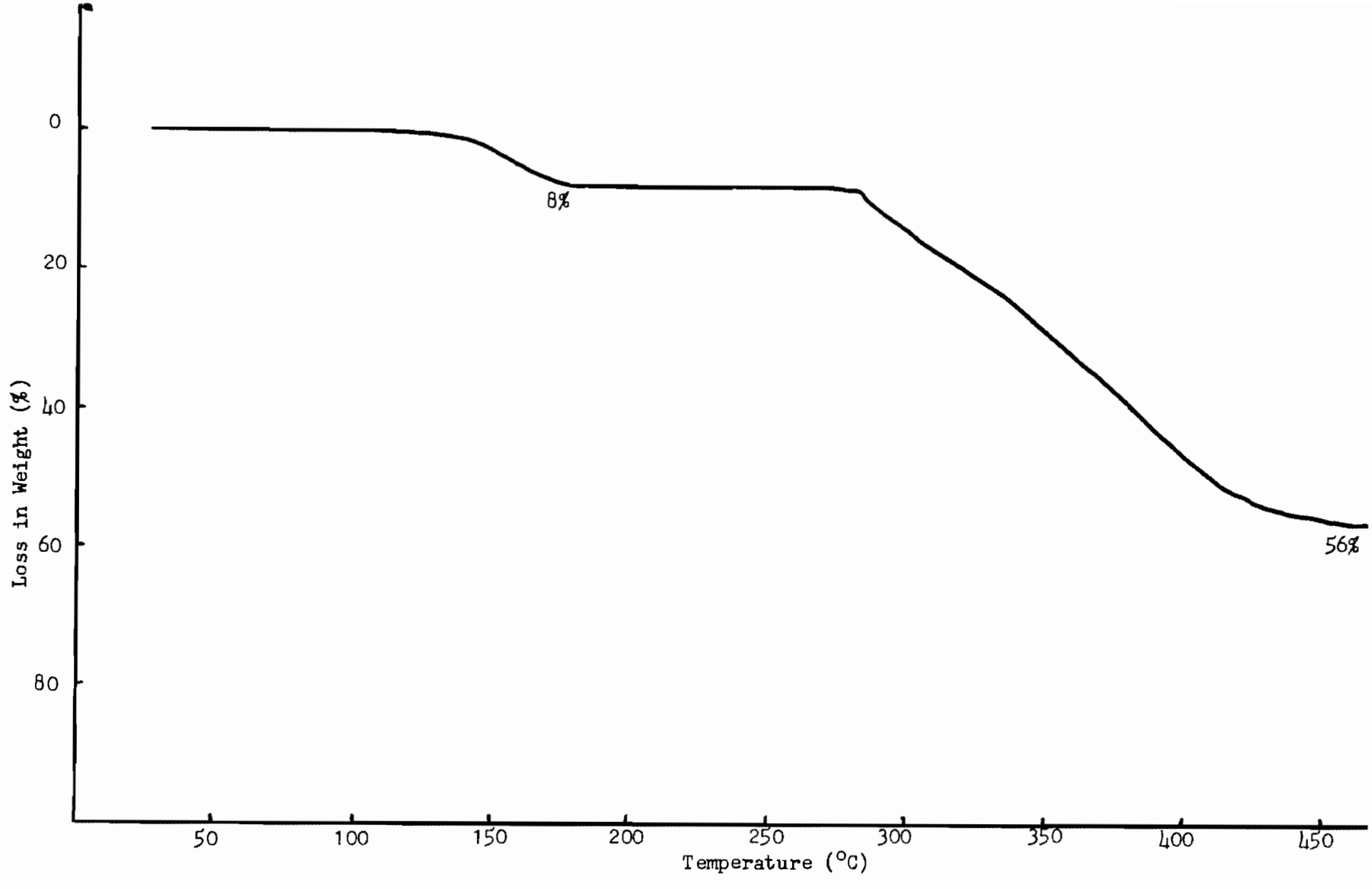


Figure 25 Thermogravimetric Decomposition Curve of Sample 79-1

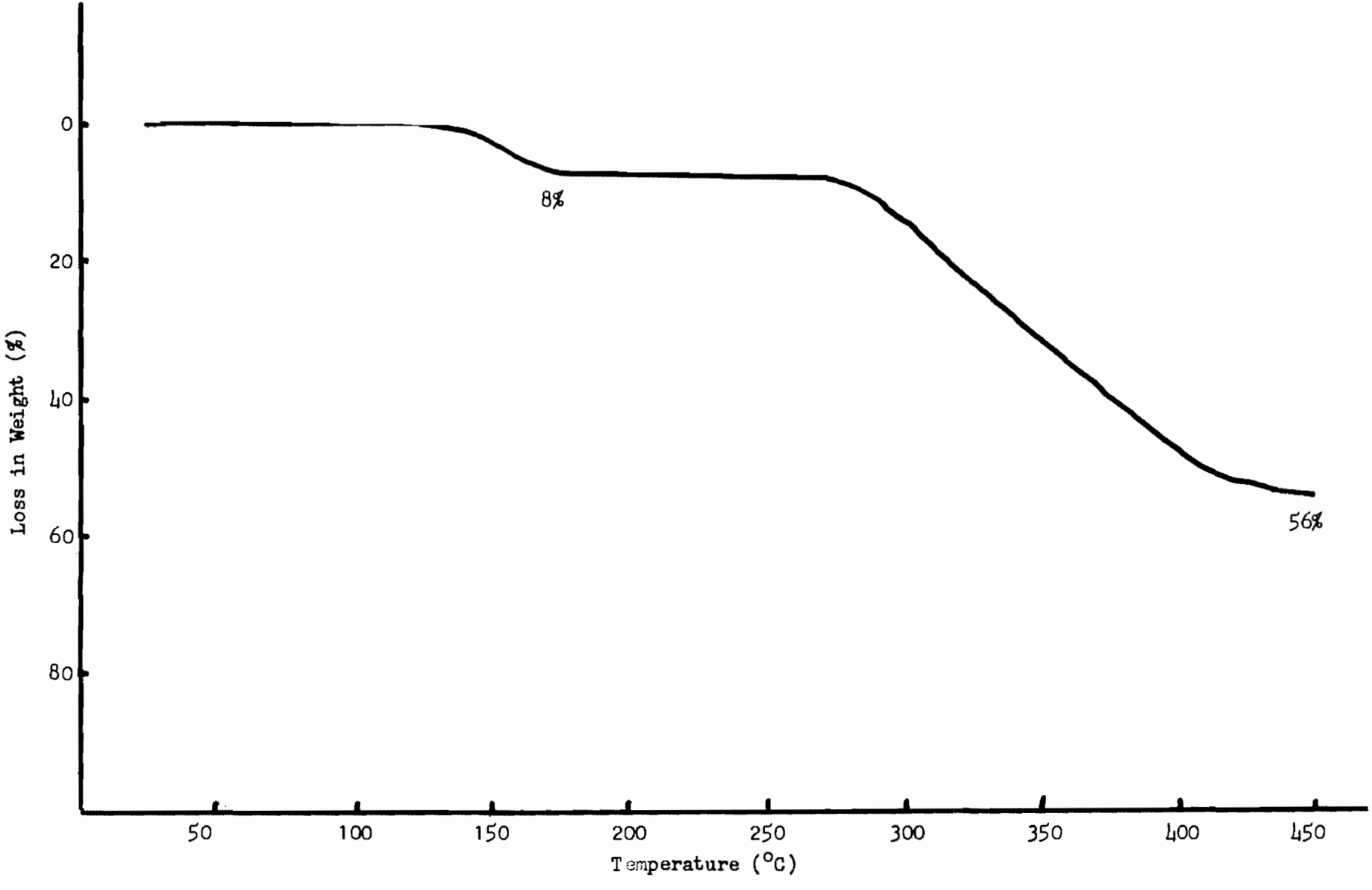


Figure 26 Thermogravimetric Decomposition Curve of National Lead Product

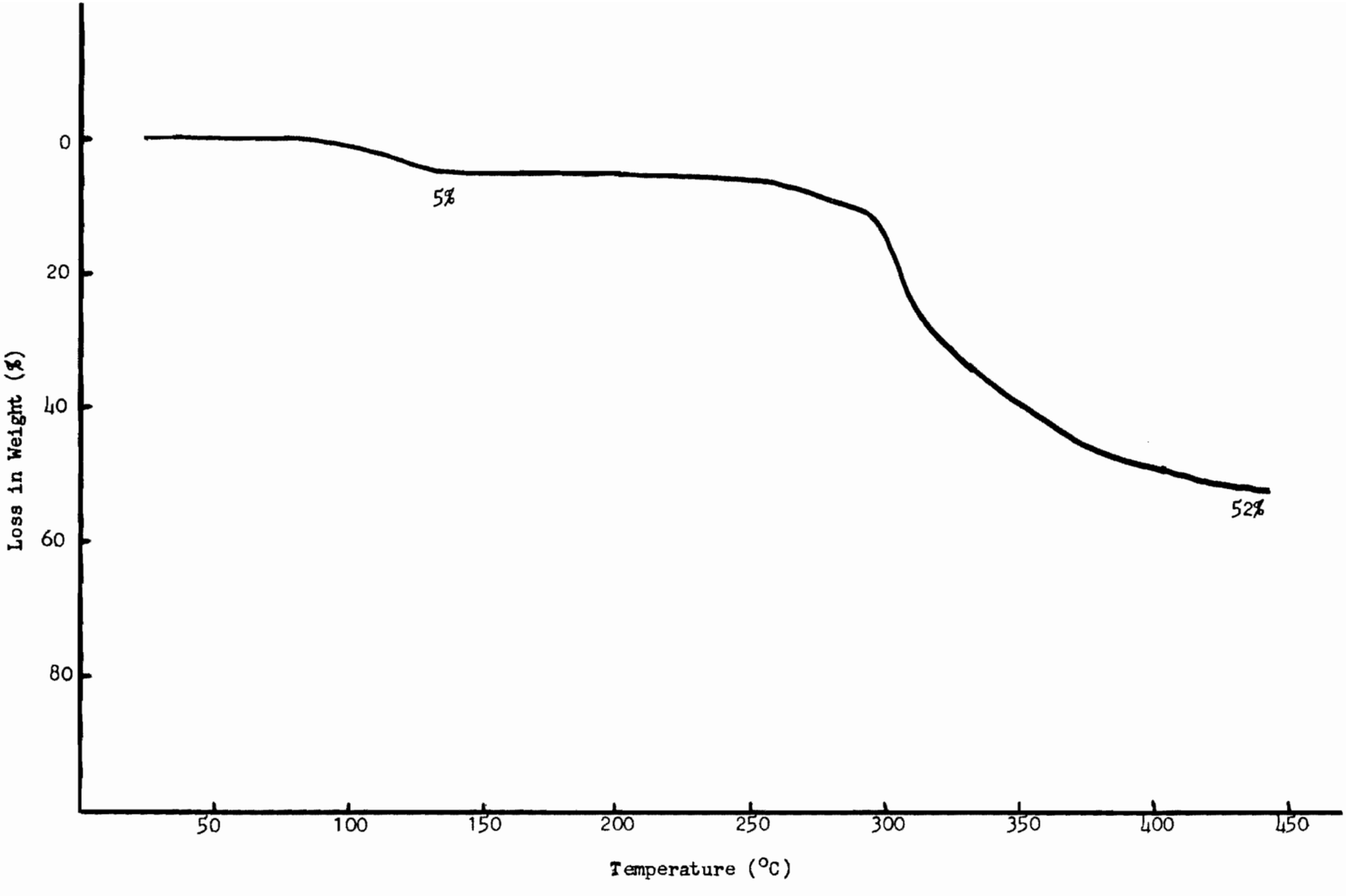


Figure 27 Thermogravimetric Decomposition Curve of the Shepherd Product

DISTRIBUTION LIST

	COPY NO.
Commanding General U. S. Army Materiel Command ATTN: AMCRD-MT AMCDL Washington, D. C. 20315	 1 2
Director Army Ballistic Research Laboratories ATTN: AMXBR-1 Aberdeen Proving Ground, Maryland 21005	 3
Commanding General U. S. Army Missile Command ATTN: AMSMI-R -RF -RK -RB Redstone Arsenal, Alabama 35809	 4 5 6 7
Commanding General U. S. Army Munitions Command ATTN: AMSMU-RE-R Dover, New Jersey 07801	 8
Commanding General U. S. Army Weapons Command ATTN: Librarian Rock Island, Illinois 61202	 9
Commanding Officer Frankford Arsenal ATTN: Librarian Philadelphia, Pennsylvania 19137	 10
U. S. Army Research Office (Durham) ATTN: Librarian Box CM, Duke Station Durham, North Carolina 27706	 11
Commanding General White Sands Missile Range ATTN: STEWS-TE-E New Mexico 88002	 12

DISTRUBUTION LIST (Cont'd)

	COPY NO.
Commanding Officer Watervliet Arsenal ATTN: Librarian Watervliet, New York 12189	13
Commanding Officer U. S. Army Engineering Research and Development Laboratory Fort Belvior, Virginia 22060	14
Office, Chief Research & Development ATTN: Missiles and Space Division Washington, D. C. 20310	15
Office, Chief Research & Development Director of Development Washington, D. C. 20310	16
Office, Chief Research & Development Department of the Army ATTN: CRDPES Washington, D. C. 20310	17
U. S. Army Foreign Science & Technology Center Munitions Building Washington, D. C. 20310	18
Office, Director Defense Research & Engineering Weapons Systems Evaluation Group The Pentagon Washington, D. C. 20310	19
Office Director Defense Research & Engineering ATTN: Director, Chemical Technology The Pentagon Washington, D. C. 20310	20
Air Force Office of Scientific Research ATTN: SREP 1400 Wilson Boulevard Arlington, Virginia 22209	21

DISTRIBUTION LIST

	Copy No.
Air Force Rocket Propulsions Laboratory (RPC)	
ATTN: RPRPT	22
RPRE	23
RPCCR	24
Edwards, California 93523	
Air Force Systems Command	
Andrews Air Force Base	
ATTN: SCTR	25
Washington, D. C. 20331	
Naval Weapons Center	
ATTN: 4522	26
4505	27
China Lake, California 93555	
Naval Air Systems Command	
ATTN: AIR-330	28
-5367	29
-604	30
Washington, D. C. 20360	
National Aeronautics & Space Administration	
Lewis Research Center	
ATTN: Ch, Lig Rkt Tech Branch	31-32
Technical Library	33
2100 Brookpark Road	
Cleveland, Ohio 44135	
National Aeronautics & Space Administration	
Marshall Space Flight Center	
ATTN: R-R&VE-P	34
I-E-MGR	35
Huntsville, Alabama 35812	
National Aeronautics & Space Administration	
ATTN: Code RPS	36
Washington, D. C. 20546	

DISTRIBUTION LIST

	Copy No.
National Aeronautics & Space Administration Scientific & Technical Information Facility ATTN: SAF/DL ACQ Div P. O. Box 33 College Park, Maryland 20740	37
Central Intelligence Agency ATTN: OCRDD-Standard Distribution 2430 E. Street, N. W. Washington, D. C. 20505	38
Chemical Propulsion Information Agency The Johns Hopkins University Applied Physics Laboratory 8621 Georgia Avenue Silver Spring, Maryland 20910	39-40
Defense Documentation Center Cameron Station Bldg. 5 ATTN: TSR Alexandria, Virginia 22314	41-52
Jet Propulsion Laboratory California Institute of Technology ATTN: TDS, Library 4800 Oak Grove Drive Pasadena, California 91103	53
Purdue University School of Mechanical Engineering Lafayette, Indiana 47907	54
Headquarters U. S. Air Force (AFRDDA) Washington, D. C. 20330	55
Headquarters Air Force Armament Laboratory (ATX) Eglin Air Force Base, Florida 32542	56
Headquarters Air Force Systems Command (SCTS) Andrews Air Force Base, Maryland 20331	57

DISTRIBUTION LIST

	Copy No.
Headquarters Air Force Weapons Laboratory (WLX) Kirtland Air Force Base, New Mexico 87117	58
Commanding Officer Picatinny Arsenal	
ATTN: SMUPA-V	59
-VG	60-64
-D	65
-DD	66
-DL	67
-RT-S Dover, New Jersey 07801	68-72

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Picatinny Arsenal, Dover, New Jersey	Unclassified
	2b. GROUP

3. REPORT TITLE

PREPARATION OF ANALYTICALLY PURE MONOBASIC COPPER SALICYLATE

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (First name, middle initial, last name)

Daniel R. Satriana

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
October 1971	27	4

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. DA 1M262302A211	Technical Memorandum 2023
c. AMCMS Code 5222.11.58500	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

Approved for public release: distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

Preparation of analytically pure monobasic copper salicylate by two distinct synthetic routes and characterization of the products by infrared spectroscopy, X-ray diffraction and thermogravimetric analysis is described.

DD FORM 1 NOV 68 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Monobasic Copper Salicylate						
Salicylic Acid						
Basic Copper Carbonate						
Copper Hydroxide