THE USE OF INFRARED SPECTROPHOTOMETRIC ANALYSIS IN THE CORRELATION OF DIFFERENT UNITS WITHIN DUNDEE LIMESTONE, DEVONIAN AGE ROGERS CITY, MICHIGAN

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
Neill H. Nutter
1958

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By

Neill H. Nutter

A THESIS

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The cooperation of Mr. Paul Thornley of the Michigan Limestone Corporation; Mr. Peter Hooper, Research director of Sturtevant Mill Company, Boston; and Dr.'s Sternberg and Schwendman of the Chemistry department, Michigan State University; is much appreciated.

And last but not least, thanks to my wife Millie, who very patiently encouraged me.

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ABSTRACT

Four samples from each of three horizons were taken from the Dundee limestone of Devonian age at Rogers City, Michigan. Because this was a rock of relative homogeneous lithology, it was hoped that an analysis of the samples on an infrared spectrophotometer would prove to be a simple and effective means of correlation. When the absorption curves were examined, it was determined that no reliable means of correlation could be found. However a very slight shift in the Ca^{++} Mg^{++} ratios was apparent. The significance of this in relation to the initial problem was not known.

PURPOSE

To the author's knowledge, little work has been done, using infrared spectroscopy as a tool for correlation. Thus, an infrared analysis of 12 samples of Devonian age Dundee limestone (four samples from each of three units) was made to determine the usefulness of such an analysis with regard to correlation within and between units.

BACKGROUND

The origin of the study of infrared radiation began in the 1800's when the Englishman, Sir William Hershel, used an ordinary glass prism to disperse sunlight into its spectrum. He discovered that as well as the visible spectrum, there existed a region invisible to the eye, that had the effect of heating substances which were placed within it. Sir William measured the resulting temperature increase of a number of substances such as water, alcohol, etc.

Nothing really significant developed in the study of infrared radiation until 1903 when William Coblentz, an American, began research in this field at Cornell University. His effort rewarded him with an appointment to the Carnegie Institute, where for two hears he plotted infrared absorption spectra for various compounds. He found that each substance had its own absorption curve which could thus be described as a fingerprint of that substance.

In the 1930's some of the larger industries experimented with the possibilities of infrared radiation and its absorption by various substances, but the equipment was handmade and extremely expensive. Since 1940, new methods of producing optical equipment of high quality and much lower expense, plus extremely sensitive electrical devices such as thermistors, thermocouples, etc. have enabled instrument companies to produce sensitive and accurate infrared spectrometers at a reasonably modest cost. It is the availability of a good instrument at a reasonable cost that has stimulated the widespread research that infrared spectroscopy enjoys today.

Organic chemistry has been well investigated, as the combinations of carbon bonds are legion and each bond has absorptions peculiar to it, and many of the compounds can be gassified or liquified, and hence are readily examined.

Inorganic materials on the other hand are not nearly as complex and varied as the organic compounds and consequently do not have the varied absorptions. Furthermore, most inorganic materials are not readily liquified or gassified as melting and boiling points are quite high. While many are soluble in water, acids or alkalies, this does not help, as aqueous solutions are nearly all opaque in the infrared region of the spectrum.

Because of this, geology has been slow in utilizing the help that infrared spectroscopy can offer. As early as 1929, quartz was used in some experiments with infrared (Plyler, 1929), but as with many others, the experimenting was being done to discover more of the phenomena of infrared, not of the quartz. Actually little work was done until 1949 when Keller&Pickett examined the absorption spectra of some silicate minerals.

One of the foremost workers in this field has been Dr. John M. Hunt of the Carter Oil Company research laboratories in Tulsa, Oklahoma. It was his work, published in 1950 (Hunt, Wisherd, and Bonham) that stimulated this study. He and his staff have utilized infrared spectroscopy in the solution of a number of geologic problems. The Union Oil Company of California is also known to have done extensive research in this field; no doubt these two organizations and others are finding the field of infrared spectroscopy a valuble key to the unlocking of many of nature's secrets.

THEORY

The infrared spectrum is that part of the electromagnetic spectrum which lies between the long wave portion of the visible, and short wave portion of the radiomicrowave region. The infrared range is generally divided into three areas. The shortest wave length portion is called the photoelectric portion and covers the wavelengths from 0.75 microns to 3.0 microns. This range sometimes is placed with the visible and sometimes with the near infrared. The near infrared is the wavelength range from 3.0 microns to 25.0 microns. The far infrared ranges from 25.0 to 500 microns.

These three divisions correspond roughly with the frequency limits of three of the four energies possessed by a molecule. The photoelectric region of the spectrum and the electronic energy of a molecule share similiar frequencies. The electronic energy is generated by movements of the outer electrons of the atom. The near infrared region has approximately those frequencies of the vibrational energy, which is exhibited in the bending and stretching of the molecular bonds. The far infrared region is of the same general frequency area as the rotational energy. The rotational energy is not important as a molecule is rarely free to rotate except when in a vapor state. The fourth energy, translational energy, has no part in molecular absorption and can be described as that energy a molecule possesses by virtue of being moved. The total energy of a molecule may be mathematically expressed;

$$W_{tot} = W_{elec} + W_{vib} + W_{rot} + W_{trans}$$

where W is the energy.

A natural or induced dipole moment must be present in a molecule to produce rotational and vibrational energies, since a change in molecular configuration necessitates changes in the dipole; therefore molecules without a dipole moment cannot respond to electromagnetic radiation.

The reaction of bond types to infrared radiation can be summed up as follows:

Groups of monatomic ions generally possess lattice vibrations which are induced by the far infrared;

Polyatomic ions possess lattice vibrations, rotatory oscillations, and internal vibrations;

Molecular solids have similar characteristics to polyatomic ions;

Covalent solids possess a combination of lattice and internal vibrations.

When radiation of a particular frequency induces a resonant vibration within a molecule, some of its energy is imparted to produce the vibration. Absorption depends upon the probability that the energy of the quantum of radiation will be absorbed by a molecule. As the concentration of the molecules increases, the probability of absorption increases. The characteristic loss in energy of the radiation, or the equal increase of energy within the substance being analysed, defines the absorption spectrum, whether infrared or otherwise, of the substance. This is expressed mathematically by the equation $dI/I = -kcdb$, where I is the radiation intensity, i.e. the quanta of radiation per square centimeter, and dI is the change of intensity produced by a thin layer of absorptive material of thickness db and concentration c. This expression is readily integrated in the following manner to give;

$$\int_{I_0}^{I} \frac{dI}{I} = -kc\int_{0}^{b} db \qquad \ln \frac{I}{I_0} = -kcb$$

and by converting the natural logarithm to base 10 logarithms, the constant k becomes a new constant a_s and the log $I_o/I = -a_s cb = A_s$ or the absorbancy. This is a development of the Beer-Lambert-Bouger law. By measuring the intensity of radiation before and after passing through a substance it is possible to determine the concentration of the substance. By the same token, if there are "n" different molecules in the substance, it is possible to calculate the individual concentrations by measuring the absorption at "n" characteristic wavelengths, and then simultaneously solving "n" equations.

A true evaluation of the absorption of a substance cannot be made if the radiation intended to pass through the substance is refracted and/or reflected. If the incident ray is normal to the surface of the substance being analysed, no refraction or reflection occurs. This is the case when a liquid or gas cell is used to hold the sample, because the cell is designed this way. In the case of solid samples however, this may not be the case. If the sample is ground to produce a powder, the irregular shaped particles will be oriented randomly, therefore much of the radiation may be reflected and/or refracted. According to Hunt et al. (1950) and Nahim (1955), if the maximum diameter of the particle is less than the wavelength of the radiation passing through the particle, reflection and refraction will be reduced to a minimum. However they also state that reducingthe size beyond 5 microns does not result in any appreciable improvement.

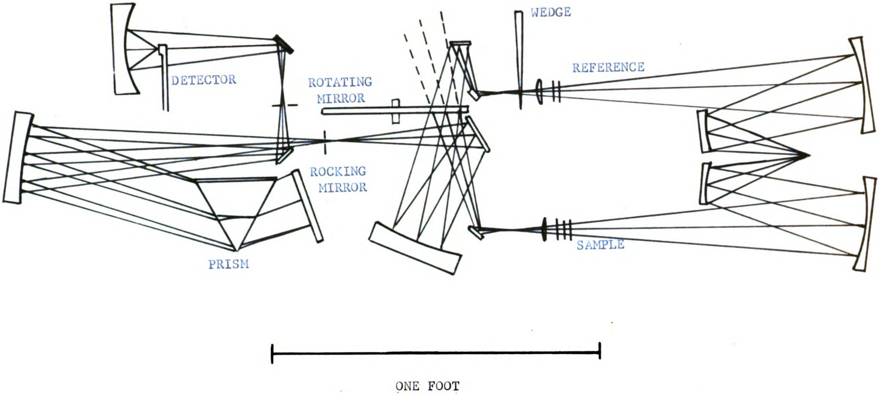
The effect of particle size is shown by the runs made with U.S.P. grade $CaCO_3$. The first run was made with $CaCO_3$ that had only been slightly ground in the agate mortar. The next runs were made with sucessively finer grinds, the last of which had an estimated 10% of the particles over 5 microns in diameter. The improvement in the definition of the curves is obvious on comparison

APPARATUS

The instrument used to determine the absorption of the limestone in this problem is the Perkin Elmer Model 21 infrared self-recording spectrometer. The optical system of the instrument is of the Littrow type. This doubles the dispersion obtained from a given prism train, and results in a more compact instrument.

The radiation from the source is split into two beams, one through the sample and the other through the reference plate and wedge whose transparency can be adjusted A rotating sector mirror and diaphragm alternately pass the two beams by way of mirrors to a curved mirror that reflects the beams through a prism which separates their wavelengths. A rocking mirror sweeps the dispersed beams across the detector by way of the prism and curved mirror. The strengths of the alternately received beams are compared at successive wavelengths. When the detector senses a difference, an alternating current is generated which adjusts the moving wedge or attenuator to equalize the signals. The motion of the wedge is transmitted to the recording pen,which gives a continuous record of the absorbancy of the sample on a moving drum.

The source of radiation in the instrument is a Nernsts glower, a filament coated with the oxides of Cerium, Thorium, Zirconium etc. The diameter of the filament is about 1½ millimeters and it is 20-30 millimeters long. It operates at 0.3 amps and uses an ordinary light bulb as a ballast resistor. The operation temperature is between 1600 and 1700 degrees centigrade In this range the peak intensity is given at about 1.4 microns in wavelength. The intensity curve of the Nernst filament is nearly that of an ideal black body radiator. At 9.25 microns a filter automatically is inserted to eliminate unwanted wavelengths at the high wavelength end. This is



OPTICAL SYSTEM OF PERKIN ELMER MODEL 21

verified by the very sharp dip on all curves at 9.25 microns. The dispersing element is a sodium chloride or potassium bromide prism. The detector used is a very sensitive vacuum thermocouple with a potassium bromide window.

PROCEDURE

The Devonian Dundee limestone samples used in this study were obtained from the quarry of the Michigan Limestone Corporation, Rogers City, Michigan.

Within the quarry, the highest convenient unit was found and some marker bed sought, namely a very thin shale seam. At a distance of a pick handle (approximately 16 inches) above this seam, four samples were taken, weighing roughly from 30 to 90 grams, at intervals of about twenty-five feet. These samples were bagged and labeled A-1, A-2, A-3, and A-4.

A second and lower unit was then sought out where four samples were taken in a similar manner. These were bagged and labeled B-1, B-2, B-3, and B-4.

The third and lowest unit that could conveniently be examined was found and again a marker bed was located and samples taken along it. These were bagged and labeled C-1, C-2, C-3, and C-4.

The shale seams used for each marker unit were not the same. The vertical separation between sampled units was estimated to be greater than twenty-five feet and the horizontal distances between sampling areas were estimated at about 1½ miles.

Each sample was broken up, utilizing a steel mortar and pestle for coarse work and an agate mortar and pestle for fine grinding. When completed, each sample would entirely pass through a 200 mesh screen. Care was taken to prevent contamination of samples.

After the samples were ground, they were bottled and labeled. As a 200 mesh grind was not satisfactory for examination, the bottled samples were boxed and sent to the Sturtevant Mill Co., Boston, Massachusetts, where the limestone samples were ground to an average size of 2½ microns in diameter, with a maximum size of 5 microns. The instrument used was a 2½ inch jet pulverizer called a "Micronizer". The samples were run individually and the machine cleaned after each run to again prevent contamination.

When the samples were returned from Boston, preparations were made for the examination on the Perkin Elmer Model 21 Spectrophotometer. Sodium chloride windows, between which the samples would be placed, and brass clamps which hold the windows were obtained.

About one gram of sample of the ground limestone was placed in a mortar and a few drops of salt saturated isopropyl alcohol added to form a suspension. This was applied to a plished salt window by touching the salt window with the pestle. A beveled glass slide was used for spreading the suspension over the window. The alcohol was allowed to evaporate and the window examined under a microscope to determine coverage. The last few steps were repeated until a satisfactory coverage was obtained. A second salt window was then placed over the sample on the first and the resulting sandwich placed in the clamp and fastened securely.

The clamped sandwich was then placed in a dessicator for transporting to the constant temperature room in which the infrared spectrophotometer was kept. This was done to prevent moisture from attacking the salt windows. Caution was taken to wear rubber fingers while handling the salt windows to again prevent moisture damage.

As the Perkin Elmer instrument is a double beam spectrophotometer, a salt window reference plate was used in the feference side of the instrument. The controls on the instrument were set as follows: Test signal - Off, Gain - 5, Response - 1, Speed - 5 (except where otherwise stated), Automatic Suppressor - 4, Source current - 0.3 amps, Slit control - 927

Graph paper lined 10 millimeters to the centimeter was used on the instrument to plot the absorption curve. Two runs were made for each sample, making a total of 24 graphs. After each sample was run, the plates were weighed, cleaned, and weighed again to determine thickness, if desired.

After all curves were obtained, U.S.P. $CaCO_3$ was ground with a mortar and pestle and four curves were run, each sample being a little more finely ground.

The wavelengths of all the peaks were then measured, and from this and the character of the peaks, correlation was attempted.

It was felt that concentration of the insolubles within the limestone might offer some help in the correlation. Forty grams of B-3, the largest sample, were dissolved in 3 N HCl. As no residue was apparent, the solution was boiled dry, dissolved inwater to remove $CaCl_2$, then filtered, producing a clear filtrate. The residue was washed and again boiled dry and this upon examination found to be only $CaCl_2$ that had not dissolved the first time. As this was not intended to be a quantitative chemical analysis of the limestone, further experimentation was discontinued, since there was not enough residue apparent for continued infrared analysis.

ANALYSIS OF DATA

A visual comparison of the absorption curves shows little of significance. There are differences in the height and configuration of all the peaks with the 7.00 micron peaks having the most apparent differences. The variation in the heights are due to the varying thicknesses of the samples, while the configuration differences may possibly be due to the uniformity, or lack thereof, of the sample on the salt window.

What is of interest becomes apparent when the wavelengths of the peaks are measured. A trend appears within each of the three units, when the average wavelength positions are compared. In the 11.40, 11.75, and 14.00 micron peaks, it is noted that the "C" unit has the greatest values and the "B" unit has the least values (see table of averages below). Although the differences are in the third decimal place, it indicates a trend, especially as it occurs three times.

Unit	Average Wavelength in Microns					
"A"	3.997	5.560	6.962	11.402	11.778	14.013
"B"	3.998	5.550	7.031	11.391	11.770	14.003
"C"	4.000	5.554	7.039	11.403	11.782	14.019

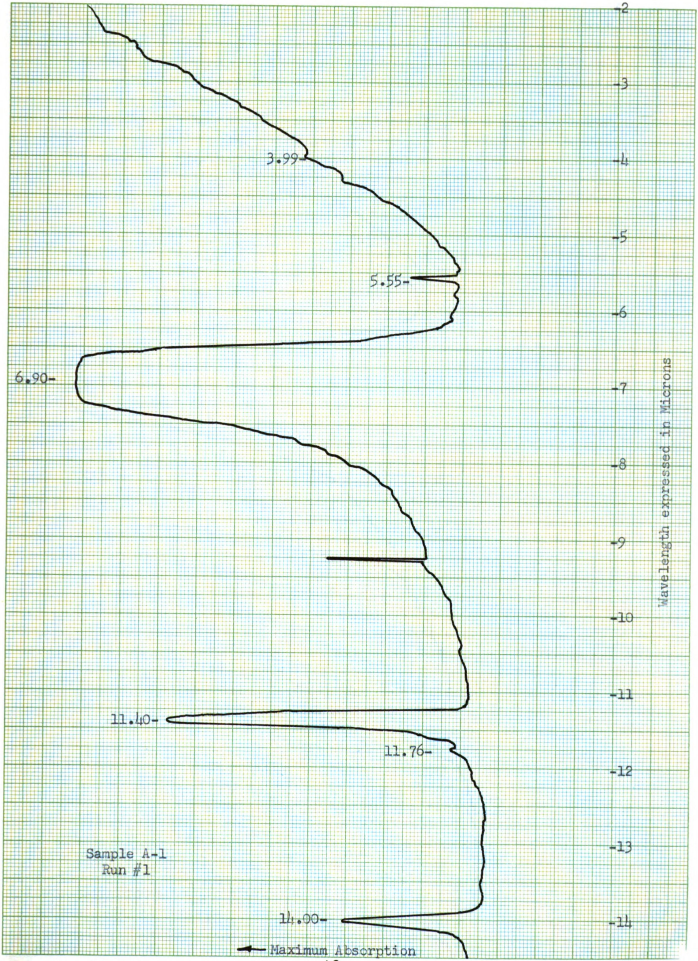
According to Hunt and Turner (1953), as the atomic weight of the cation increases, the wavelength about the 11.40 micron peak tends to move toward the longer wavelengths. The magnesium cation is usually associated with the calcium cation in limestone to a varying degree. The magnesium cation has an atomic weight of 24.32 as compared with 40.08 for the calcium cation. Therefore using this information, it would appear that the "B" unit would contain more of the magnesium cation while the "C" unit contained the least. The following table will show this wavelength shift between lighter and heavier cations.

DATA

Sample		Wt. in grams	Wavelength of peaks in Microns					
A-1	1	0.0025	3.99	5.55	6.90	11.40	11.76	14.00
	2	0.0057	4.00	5.57	6.90	11.42	11.78	14.03
A-2	1	0.0042	3.98	5.56	7.00	11.40	11.77	14.01
	2	0.0037	4.00	5.57	6.95	11.40	11.78	14.03
A-3	1	0.0038	4.00	5.57	6.90	11.40	11.78	14.03
	2	0.0038	4.00	5.55	7.00	11.40	---	14.00
	3	0.0038	4.00	5.57	7.00	11.40	11.75	14.02
A-4	1	0.0028	4.00	5.55	7.03	11.40	11.80	14.00
	2	0.0024	4.00	5.55	6.98	11.40	11.80	14.00
AVERAGE			3.997	5.560	6.962	11.402	11.778	14.013
B-1	1	0.0036	4.00	5.55	7.05	11.40	---	14.00
	2	0.0038	4.00	5.55	7.05	11.40	11.75	14.00
B-2	1	0.0011	4.00	5.55	7.00	11.39	---	14.00
	2	0.0033	4.00	5.55	7.00	11.38	---	14.00
B-3	1	0.0015	4.00	5.57	7.00	11.40	11.80	14.02
	2	0.0019	4.00	5.55	7.10	11.40	11.75	14.00
B-4	1	0.0014	4.00	5.55	7.05	11.33	11.80	14.00
	2	0.0029	3.98	5.53	7.00	11.38	11.75	14.00
AVERAGE			3.998	5.550	7.031	11.391	11.770	14.003
C-1	1	0.0018	4.00	5.55	7.00	11.40	11.80	14.00
	2	0.0015	4.00	5.55	7.05	11.40	11.75	14.03
C-2	1	0.0021	4.00	5.57	7.10	11.42	11.80	14.05
	2	0.0018	4.00	5.55	7.09	11.40	11.80	14.02
C-3	1	0.0023	4.00	5.55	7.07	11.40	11.78	14.00
	2	0.0039	---	5.56	7.00	11.40	11.75	14.02
C-4	1	0.0043	4.00	5.55	7.00	11.40	11.78	14.00
	2	0.0014	4.00	5.55	7.00	11.40	---	14.03
AVERAGE			4.000	5.554	7.039	11.403	11.782	14.019
U.S.P. $CaCO_3$			4.00	5.55	7.00	11.42	11.75	14.05
$CaCO_3$ (Hunt et al. 1950)			4.02	5.58	6.95	11.40	11.80	14.02

MINERAL	FORMULA	CATION ATOMIC WEIGHT	CRYSTAL SYSTEM	WAVELENGTH OF ABSORPTION PEAKS IN MICRONS Letters stand for strength of curves s-strong, m-medium, w-weak						
Magnesite	$MgCO_3$	24.32	Hexagonal	4.00w	5.52w	6.90s	11.25m	11.70w	13.33m	
Dolomite	$CaMgCO_3$		Hexagonal	4.00w	5.52w	6.90s	11.30m	11.70w	13.70m	
Calcite	$CaCO_3$	40.08	Hexagonal	4.02w	5.58w	6.95s	11.40m	11.80w	14.02m	
Aragonite	$CaCO_3$	40.08	Orthorhombic	4.02w	5.58w	6.95s	11.40m	11.65m	14.02m	14.30w
Rhodochrosite	$MnCO_3$	54.93	Hexagonal	4.05w	5.58w	7.00s	11.50m	11.95w	13.72m	
Siderite	$FeCO_3$	55.85	Hexagonal	4.05w	5.58w	7.00s	11.50m	11.95w	13.50m	
Smithsonite	$ZnCO_3$	65.38	Hexagonal	4.05w	5.58w	7.00s	11.47m	11.90w	13.40m	

Absorption data from Hunt et al. 1950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Wavelength expressed in Microns
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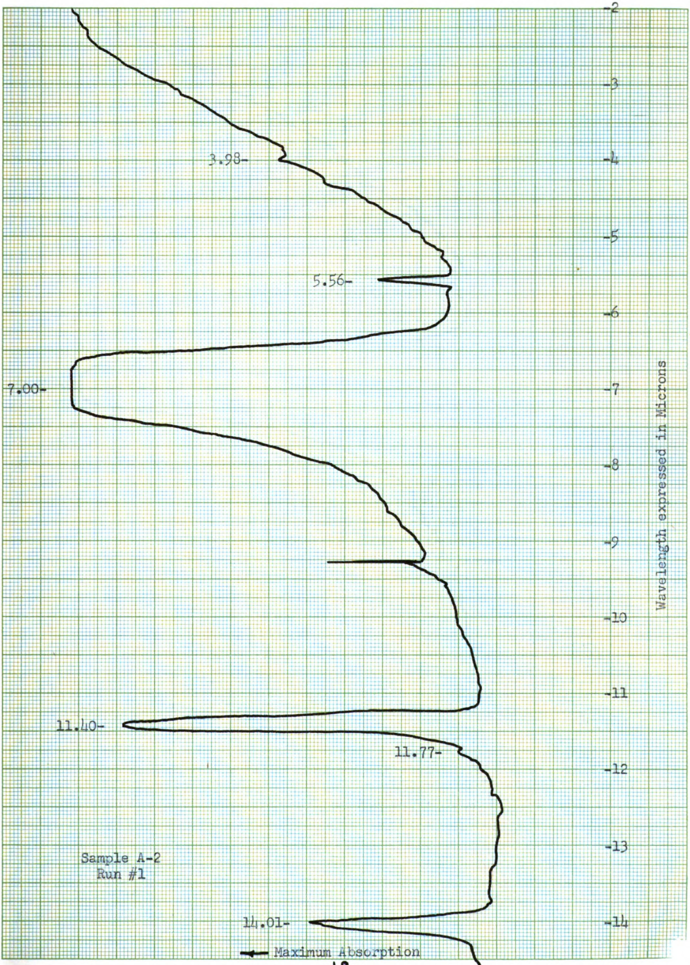
Maximum Absorption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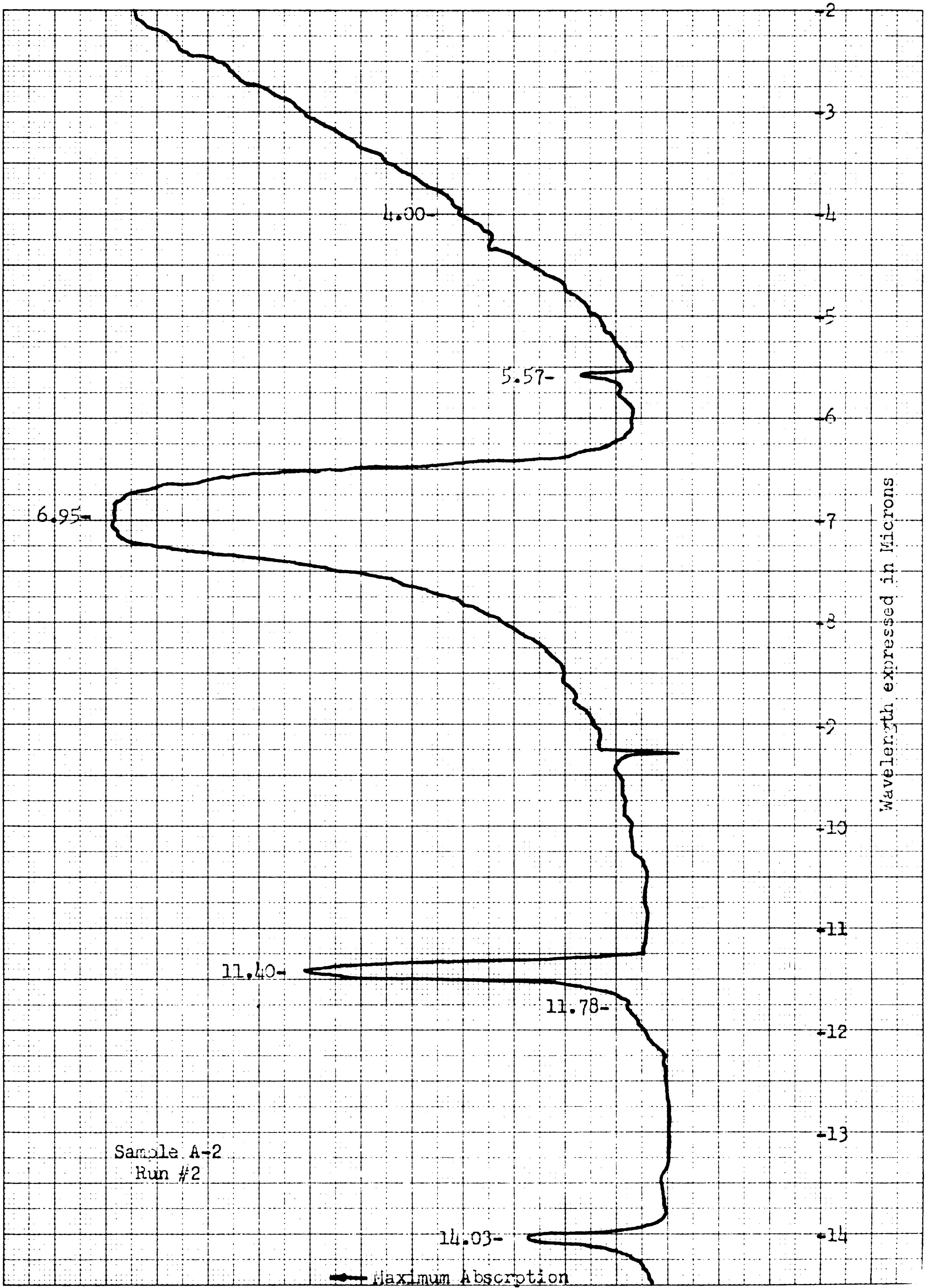
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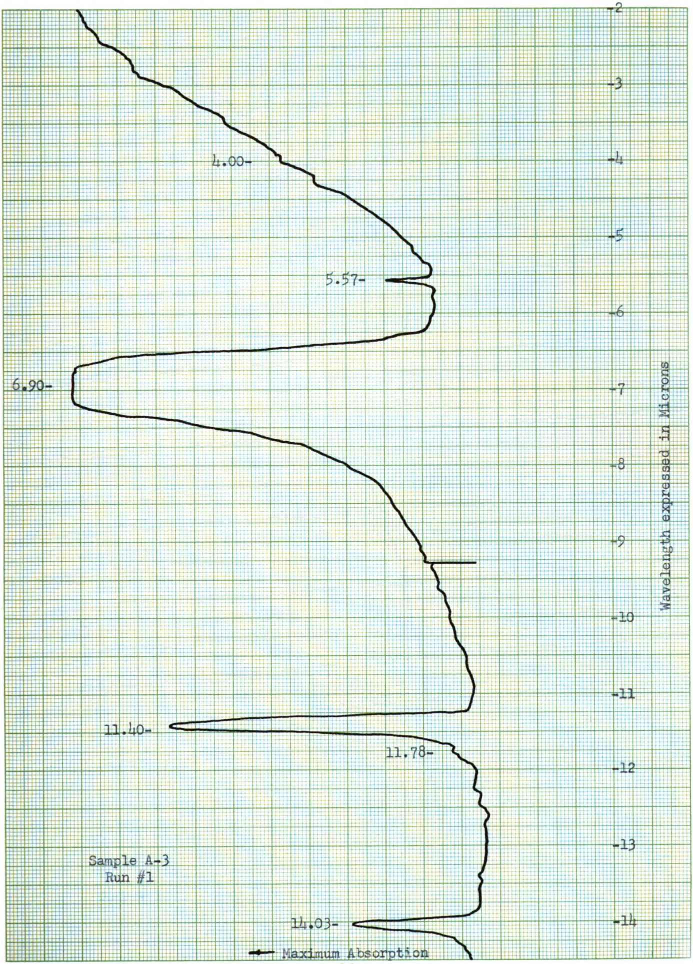
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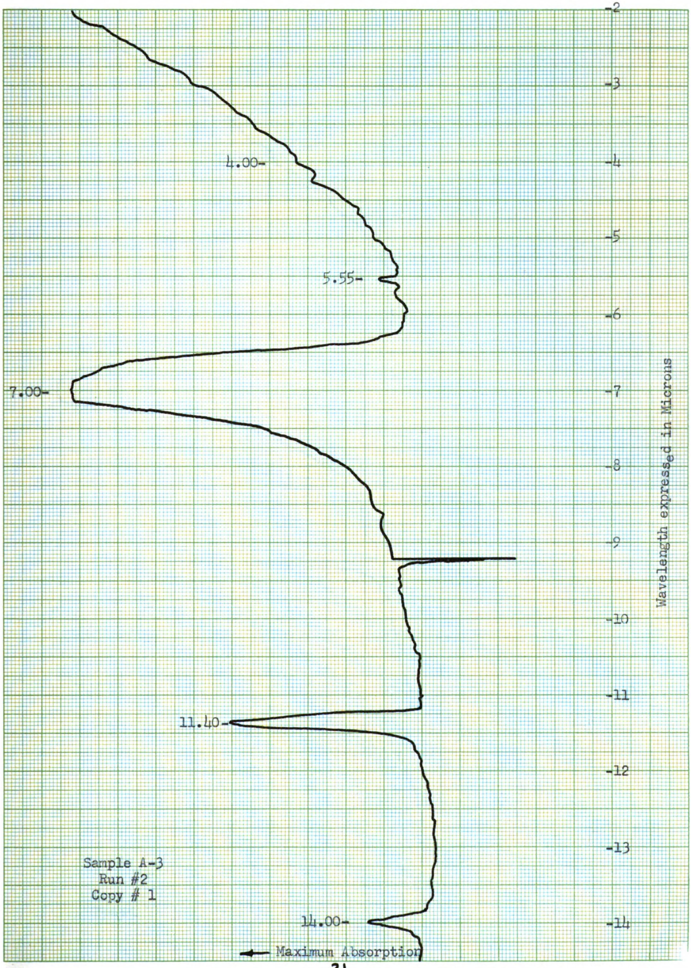

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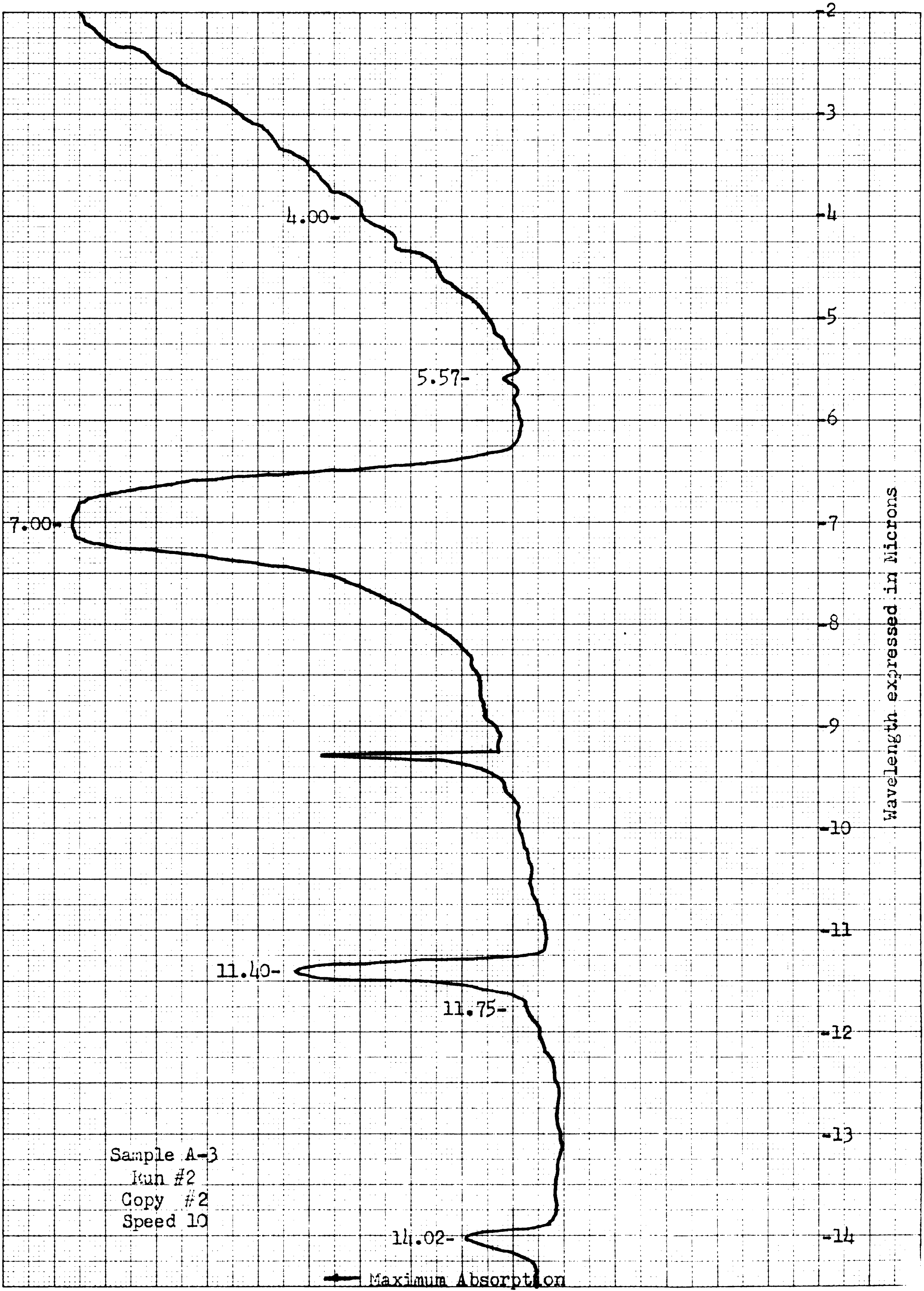
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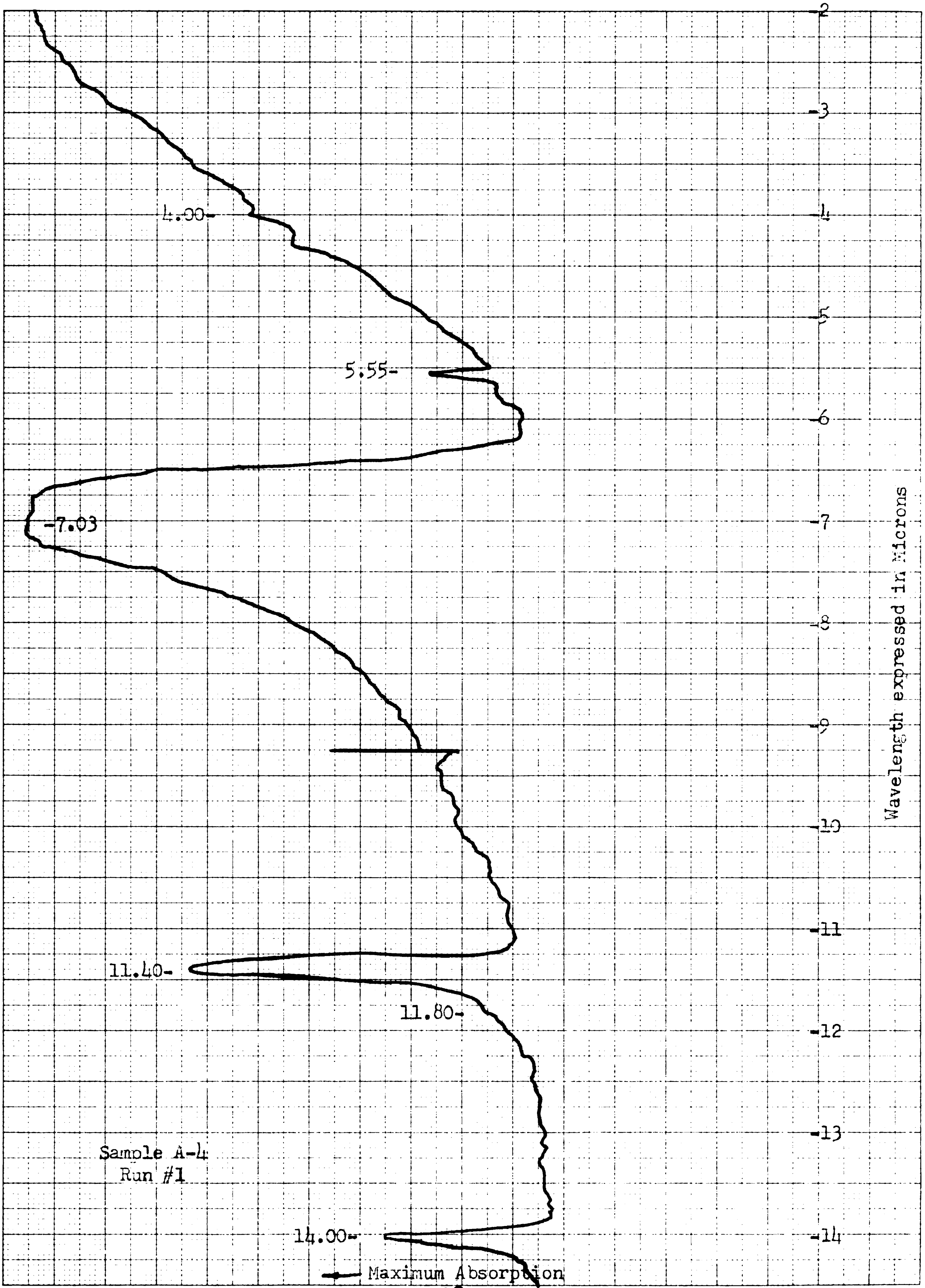
Maximum Absorption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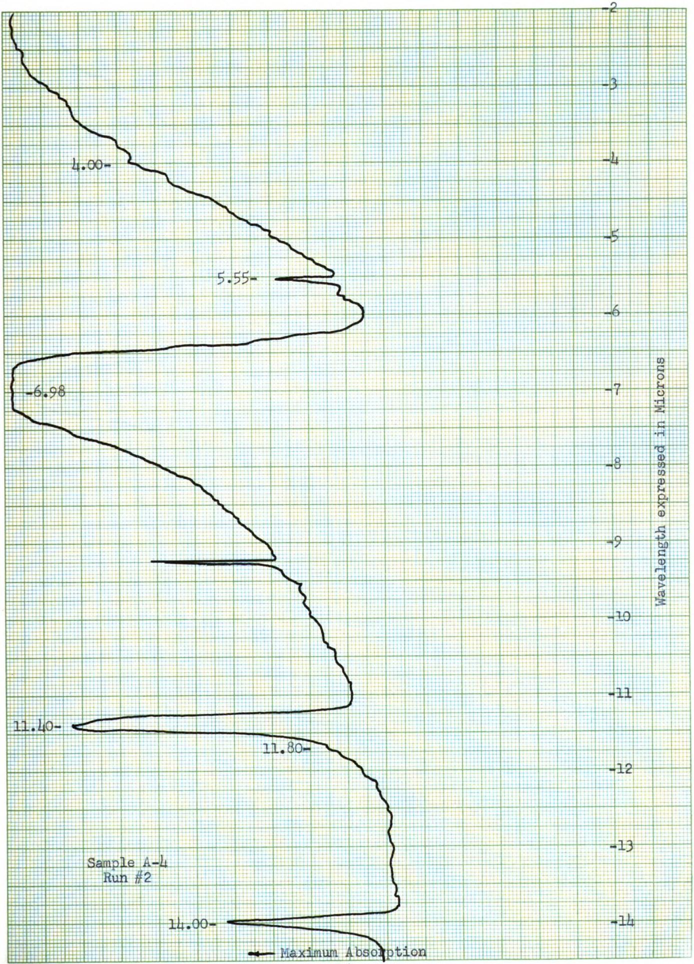
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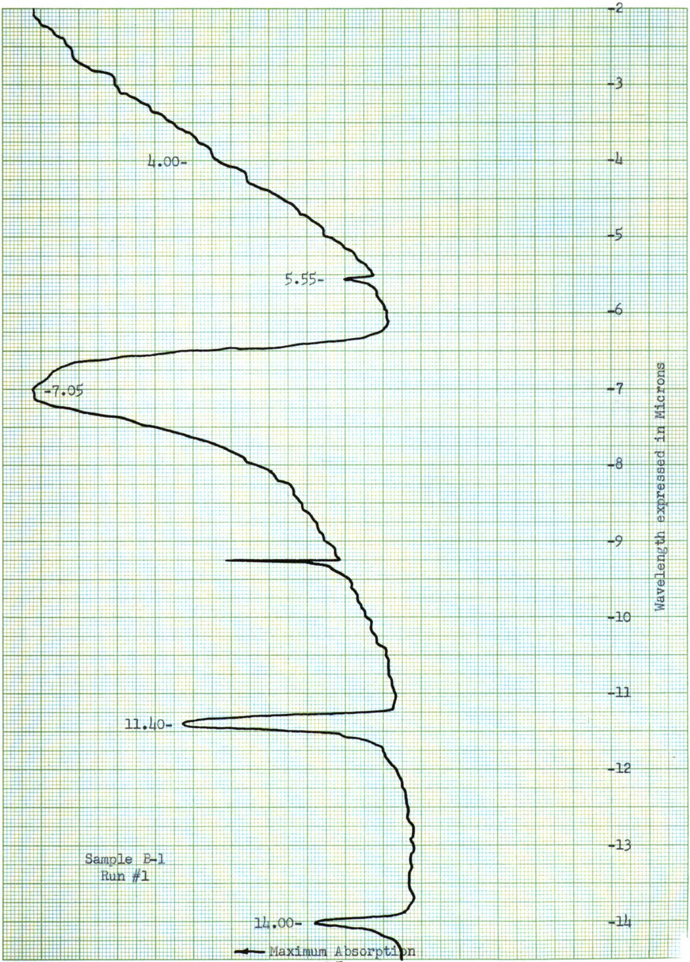
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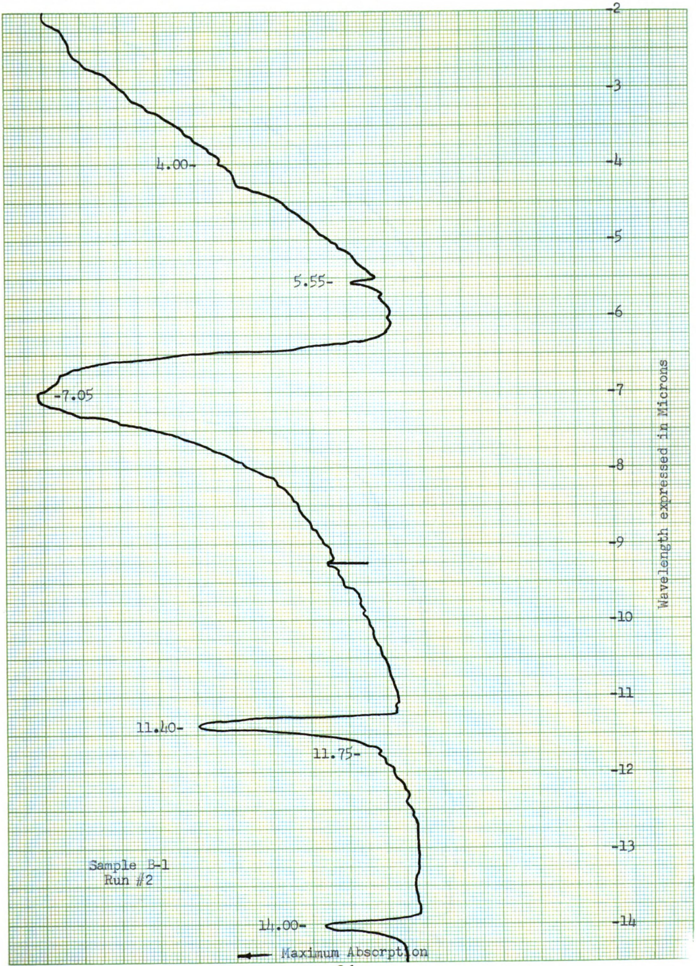
Wavelength expressed in Microns
Sample B-1
Run #1
Maximum Absorption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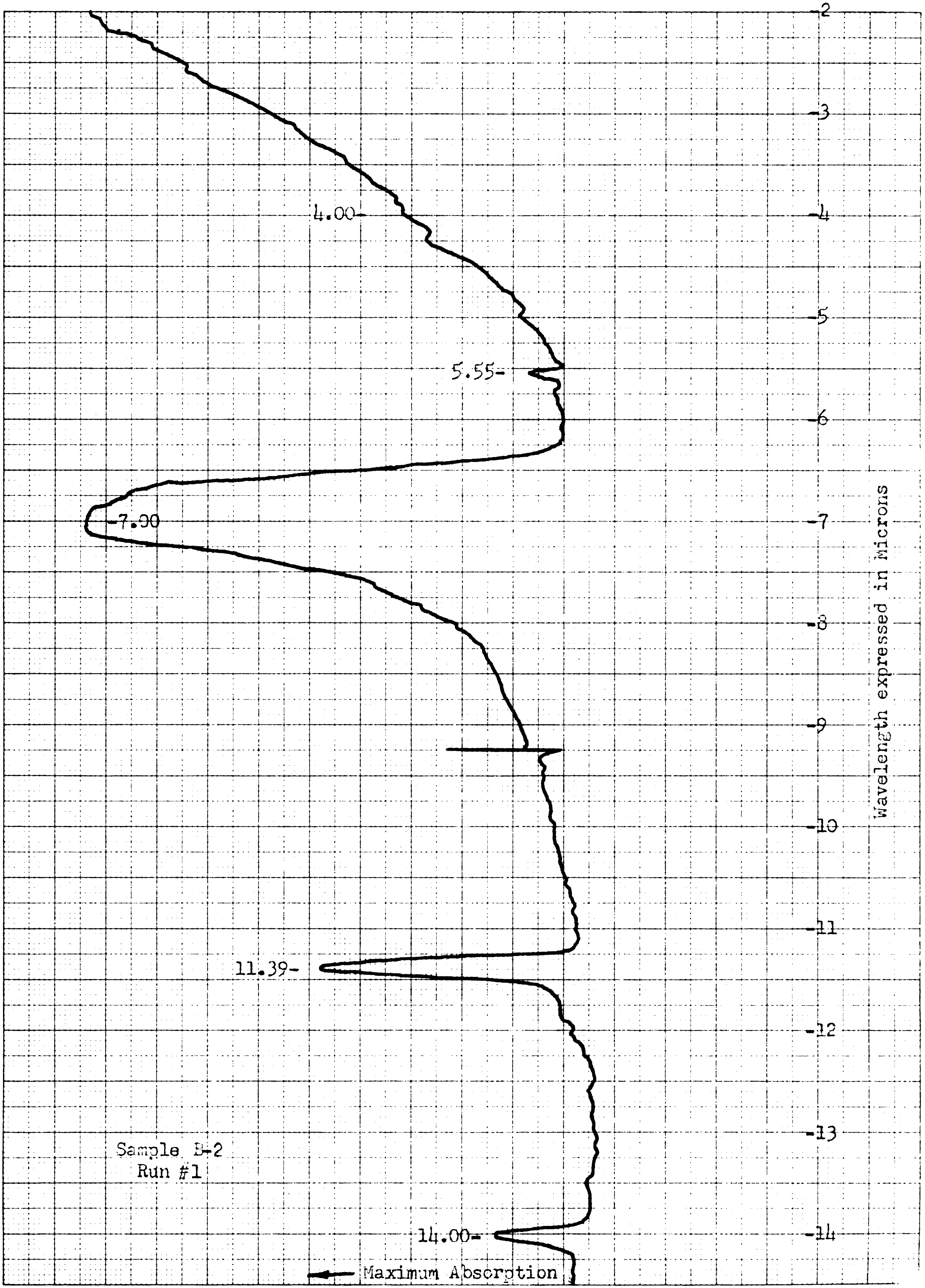
Wavelength expressed in Microns



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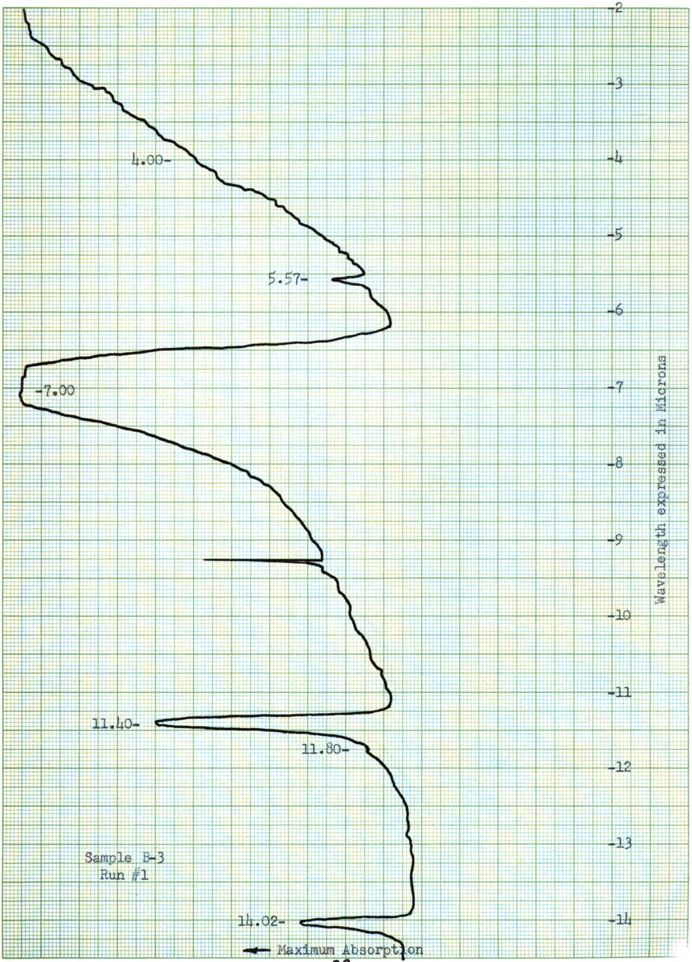
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Wavelength expressed in Microns
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11.80-
-12
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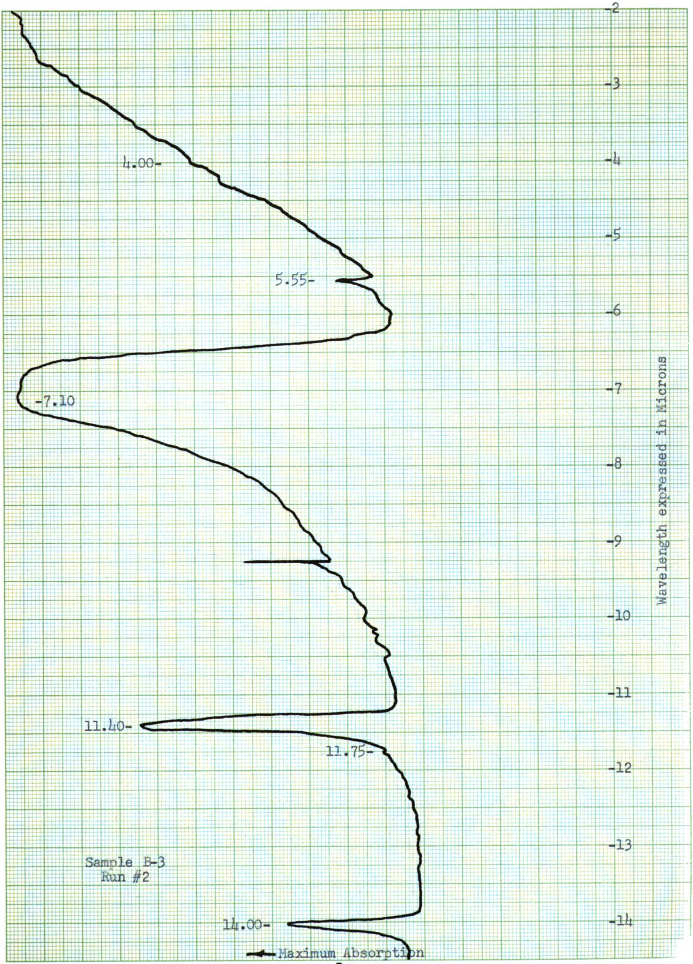
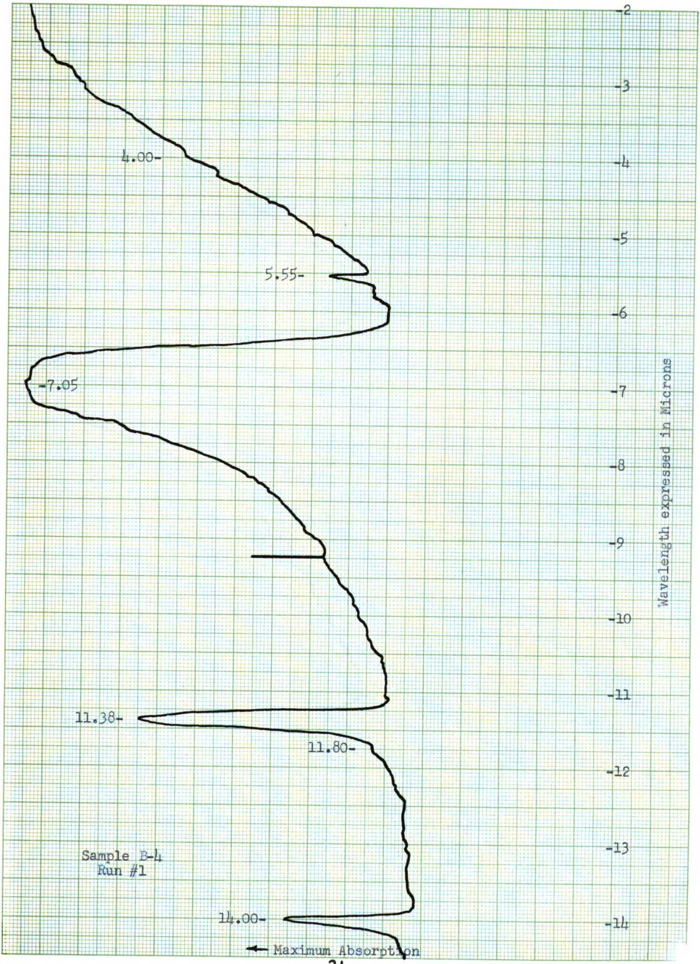
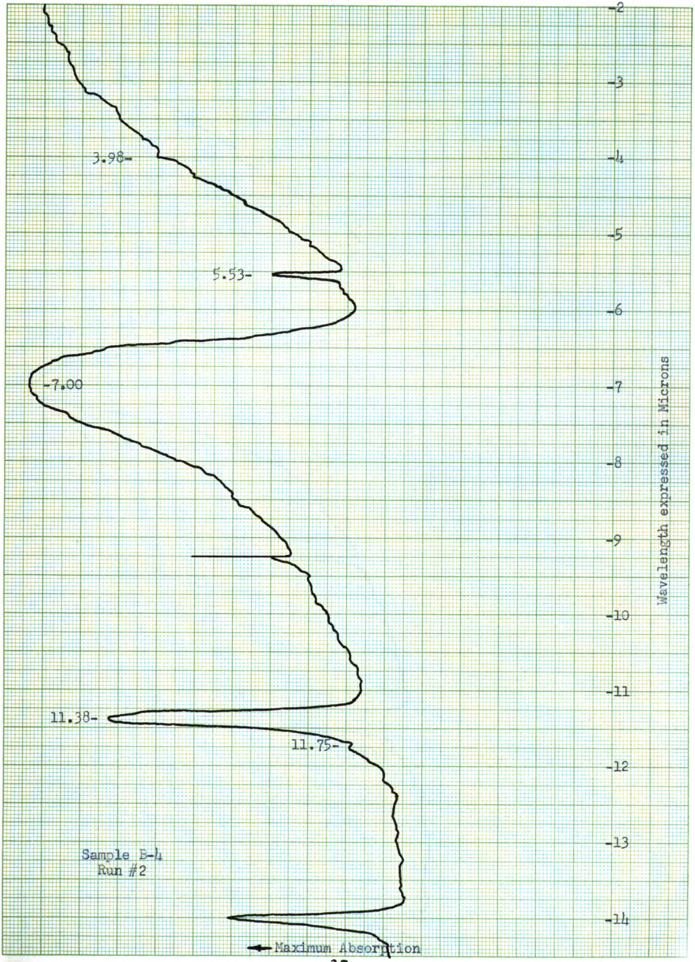
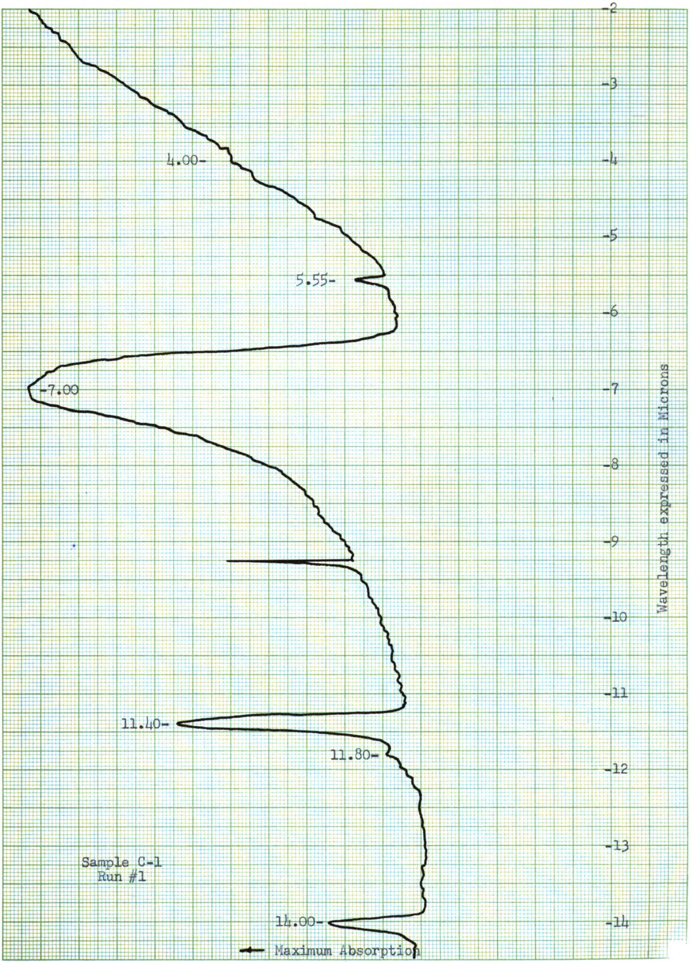
Sample B-3
Run #1
14.02-
-14
← Maximum Absorption

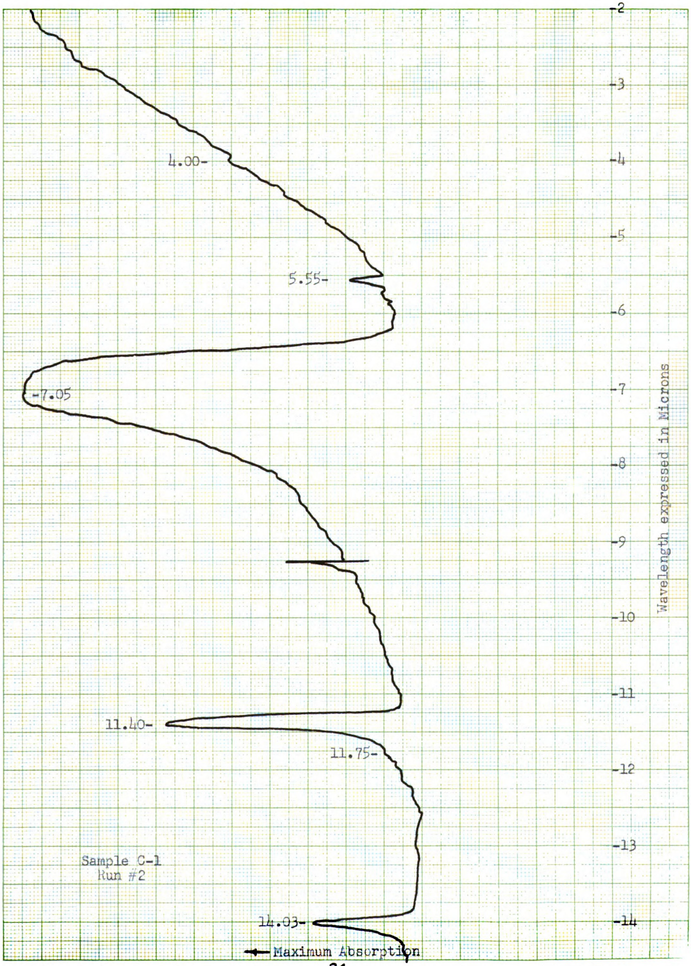

4.00-
5.55-
-7.10
11.40-
11.75-
14.00-
Sample B-3
Run #2
Maximum Absorption
Wavelength expressed in Microns
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14

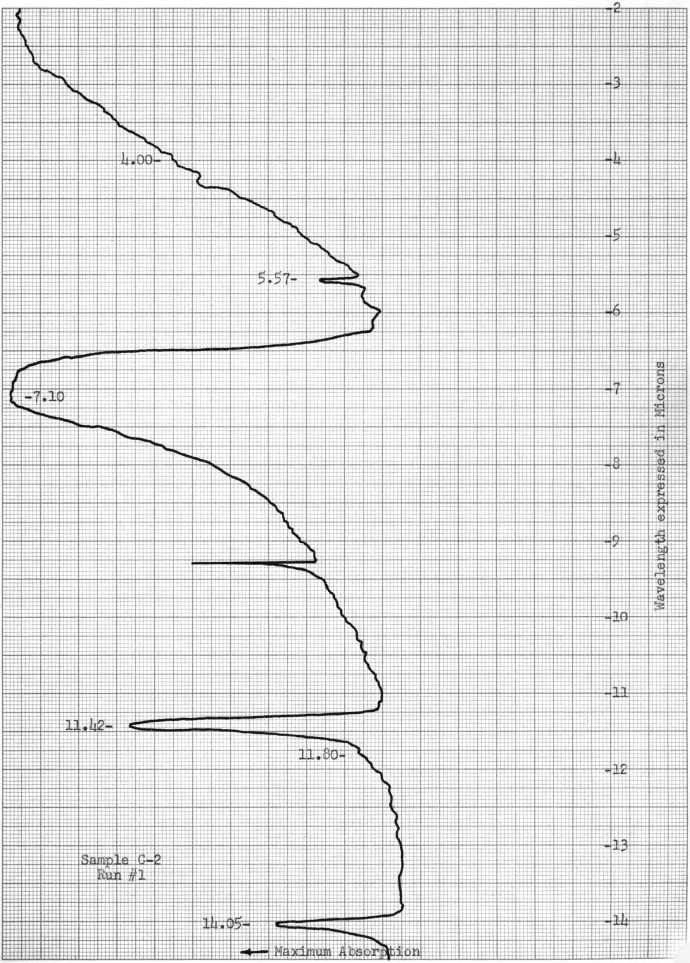

-2
-3
4.00-
-4
-5
5.55-
-6
-7.05
-7
-8
-9
-10
-11
11.38-
11.80-
-12
-13
Sample B-4
Run #1
14.00-
-14
Wavelength expressed in Microns
← Maximum Absorption

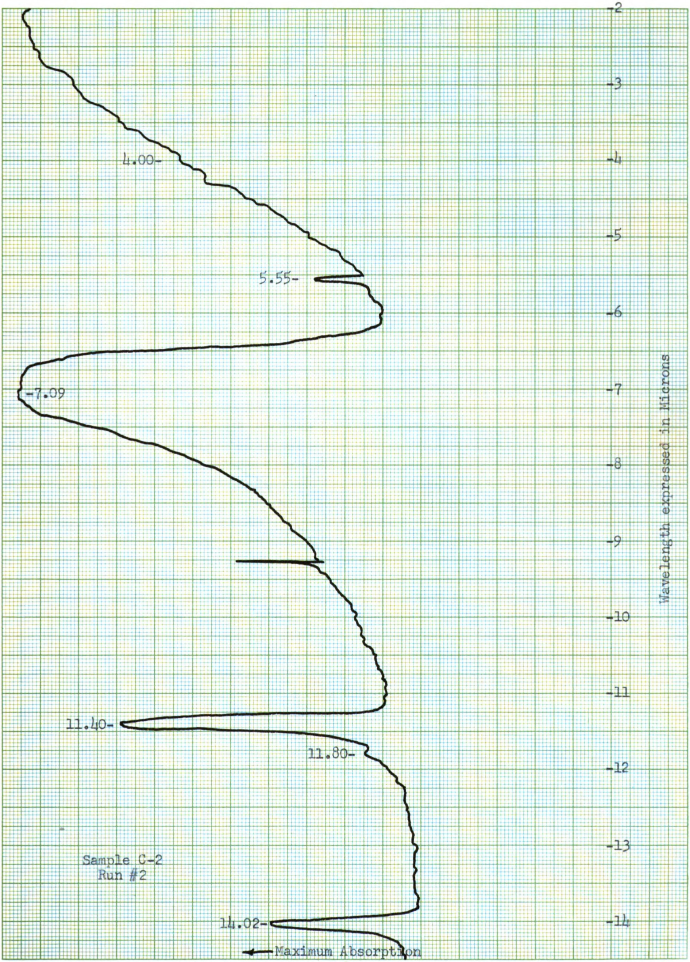

-2
-3
3.98-
-4
-5
5.53-
-6
-7.00
-7
-8
-9
-10
-11
11.38-
11.75-
-12
-13
Sample B-4
Run #2
-14
← Maximum Absorption
Wavelength expressed in Microns



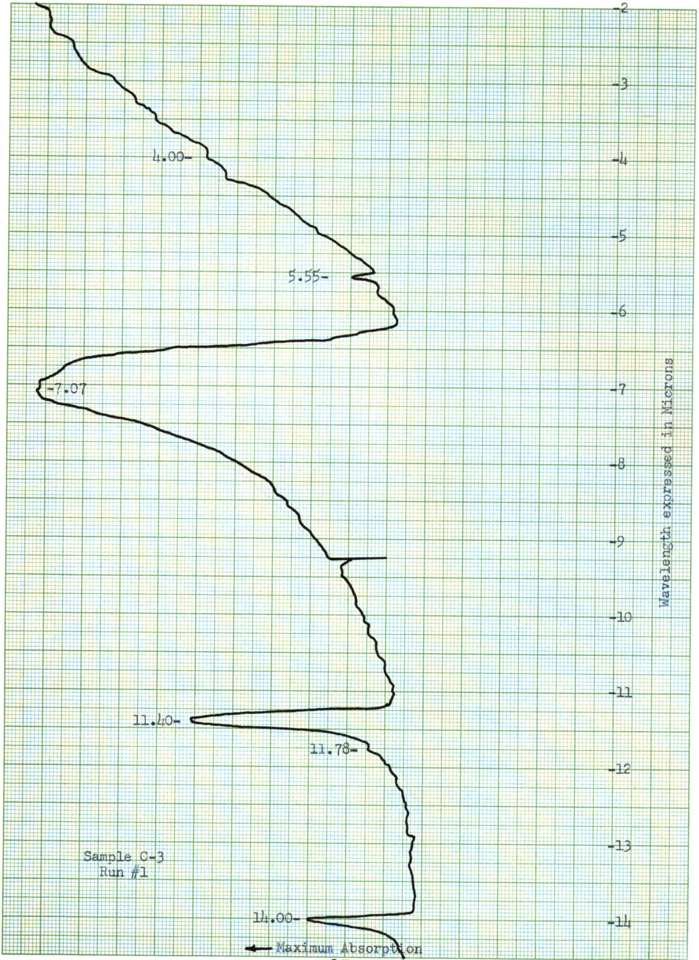
Sample C-1
Run #1

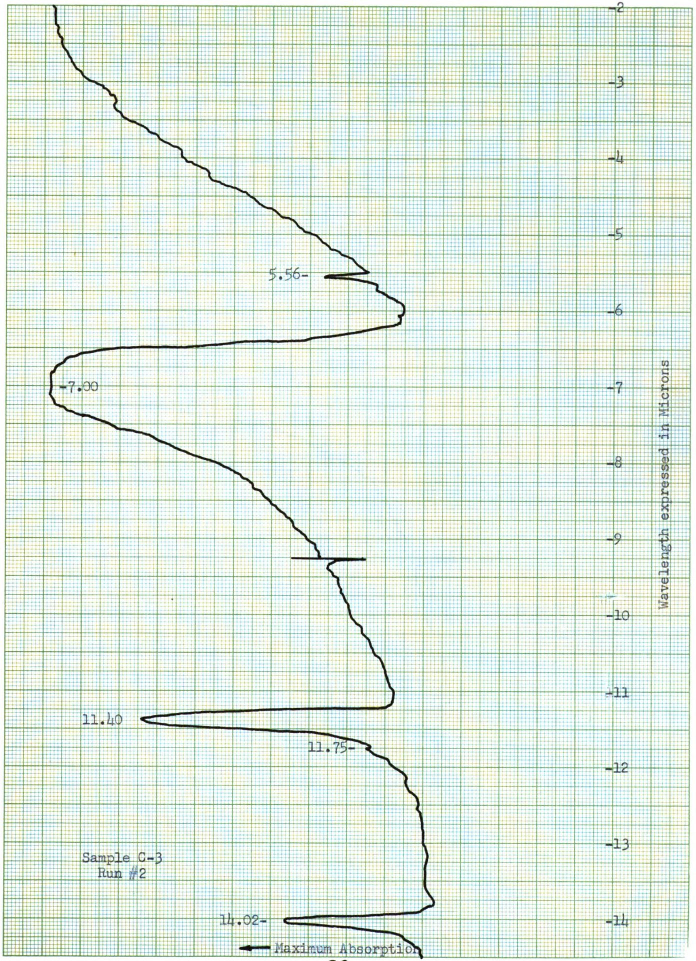

2
3
4
5
6
7
8
9
10
11
12
13
14
Wavelength expressed in Microns
4.00
5.55
7.05
11.40
11.75
14.03
Sample C-1
Run #2
Maximum Absorption

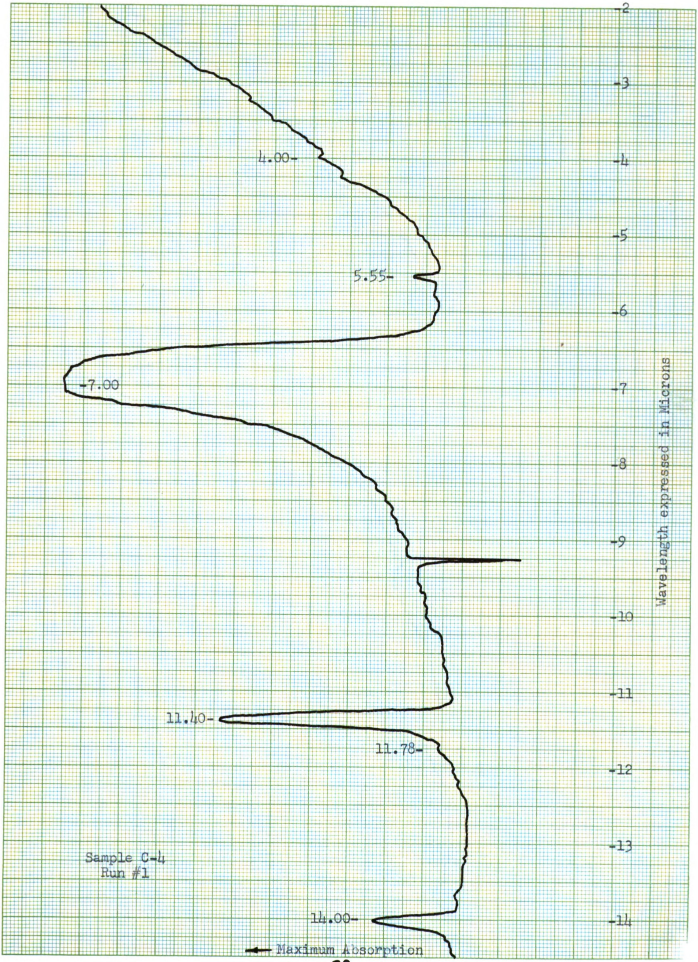

4.00-
5.57-
-7.10
11.42-
11.80-
14.05-
Sample C-2
Run #1
← Maximum Absorption
Wavelength expressed in Microns
2
3
4
5
6
7
8
9
10
11
12
13
14

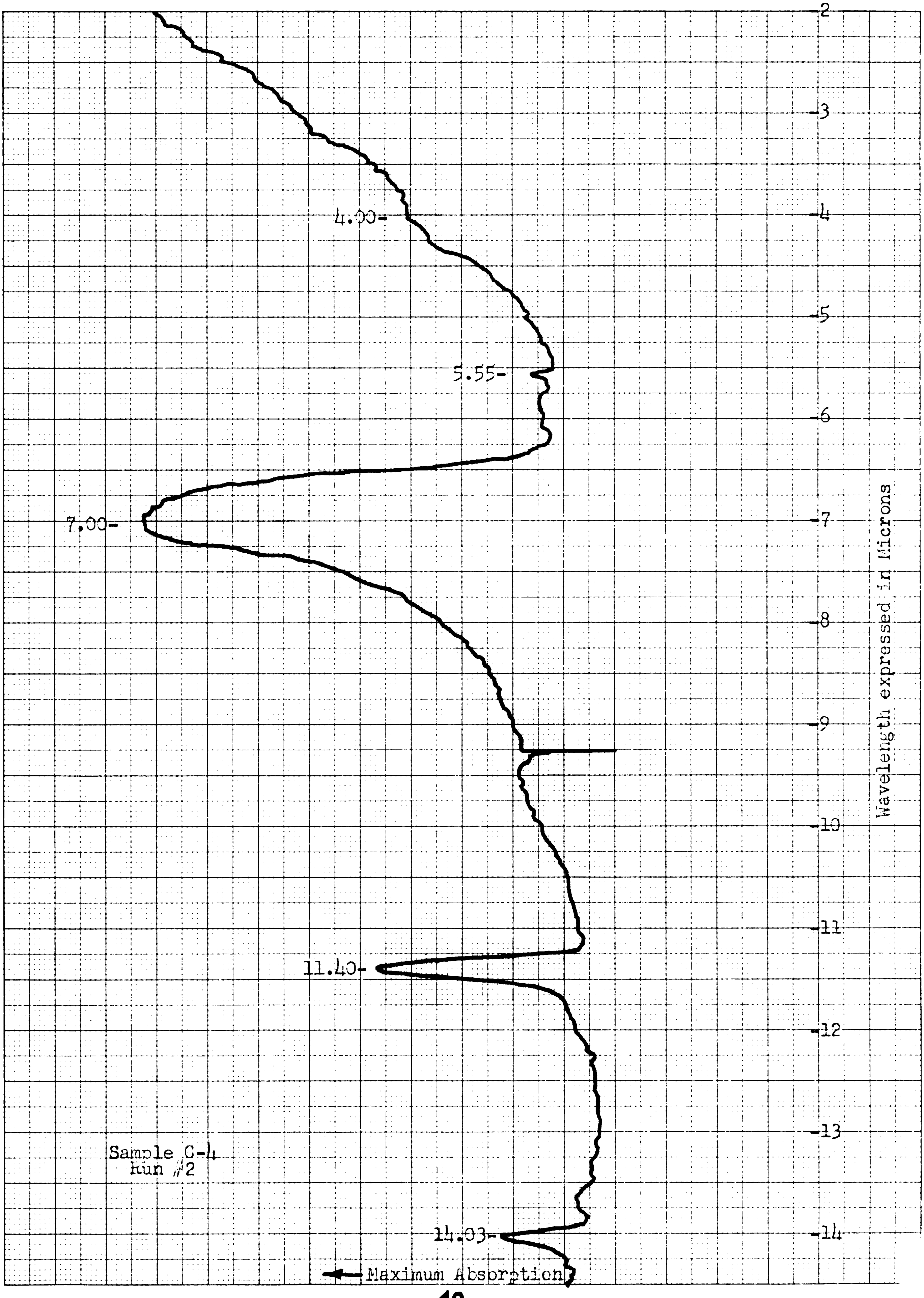


Sample C-2
Run #2

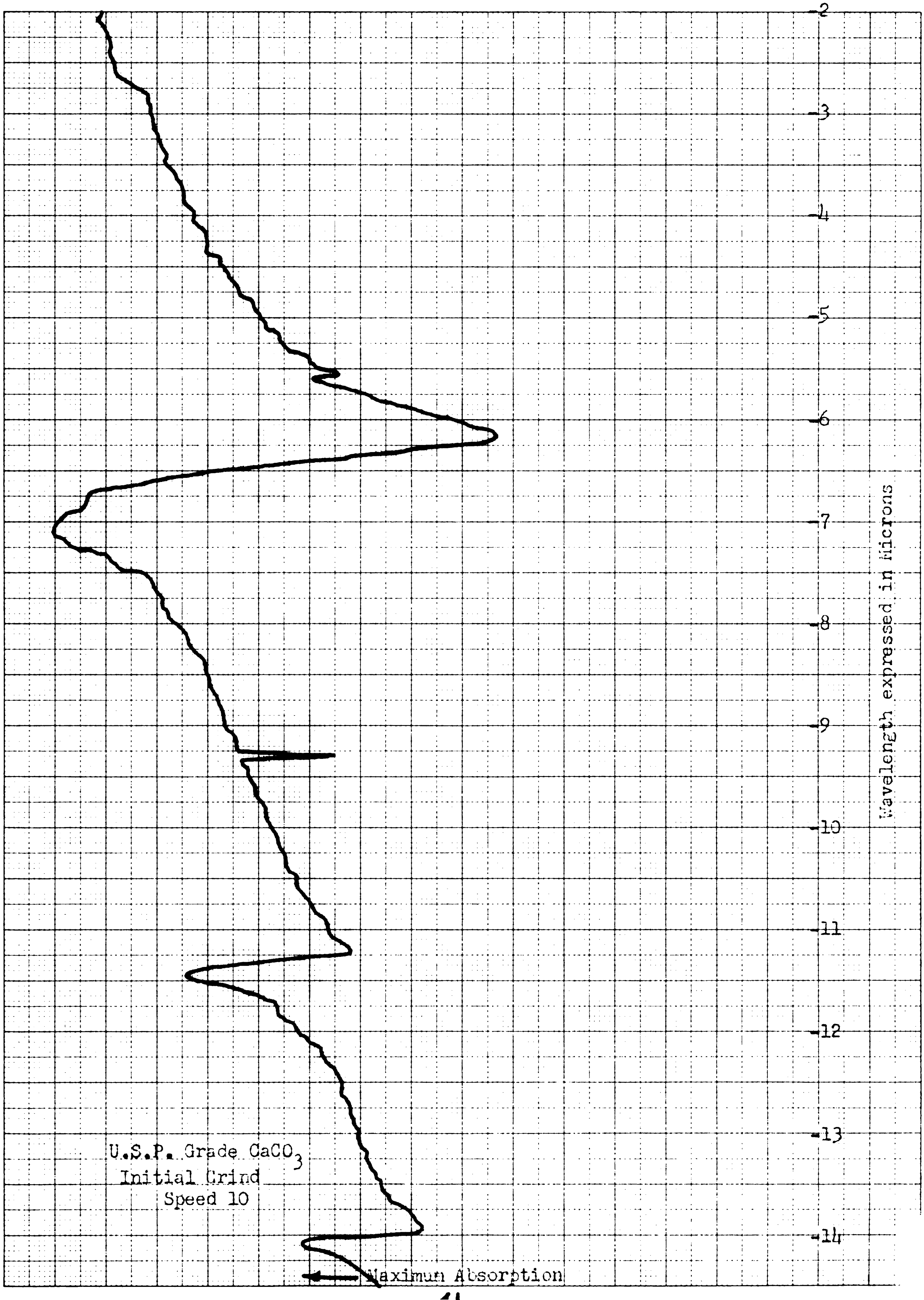

-2
-3
4.00-
-4
-5
5.55-
-6
-7.07
-7
Wavelength expressed in Microns
-8
-9
-10
-11
11.40-
11.78-
-12
-13
Sample C-3
Run #1
14.00-
-14
← Maximum Absorption


-2
-3
-4
-5
5.56-
-6
-7.00
-7
-8
-9
-10
-11
11.40
11.75-
-12
-13
Sample C-3
Run #2
14.02-
-14
Maximum Absorption
Wavelength expressed in Microns
5788

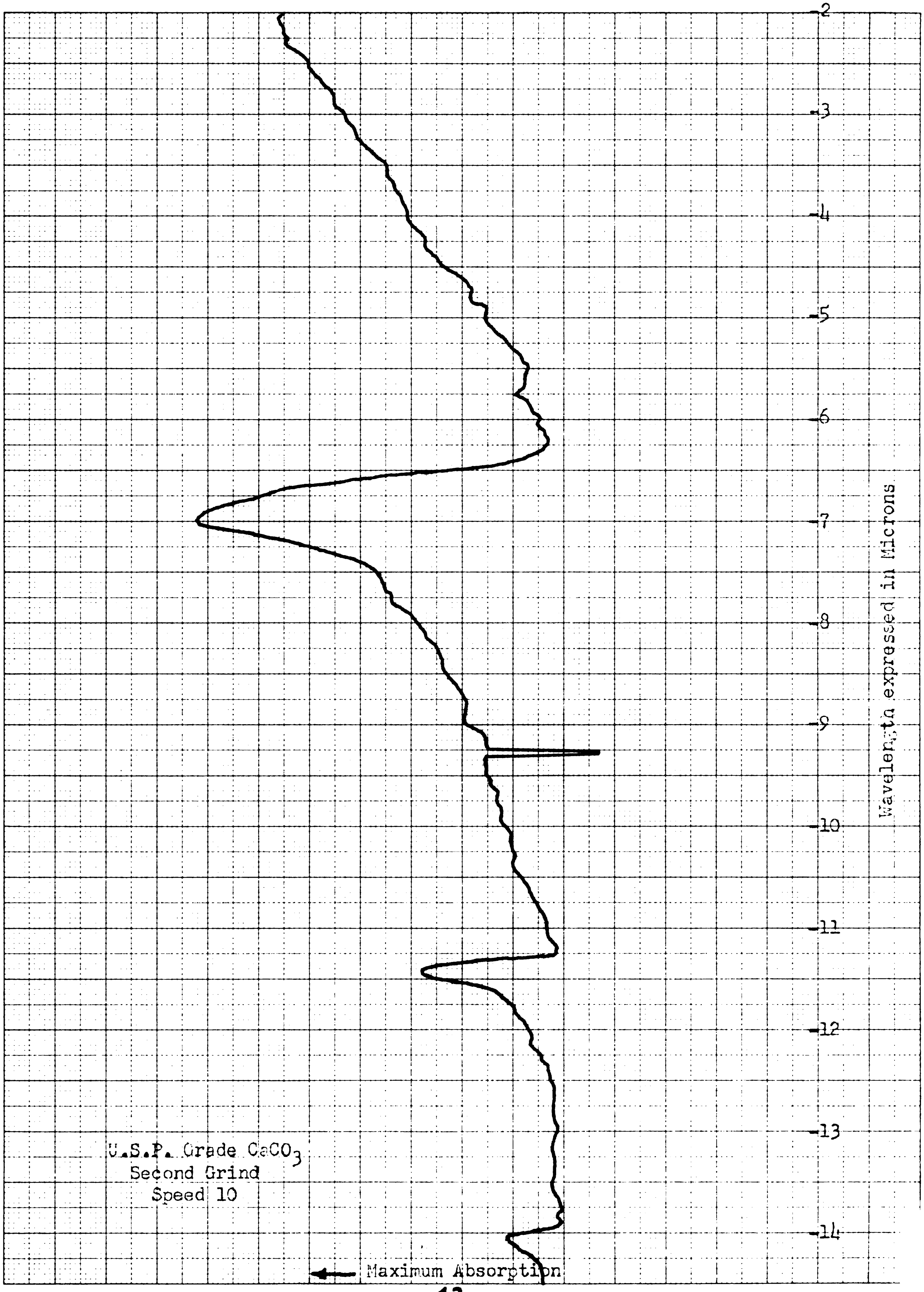

-2
-3
4.00-
-4
-5
5.55-
-6
-7.00
-7
-8
-9
-10
-11
11.40-
11.78-
-12
-13
Sample C-4
Run #1
14.00-
-14
Maximum Absorption
Wavelength expressed in Microns



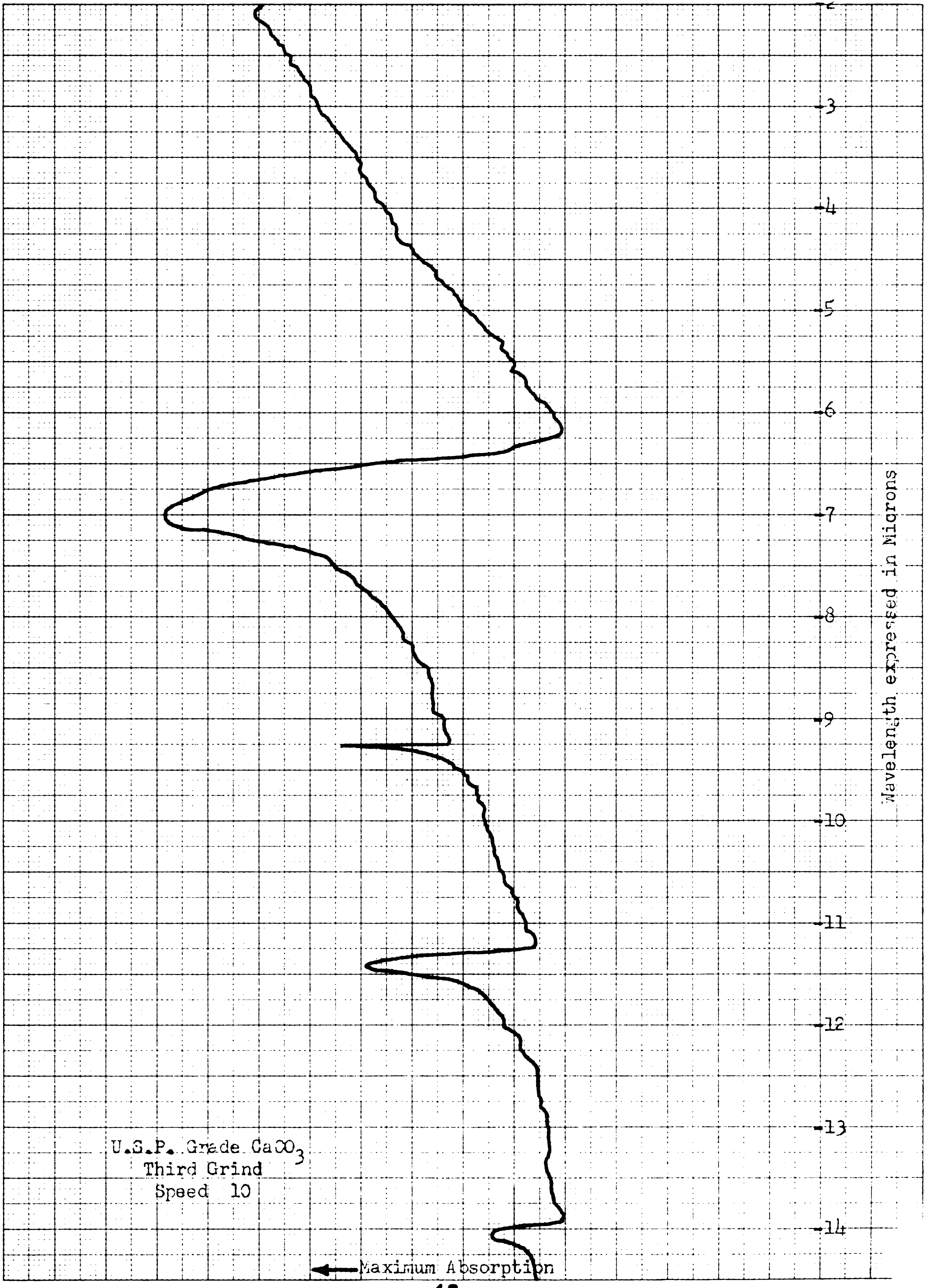
2
3
4.00-
4
5
5.55-
6
7.00-
7
8
9
10
11
11.40-
12
13
Sample C-4
Run #2
14.03-
14
Wavelength expressed in Microns
Maximum Absorption

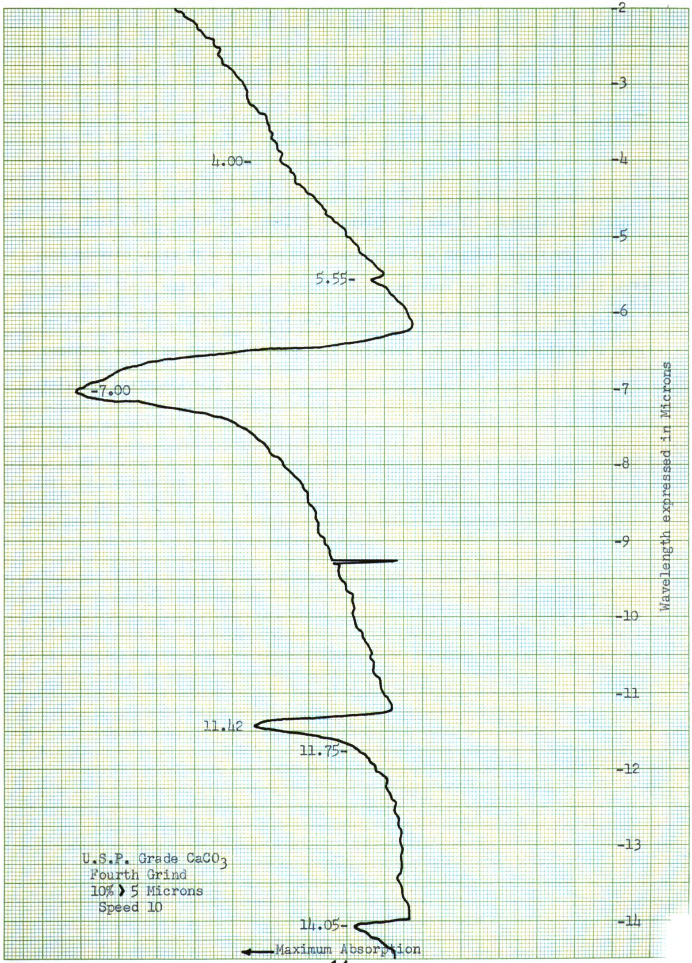

2
3
4
5
6
7
8
9
10
11
12
13
14
Wavelength expressed in Microns
U.S.P. Grade $CaCO_3$
Initial Grind
Speed 10
Maximum Absorption

12.188
5788



U.S.P. Grade $CaCO_3$
Second Grind
Speed 10


2
3
4
5
6
7
8
9
10
11
12
13
14
Wavelength expressed in Microns
U.S.P. Grade CaCO$_3$
Third Grind
Speed 10
Maximum Absorption



U.S.P. Grade $CaCO_3$
Fourth Grind
10% > 5 Microns
Speed 10

CONCLUSION

This research is not conclusive enough for use in correlation within and between units of a rock as homogeneous as the Dundee limestone. However, there was a trend indicated which may show varying degrees of Mg^{++} in the different units and this may or may not be significant. Further research would no doubt indicate that infrared spectroscopy could be a very valuable correlative tool.

RECOMMENDATIONS FOR FURTHER WORK

A study should be made using C.P. $CaCO_3$ and $MgCO_3$ in varying amounts as standards to determine the interdependance on each other of the shift of the wavelength absorption peaks. The percentage of Mg^{++} to Ca^{++} plotted against the absorptions particularly in the 11.40, 11.80, and 14.02 micron wavelength ranges, should result in a straight line function. A plot of this type would be invaluable in determining the amount of secondary dolomitization that occurs in a limestone. It is acknowledged that cations of the carbonates other than Mg^{++} and Ca^{++} will affect absorption peak shift but these would generally be limited to no more than one or two percent of the total.

The techniques used in preparing samples for examination could be improved. Potassium bromide disks have been used with the substance to be analysed dispersed throughout them, in place of the sodium chloride windows used conventionally, for work with inorganic chemicals,and possibly rock and mineral samples could be prepared in a similar fashion. Thin sections of the samples would offer some advantages in analysis but the difficulty in preparing a sample of desired thickness would prohibit most studies.

Further studies should include wavelength regions beyond the limits of this study, as significant absorptions may occur outside the 2 to 15 micron wavelength regions.

BIBLIOGRAPHY

Barnes, R.B., Gore, R.C., Liddel, A., Williams, V.Z., 1944, Infrared Spectroscopy; Reinhold Pub. Corp., New York.

Crawford, B. Jr., Sci. Am., 189, p. 42 (1953).

Daniels, F., Alberty, R.A., 1955, Physical Chemistry; Wiley and Sons, New York.

Harrison, G.R., Lord, R.C., Loofbourow, J.R., 1948, Practical Spectroscopy; Prentice-Hall Inc. New York.

Heigl, J.J., Bell, M.F., White, J.V., Anal. Chem., 19, p. 293, (1947).

Hunt, J.M., Wisherd, M.P., Bonham, L.C., Anal. Chem., 22, p. 1478, (1950).

Hunt, J.M., Turner, D.S., Anal. Chem., 25, p. 1169 (1953).

Keller, W.D., Pickett, E.E., Am. Mineralogist, V.34, p. 855, (1949).

Lipson, H., Cochran, W., 1953, The Determination of Crystal Structures Vol. III; Bell and Sons, London.

Miller, F.A., Wilkins, C.H., Anal. Chem., 24, p. 1253 (1952).

Nahin, P.G., Bull. 169, State of California, Div. of Mines, p. 112 (1955).

Plyler, E.K., Phys. Review, V. 33, p. 48 (1929).

Randall, H.M., Fowler, R.G., Fuson, N., Dangl, J.R., 1949, Infrared Determination of Organic Structures; D. Van Nostrand Co. Inc. New York.

Wilson, E.B. Jr., Decius, J.C., Cross, P.C., 1955, Molecular Vibrations; McGraw Hill Co. Inc. New York.