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ANALYSIS OF ROCKS AND MINERALS BY ATTENUATED TOTAL REFLECTION WITH ATLAS

A Dissertation
Presented to
the Graduate Faculty of the
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Donald Franklin Anderson
July 1975

This thesis, written and submitted by

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Dated May 5, 1976

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Chapter 1

INTRODUCTION

Routine non-destructive analyses of rocks and minerals in slab or powder form may be practicable by the application of the technique of attenuated total reflection [ATR] in infrared [IR] spectrophotometry.

An atlas of spectra would serve the analytical chemist and geologist, who in turn would serve the miner, the lapidarist, and other groups interested in rocks and minerals.

No effort has been made to produce an atlas of spectra of rocks and minerals by ATR. No ATR spectra of rocks and minerals were found in the literature. The history of ATR indicates that it is still in its early stages of development. The application of all phases of IR to the study of minerals has been employed much less than to the study of organics. Lyon [1962] in a seven-year search and bibliography compilation lists a total of 440 papers that have been published by September, 1962, concerning mineral-related IR studies worldwide. A listing for each year since 1943 showed a gradual increase in papers; the greatest number of papers in one year was 57 in 1961. Modern methods of IR analysis involve modifications either of IR transmission through the sample or reflection from the sample. Fahrenfort [1961] introduced the technique of ATR as an application to IR spectrophotometry. Harrick [1967] in a bibliography of 450 references attempted to include "all the literature on internal reflectance spectroscopy available" by February, 1967; 182 references were dated pre-1962 or previous to the introduction of ATR; the titles of 44 of the references specifically included ATR; one title indicated ATR of inorganic ions; no title indicated ATR of minerals. Nyquist [1971] lists approximately 900 IR spectra of inorganic compounds, including 9 minerals, none by ATR. A literature search of abstracted articles through 1974 indicated no titles of articles involving ATR of minerals.

For the analysis of rocks and minerals, ATR is more versatile and more convenient than most methods. It is applicable for both opaque and transparent materials of thick or thin films. It often requires no sample preparation.

This study of ATR of minerals involves the development of an atlas of mineral powder spectra and of mineral slab spectra, the comparison of the two sets of spectra with each other, and the comparison of powder spectra from ATR with transmission spectra in the literature. The study is confined to the spectral range of 0.5 - 15.5 microns.

Chapter 2

ROCKS AND MINERALS

The composition of minerals varies from simple binary compounds to very complex compounds. The composition of rocks varies from pure stoichiometric compounds, through a major intermediate group of variable but predictable composition, to unpredictable conglomerate mixtures. Probably every natural nuclide, with the exception of the rare gases, can be found as an integral constituent of rocks.

Mineralogists typically classify the rock-forming minerals according to the classifications by Deer [1967]. The five classes are: 1. Ortho and ring silicates; 2. Chain silicates; 3. Sheet silicates; 4. Framework silicates; 5. Non-silicates. An IR study of minerals is more informative to the analytical chemist if the minerals are grouped from the simplest to the most complex, instead of being grouped in mineralogists' classifications.

Rocks consisting of simple binary compounds may show IR activity if there is covalent bonding between the two elements. ATR provides an opportunity to study the bonding of metals with non-metals without involving the complications of solvents, heat, or chemical reagents. Minerals consisting of relatively pure binary compounds---such as galena [PbS], pyrite [FeS_2], or hematite [Fe_2O_3]---are common. In binary compounds, there may be bonding between metal and non-metal, but if the bonding is only between two atoms of non-metal, as in FeS_2, there would not be any IR activity, because there would not be any change in dipole moment. The spectral range of 0.5 - 15.5 microns is inadequate in the study of bonding and identification of binary compounds. Nyquist [1971] has extended the range up to 25 microns with adequate results.

A second group of rocks consists of relatively pure single compounds of only two kinds of ions, but in which at least one of the ions is complex---such as carbonates, sulfates, titanates, phosphates, and silicates. In these cases ATR sensitivity is usually sufficient to determine the effect of the metallic ion upon the complex and therefore identify the metallic ion. The identification of the complex species is unambiguous.

The third group of rocks consists of mixtures of two similar compounds---as in the case of dolomite, a mixture of $CaCO_3$ and $MgCO_3$. Other examples are serpentine, talc, and kaolinite---all somewhat stoichiometric combinations of oxides of metals with silicon dioxide. In these cases quantitative abundance of the compounds can be determined by ATR.

All other rocks can be grouped as complex, with three or more metallic elements possible. Mixtures involving complex minerals are difficult but not impossible to identify in quantitative ATR analysis.

Chapter 3

INFRARED SPECTROMETRY

That part of the electromagnetic spectrum consisting of wavelengths 0.2-200 microns has been designated as infrared [IR].

The energy of a molecule can be described in terms of translational, rotational, vibrational, and electronic contributions. Those contributions involving IR are rotational and vibrational. In the solid state molecular rotational energy is negligible. Vibrational energy is the only type that is of importance in the IR studies of solids.

Vibration of atoms of a molecule with respect to each other is a type of molecular motion. Electromagnetic radiation can induce transitions among the vibrational-energy levels. For energy to be transferred between the radiation and the vibrating molecule, an electrical coupling must be present. This coupling can occur if the vibrating molecule produces an oscillating dipole moment that can interact with the oscillating electric field associated with all electromagnetic radiation. During the interaction, energy is transferred from the radiation to the molecule, or vice versa. Homonuclear diatomic molecules do not interact with the radiation.

The vibrations between any two adjacent atoms in a molecule involve deformation of the chemical bond between them. The bond behavior can with good approximation be compared to behavior of a spring and is governed by Hooke's law:

$$\bar{v} = \frac{1}{2c[pi]} \frac{k[m_1 + m_2]}{m_1 m_2}^{1/2} \text{, where:}$$

$\bar{v}$ = the wave number [which is the frequency divided by the speed of light] in cm^{-1}; m_1 = the mass of one atom in grams; m_2 = the mass of the other atom in grams; c = the speed of light in cm sec^{-1}; k = the force constant in dyne cm^{-1}.

The force constant measures the force required to deform a bond by a given amount and is characteristic for each bond in a specific molecular species; it is approximately characteristic for the same bond in various differing molecules. The value of the force constant can be determined by observed absorption; its value can be approximately predicted by use of the empirical equation of Gordy [1946]:

$$k = aN[x_A x_B / d^2]^{3/4} + b, \text{ where:}$$

k = the force constant in dyne cm^{-1}; a = a constant of value 1.67; N = the bond order; x_A and x_B = the Pauling electronegativities of atoms A and B respectively; d = the internuclear distance in angstroms; b = a constant of value 0.30.

The maximum number of normal modes of vibration of a molecule is determined by the fact that each nucleus has three degrees of freedom of motion; the total number of degrees of freedom in the molecule of n number of atoms is 3n. Three degrees most be deducted from this for translation of the molecule as a rigid unit and three for rotations about each principal axis. The maximum number reduces to 3n - 6, excepting for a linear molecule which has 3n - 5. The number may be reduced further if the symmetry of the molecule may be such that certain pairs or triads of the fundamental vibrations are exactly equal.

Almost all molecules occupy the zero-point vibrational energy level at ordinary temperatures; therefore the most dominant interaction with electromagnetic radiations is that of absorption. Each absorption yields an absorption band. The number of absorption bands exhibited by the IR spectrum of a molecule can be increased by the production of overtones and by combinations of fundamental or harmonic bands. The intensity of an IR absorption band is proportional to the square of the rate of change of dipole moment with respect to the displacement of the atoms. Weakly polar bonds yield weak absorption bands, and partially ionic bonds yield strong absorption bands. The intensity of all bands is proportional to the amount of the sample in the path of the IR radiation.

Increasing the masses of the atoms decreases the frequency of the absorption band, and increasing the bond length decreases the frequency of the absorption band. The recording of all absorptions over a span of wave-lengths yields a consistently reproducible "fingerprint" of a substance.

Differing crystalline forms of the same compound have differing spectra. Differing lattice structures result in different symmetries, and thus in different vibrations. These lattice vibrations often result in additional absorption bands for crystalline polyatomic inorganic compounds. The lattice vibrations result in mutually displaced absorption bands in different crystalline forms of the same compound. Non-identical spectra of two crystalline forms of the same compound make it analytically possible to distinguish between them.

Chapter 4

ATTENUATED TOTAL REFLECTION

The following terms dealing with internal reflection spectroscopy have been approved by the sponsoring committee and accepted by the American Society for Testing Materials [ASTM] [1971]:

1. INTERNAL REFLECTION SPECTROSCOPY [IRS]. The technique of recording optical spectra by placing a sample material in contact with a transparent medium of greater refractive index and measuring the reflectance [single or multiple] from the interface, generally at angles of incidence greater than the critical angle.

2. SPECTRUM, INTERNAL REFLECTION. The spectrum obtained by the technique of Internal Reflection Spectroscopy. Note: Depending on the angle of incidence the spectrum recorded may qualitatively resemble that obtained by conventional transmission measurements, may resemble its mirror image or may resemble some composite of the two.

3. ATTENUATED TOTAL REFLECTION [ATR]. Reflection which occurs when an absorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity. Note: In this process, if an absorbing sample is placed in contact with the reflecting surface, the reflectance for total internal reflection will be attenuated to some value between greater than zero and unity in regions of the spectrum where absorption of the radiant power can take place.

4. INTERNAL REFLECTION ELEMENT [IRE]. The transparent optical element used in Internal Reflection Spectroscopy for establishing the conditions

necessary to obtain the internal reflection spectra of materials. Note: Radiant power is propagated through it by means of internal reflection. The sample material is placed in contact with the reflecting surface or it may be the reflecting surface itself. If only a single reflection takes place from the internal reflection element, the element is said to be a single-reflection element; if more than one reflection takes place, the element is said to be a multiple-reflection element. When the element has a recognized shape it is identified according to each shape, for example, internal reflection prism,....internal reflection plate,....etc.

5. SINGLE-PASS INTERNAL REFLECTION ELEMENT. An internal reflection element in which the radiant power traverses the length of the element only once; that is, the radiant-power enters at one end of the optical element and leaves via the other end.

6. FIXED-ANGLE INTERNAL REFLECTION ELEMENT. An internal reflection element which is designed to be operated at a fixed angle of incidence.

In his studies of the total reflection of light at the interface between two media of different refractive indices Newton discovered, more than 250 years ago, that an evanescent wave extends into the rarer medium beyond the reflecting surface that is in contact with the rarer medium. Since 1959 it has been known that optical absorption spectra can conveniently be obtained by a measure of the interaction of the evanescent wave with the external medium. A standing wave normal to the reflecting surface is established in the denser medium and there is an evanescent, non-propagating field in the rarer medium whose electric-field amplitude decays exponentially with the distance from the surface. The evanescent ray can either be reflected at a displaced position or be absorbed by the rarer medium.

When the sample constitutes the rarer medium, the reflectivity is a measure of the interaction of the evanescent wave with the sample material and the resulting spectrum is also a characteristic of the sample material. Strong absorptions of the evanescent wave by the sample can be obtained at certain angles of incidence. Relative to Transmission[T] spectra, the absorption bands of reflection are slightly displaced to longer wave-lengths [never more than one wave-length] and are broadened on the long wave-length side. At larger angles of incidence reflection spectra resemble T spectra more closely than with smaller angles.

Light striking an interface between two transparent semi-infinite media of different refractive indices will be partially reflected and partially transmitted. The transmitted ray travels at a different velocity from the reflected ray. The velocity of monochromatic light is a characteristic for each medium. Because of its different velocities in the two media, the transmitted ray is refracted as described by Snell's law:

$n_1 \sin \theta = n_2 \sin \phi$, where:

n_1 and n_2 are the refractive indices of the two respective media, and θ and ϕ are the angular deviations of the light beam from the normal in media 1 and 2 respectively. When $n_1 \neq n_2$, the beam is refracted at the interface. When n_1 is greater than n_2, then θ is less than ϕ. θ, ϕ and interfacial normal angles are always in the same plane; this plane is called the plane of incidence. If θ is the angle of the incident beam, there is a value of θ less than 90° at which ϕ is 90° or parallel to the interface; such angle θ is called the critical angle [θ_c]. All values of θ larger than θ_c result in 'total reflection'. Because of the evanescent ray, the term 'total reflection' is not precisely total.

When the second medium is absorbing, the extent of the interaction of the evanescent wave with the absorbing medium when n_1 is greater than n_2 can be determined through the classical reflection equations of Fresnel. It is advantageous to first consider the relatively simple equations for non-absorbing media and then modify them for the case of absorbance by the second medium. It is known that all reflected light is partially polarized and that there is an angle of incidence for the interface between any two media in which the reflected light is completely polarized; this angle is called the polarizing angle or Brewster's angle, and its value is a characteristic of the two media. Fresnel's equations describe the reflected amplitudes separately for perpendicular polarization and parallel polarization:

$$r_{\perp} = \frac{-\sin [\phi - \theta]}{\sin [\phi + \theta]} \quad \text{and} \quad r_{\parallel} = \frac{\tan [\phi - \theta]}{\tan [\phi + \theta]}, \quad \text{where:}$$

$r_{\perp}$ is the reflected amplitude for the perpendicular polarized beam [the electric vector vibrates in the plane perpendicular to the plane of incidence] and $r_{\parallel}$ is the reflected amplitude for the parallel polarized beam. Both $r_{\perp}$ and $r_{\parallel}$ are expressed as fractional values of the incident beam amplitude. θ is the angle of incidence and ϕ is the refracted angle.

At values of θ greater than θ_c, ϕ becomes imaginary and the Fresnel equations become:

$$r_{\perp} = \frac{\cos \theta - i\,[\sin^2\theta - [n_2/n_1]^2]^{1/2}}{\cos \theta + i\,[\sin^2\theta - [n_2/n_1]^2\;{}^{1/2}} \qquad \text{and}$$

$$r_{\parallel} = \frac{[n_2/n_1]^2 \cos \theta - i \, [\sin^2 \theta - [n_2/n_1]^2 \,]^{1/2}}{[n_2/n_1]^2 \cos \theta + i \;\; \sin^2 \theta - [n_2/n_1]^2 \;\;^{1/2}}$$ where:

$i = [-1]^{1/2}$.

When n_2 is less than n_1, and the rarer medium is absorbing, Fresnel's equations are valid if the refractive index of the rarer medium is replaced by the complex refractive index:

$\hat{n}_2 = n_2 \, [1 - ik_2]$, where

$\hat{n}_2$ = the complex refractive index and k_2 = the attenuation index or absorption index. The attenuation index of a medium is related to the absorption coefficient $[\alpha]$ through the Lambert absorption law, which yields the relationship:

$nk = \alpha c/4\pi v$, where

n = the refractive index, k = the attenuation index, c = the speed of light, and v = the frequency of the radiant beam. Solutions to the substituted Fresnel equations are laborious without the aid of a computer.

The reflectivity, which represents the percentage of reflected power relative to the incident power is given by the square of the amplitude. For non-absorbing media the squares of the Fresnel equations give the total reflectivity and are reduced to :

$R = [n_2 - n_1]^2 \, / \, [n_2 + n_1]^2$, where

R = the reflectivity, and n_1 and n_2 are the refractive indices of the respective media. The reflectivity of an absorbing rarer medium becomes:

$$R = \frac{[\, n_2 - n_1 \,]^2 + [\, n_2 k_2 \,]^2}{[\, n_2 + n_1 \,]^2 + [\, n_2 k_2 \,]^2} \, .$$

Use of Fresnel's equations reveals that during total reflection the refractive index of an absorbing medium is not a constant but is dependent on the angle of incidence; the critical angle becomes a range of angles rather than a precisely located angle; the penetration depth by the evanescent ray is greatest near the critical angle; the penetration depth increases with increasing wave-length of radiation [Khortüm: 1969].

The application of reflection theory to analysis involves the desirability of strong absorption of the evanescent ray by the sample to yield significant absorption bands. Strong absorption can be achieved when the angle of incidence is near the critical angle to allow deep penetration of the evanescent ray: this deeper penetration, however, is accompanied by a greater lag of the subsequent reflection of that portion of the evanescent ray that is not absorbed; this results in broader absorption bands displaced toward the longer wave-length.

The process of attenuated total reflection [ATR] achieves the combination of both strong absorption and sharp relatively undisplaced spectra by adjusting the incident angle to be considerably larger than the critical angle to yield only small absorption per reflection, while the same incident beam is reflected many times. For example, a trapezoidal prism of the optically denser medium can have the beam enter one of the sides that forms an oblique angle with the two parallel faces. When both faces are in contact with the rarer medium and the angle of incidence to the two faces is much greater than the critical angle, the beam will be reflected from face to face as it progresses between them. The evanescent wave can be absorbed during each reflection, resulting in multiple identical weak absorptions. The beam is progressively attenuated. The absorption band is not only strong but also sharp and only slightly displaced. Under these conditions the lack of deep penetration of the evanescent ray [Penetration may be as low as one-tenth wave-length.] makes total absorption insignificant unless the rarer medium is in intimate contact with the prism. For strong absorption the rarer medium can be a gas, liquid, or polished solid that makes abundant contact along the path of the reflected beam.

Chapter 5

OTHER ANALYTICAL METHODS

Every successful analytical method has its advantages and disadvantages. Wainerdi's [1971] monograph has surveyed the methods of mineral analysis and has an extensive bibliography. A brief discussion of some of the most used methods for mineral analysis follows.

IR TRANSMISSION

IR transmission problems involving inorganic crystalline materials center primarily around the sample; they include:

1. Typical windows necessary when using mulls are prone to ion-exchange with the sample; this eliminates KBr, NaCl, CsBr, and CsI as windows for most samples. BaF_2 windows have been employed with some success.
2. It is necessary to use more than one mulling agent for each spectrum unless only a narrow range is needed; the absorption bands from the mulling agent would otherwise interfere with the spectra. Fluorolube is satisfactory in the range 2.63 - 7.50 microns, and Nujol is adequate for 7.50 - 25.
3. The sample must be ground to less than 5 micron diameter; large size causes refraction, distorts spectra, and reduces contrast in absorption bands.
4. It is difficult to accurately regulate the thickness of the sample, making quantitative analysis difficult.
5. Use of compressed disks involving diluting agents such as KBr, intro-

duces ion-exchange probabilities between sample and KBr.

The general descriptions of many inorganic transmission spectra have been established. Transmission spectra are similar but not identical to reflection spectra. Transmission spectral data for some specific minerals are listed in the section on data discussion. Some generalities by Nyquist [1971] are listed here in microns:

2.94 - 5.00	Strong to medium-strong multipeaked O-H stretching that is characteristic of very acidic protons of acid salts, including HCO_3^{-1}, and HPO_4^{-2}, and HSO_4^{-1}.
2.70 - 3.13	Strong sharp band for O-H stretching of hydroxyl groups and water.
2.78	Strong sharp band for O-H stretching of water of hydration.
2.94	One or more strong sharp bands for O-H stretching of water of hydration.
2.94 - 3.13	Strong broad band for O-H stretching of free water.
2.70 - 2.73	Strong sharp O-H stretching of hydroxyl groups.
6.06	H-O-H bending
6.06 - 6.25	H-O-H bending, medium multicomponent water of hydration.
6.67 - 33.3	Polyatomic anions stretching and bending.
16.67 - 1000	Most inorganics.
25 - 1000	Lattice modes.
33.3 - 1000	Most lattice modes.
33.3 - 1000	Heavy metal oxides.

WET CHEMICAL ANALYSIS

In wet chemical analysis the sample is first dissolved either directly by suitable acids or fused with a flux and then dissolved in acid. The constituents to be determined are separated from interfering substances, either by precipitating the interfering substances or the desired constituents, or they are separated by selective solvent extraction. The constituents are then determined by gravimetric, volumetric, or fire assay analysis.

The technique of wet chemical analysis is still, perhaps, the most valuable technique in the analysis of natural materials, since many of the modern physical methods are dependent on standards analyzed in the classical way. It is a laborious method, however, and for many elements the detection limits are poor. Further, except for the simple routine analysis, experienced analysts are required to conduct delicate chemical manipulations.

MICROSCOPIC METHODS

Heinrich [1965] asserts that the recognition of minerals by means of their optical properties is the single most widely used and most widely applicable method of mineral identification. Optical methods applied to minerals in thin section have long been used and were developed to a state of considerable refinement before the immersion method became widely known.

Microscopic methods of mineral analysis have now become virtually synonymous with the determination of the refractive index by the immersion method. The immersion method has been the only technique available for determining the refractive index or indices of minute, translucent solid particles. In this method the particles are placed in liquids of known refractive indices and examined with a petrographic microscope, which reveals that the particle has either a higher or lower refractive index than the liquids.

For purposes of identification only, the refractive index of a mineral typically needs to be measured no more accurately than to 0.01. But to determine the approximate composition in a series, the accuracy needs to be in the order of 0.005.

Factors that influence the accuracy of refractive index determinations of solids via immersion have been summarized by Allen [1954]:

1. Limitations inherent in the mechanical design and optical characteristics of the microscope.
2. The skill, experience, and visual acuity of the observer.
3. The size and shape of the particles, their visibility and their indices---the lower indices can be determined more accurately. Accuracy in birefringent crystals is more difficult to attain.
4. The uniformity of the index throughout the specimen.
5. The precision with which the liquids of a set are calibrated for their indices and the accuracy of the temperature coefficients, combined with the smallness of the intervals between adjacent members of the series.
6. The accuracy with which the actual working temperatures of the liquids are determined.

ION EXCHANGE CHROMATROGRAPHY

Ion exchange chromatography is a versatile method of separation and concentration of ions. It is applicable to many kinds of analyses, including mineral analysis. Many minor elements commonly occur in concentrations below the limit of spectrographic detection, and for this reason alone separation and preconcentration is required.

The experimental technique is simple and in most cases fairly rapid. After the sample has been dissolved, the ions are isolated or concentrated by use of substances, usually resins, which will give up a cation, such as hydrogen ion, for the cations in the sample. Or another resin will give up an anion, such as hydroxide ion, for the anions in the sample.

The net result, however, is that ion-exchange is merely a step in another analytical process.

COLORIMETRY

Chemical colorimetry has been a leading analytical method for the determination of small amounts of inorganic constituents in the range of 10^{-5} to 5% by weight concentrations. This method lends itself well to trace element analysis in minerals. Even lower concentrations can be determined through the use of ion-exchange to concentrate the constituent. This method is now more commonly called visible spectrophotometry and no longer depends upon the human eye to determine concentrations. The method is often reliable to less than -% relative error.

Solution spectrophotometry is based on Beer's Law, which accurately predicts the percentage of incident light that will be transmitted through a solution. Expressed mathematically in one of the most useful forms:

$\log P_o/P = abc$, where:

P_o = the intensity of the incident light [monochromatic],

P = the intensity of the transmitted light through a medium containing ing the absorbing constituent being measured,

a = a constant characteristic of the absorbing constituent,

b = the length of the path of light through the medium,

c = the concentration of the absorbing constituent.

As in so many methods, standards need to be used from known values.

OPTICAL EMISSION SPECTROSCOPY

Emission spectroscopy, often referred to as spectrochemistry, was the first direct instrumental analytical technique to be widely used in geochemical investigations. Its detection limits are often in the low-ppm range. Recently, with sophistication of comparators and with computerization, the method now gives quantitative results in many cases. No solutions nor separations are necessary. Nevertheless, the average laboratory has at best the ability to determine only semi-quantitatively.

The method is based on the fact that excited planetary electrons emit discrete quanta of energy when they fall back to a lower energy level. The various quanta can be separated by a prism or diffraction grating. Photographs of the many diffracted emissions possible show up as lines representing specific wave-lengths in the ultra-violet and visible range. Some emissions happen more commonly than others for each element, and the pattern of intensity is characteristic of each element.

The sample is often powdered, but often even this is unnecessary. Its greatest value is in the determination of metallic elements. Aside from high cost and the need for an experienced operator, spectrochemistry is an excellent and valuable tool for geochemical analysis for elements in which all the elements are experimentally determined simultaneously.

Nevertheless, this method yields essentially no information on molecular structure or on bonding.

ATOMIC ABSORPTION

Atomic absorption depends on the phenomenon whereby atoms of an element are able to absorb electromagnetic radiation. This occurs when the atoms are unionized and unbonded to other kinds or to similar atoms. The wave-length of light at which atomic absorption proceeds is specific for the type of atom and occurs at its resonant frequencies. These frequencies correspond to the electronic transition between the first allowable energy level and the ground state of the atom.

Atomic absorption provides a simple and inexpensive technique wherein a wide range of elements in many different types of materials may be determined accurately and precisely. It is a powerful, relatively new tool. The prime disadvantages seem to be the facts that the sample must be brought into solution and that only one element can be analyzed at one time.

It is true that sometimes there are interferences of the chemical, molecular, and spectral categories. The molecular interferences could possibly result in information on bonding, as the tachnique gains in its spectacular rise in popularity.

X-RAY DIFFRACTION

X-ray diffraction establishes crystal structure. If the substance being studied has ever undergone this process in the past and has had its identity established, merely referring to the library, or index, of diffraction patterns on file can match this unknown with a substance in the index and thereby establish its identity.

The method utilizes the fact that many X-rays have wave-lengths of approximately the same value as the distance between planes of atoms in a crystal; therefore, the crystals are able to act as diffraction gratings for the X-rays, as illustrated in figure A:

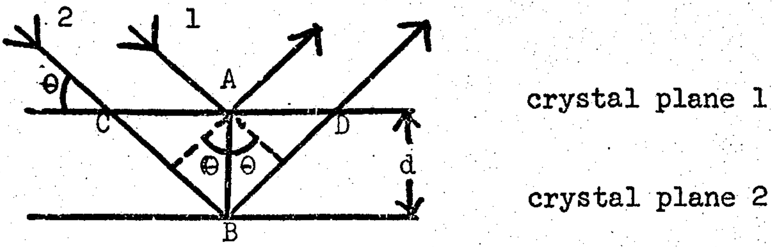

Figure A. Diffraction of X-rays by a Set of Crystal Planes.

The only way that the X-ray beam 2 can reinforce beam 1 is for distance CBD to be an integral multiple of the wave-length of the X-ray. The distance CBD is equal to 2d sin θ; From this information Bragg formulated the equation:

$n\lambda = 2d\sin\theta$, where:

n = an integer, λ = the wave length of the X-ray,

d = the distance between crystal planes, and

θ = the angle of incidence.

The above equation is an expression of Bragg's Law. If the X-ray beam is monochromatic, there will be a limited number of angles at which diffraction of the beam will occur. This pattern can be photographed. Every crystalline substance scatters the X-rays in its own unique diffraction pattern, producing a "fingerprint" of its atomic and molecular structure. One unique feature of X-ray diffraction is that components are identified as specific compounds.

Cost, dangers of high voltage systems, dangers of exposure to X-rays, and therefore the necessity for an expert operator tend to limit the use of X-ray diffraction more than otherwise.

NUCLEAR ACTIVATION ANALYSIS

Nuclear activation analysis is a technique for determining qualitative and quantitative composition by means of nuclear transmutation and the subsequent measurement of emitted radiation from an unknown substance. Basically, some of the atoms present in the unknown material interact with the bombarding particles and, in many cases, are converted into radionuclides with known nuclear characteristics.

The three basic steps in nuclear decay activation analysis are:

1. irradiation of the sample to induce the desired radioactivity.
2. measurement of the emitted radiations from the sample.
3. interpretation of the data to obtain the qualitative and quantitative analysis of the sample.

The method is limited primarily to availability of radiation source and to the kinds of nuclides that will respond to a specific source. There are also the dangers of human exposure to radiation.

Chapter 6

INSTRUMENTATION

The instruments and equipment used in this project were the Perkin-Elmer Model 21 Double Beam Recording Infrared Spectrophotometer, the Wilks Model 12 Double Beam Attenuated Total Reflection Attachment, KRS-5 reflector plates with 45° entrance edge, and the slab sample-holder.

DOUBLE BEAM RECORDING INFRARED SPECTROPHOTOMETER

In a double beam spectrophotometer [Figure B] two equivalent beams are taken from the source. One beam travels through the sample, the other travels either through a blank or through air only. Each one is alternately interrupted by a rotating mirror-chopper or directed to a monochromator-detector system. While one beam is interrupted, the other is directed. The detector changes the IR signals to electric signals. These signals are then amplified, and if the sample signal differs from the reference signal an alternating current results. The current activates a servo mechanism which governs the amount of reference beam allowed to reach the detector. The reference beam is regulated until both beams are the same intensity. The servo mechanism is also connected to a recorder pen. The movement of the recorder pen as the beams are gradually equalized constitutes a measurement of the relative transmittance of the sample.

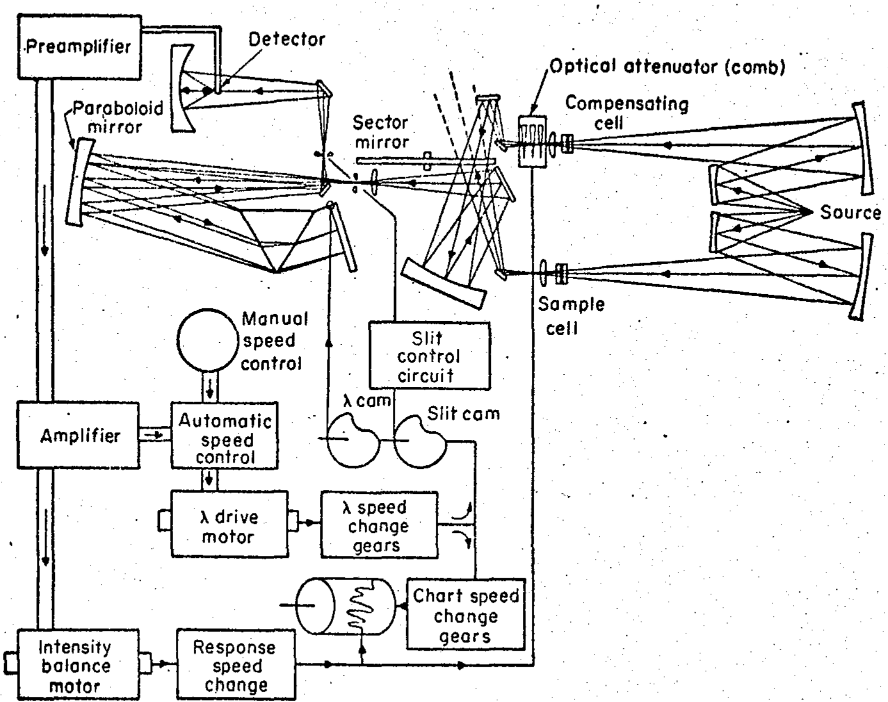

Figure B. Perkin-Elmer Model 21 Optical System [Willard: 1965]

WILKS MODEL 12 DOUBLE BEAM ATTENUATED TOTAL REFLECTION ATTACHMENT

The Model 12 [Figure C] is an ATR attachment for a double beam infrared spectrophotometer; it is attached externally between the IR source and the chopper. The attachment consists of two identical parts; one part directs the reference beam, and the other part directs the sample beam. Each part consists of four rotatable mirrors and of anchor pins to position the removable sample reflector plate holder or reference reflector plate holder. When the sample plate and holder are in position, two mirrors are employed to reflect the sample beam into the plate and two mirrors direct the beam from the plate to the chopper. The same process occurs with an identical system to direct the reference beam through the reference plate.

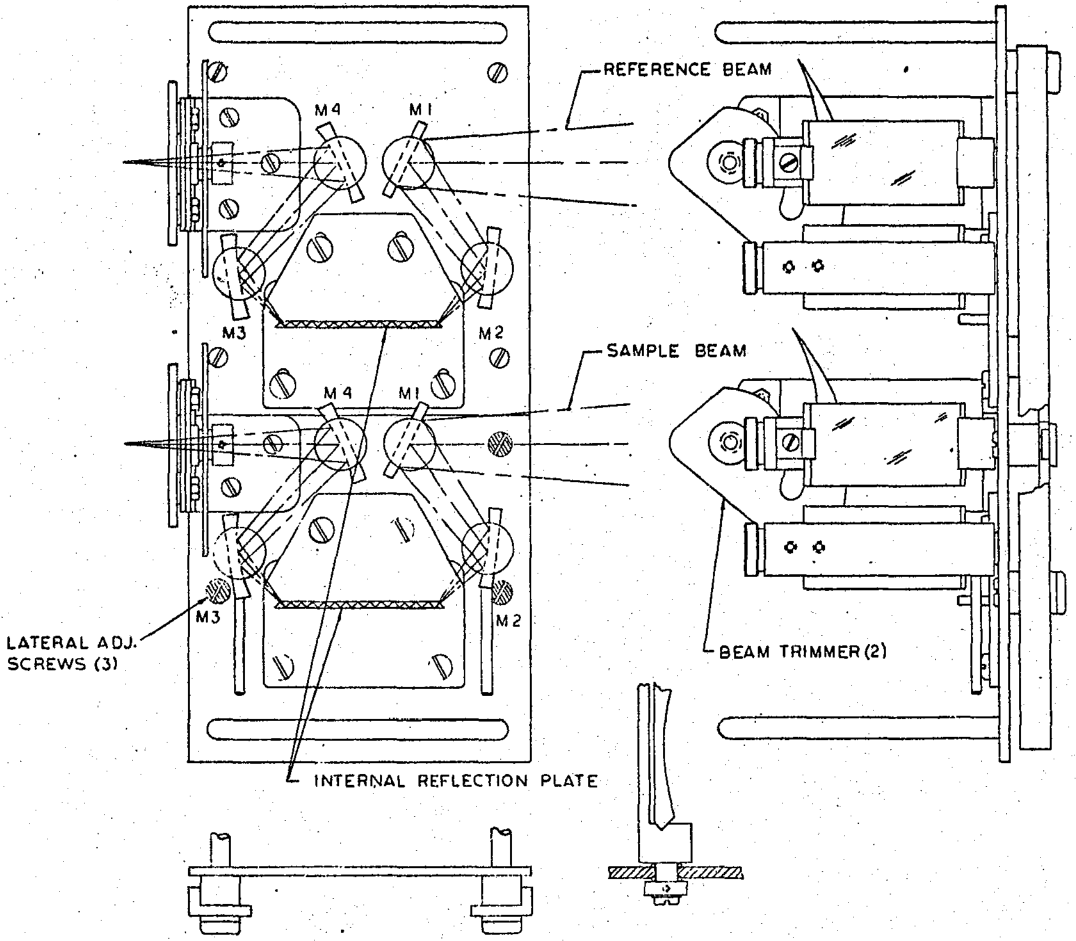

Figure C. Wilks Model 12 ATR Attachment [Wilks: 1965]

KRS-5 INTERNAL REFLECTION ELEMENT

Internal Reflection Element [IRE] is the transparent optical element used in internal reflection spectroscopy for establishing conditions necessary to obtain the internal reflection spectra of materials. IRE of many designs have been employed to fit the needs of the various ATR attachments. One of the most common shapes is the trapezoid [Figure D]. The distance between the parallel faces, the thickness, is much less than the dimensions of either face, creating a thin plate. The slope of the edges of the IRE is typically 45°; some are 60°; a few are 30°. IRE with edges of any angle can be used; they are limited in use only to limitations of the ATR attachment and to the critical angle created by the sample. IRE and attachments are designed to allow the IR beam to enter the plate through the center of one of the edges at an angle normal to the edge. The beam exits through the center of the opposite edge and normal to it. The ratio of the length to the thickness of the IRE is critical for maximum transmittance. The ratio of the length to thickness should be chosen so that the central ray enters and leaves via the center of the entrance end exit apertures respectively. IRE facial surfaces must be highly polished for maximum internal reflection. There is an optimum length of IRE in each ATR system which attains the maximum absorption via maximum number of reflections before the radiation loss by diffusion attendant with each reflection reduces the response of the spectrophotometer below a significant and discriminating value.

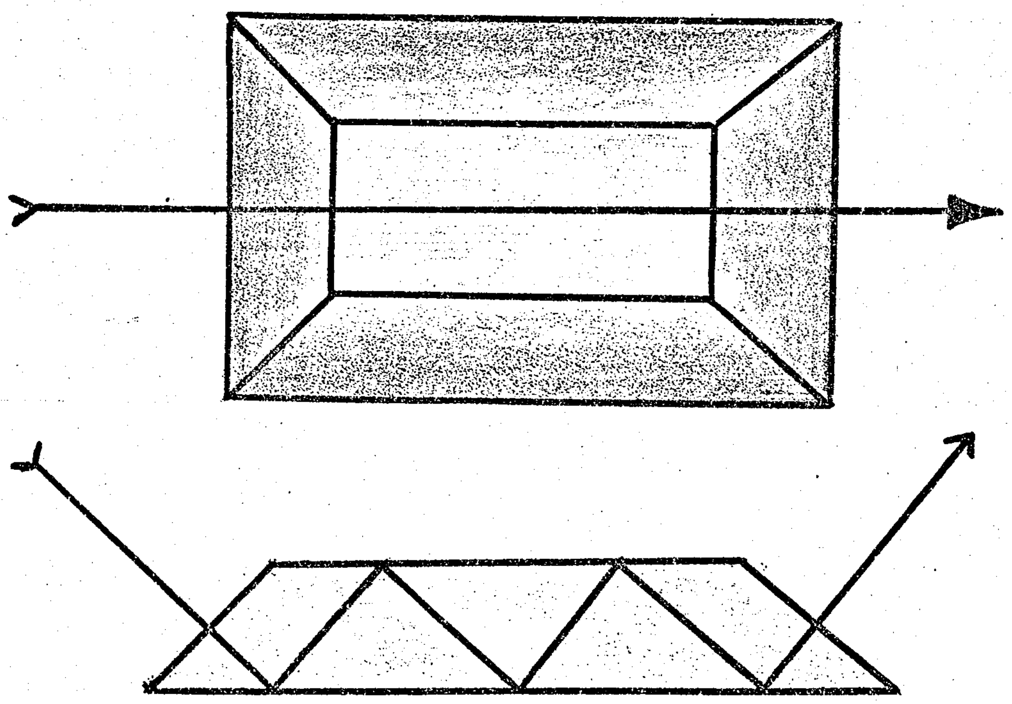

Figure D. Internal Reflection Element.

IRE materials [IREM] typically have high refractive indices. Any IREM needs to have a higher refractive index than the substance being analyzed. The IREM need to be IR transparent with no significant absorbance within the spectral range of the analysis to avoid interference with the sample spectrum. The IREM must be chemically inactive; with certain types of samples one IREM is satisfactory but not for others and vice versa. The IREM should be durable--hard, tough, able to keep a high surface polish on the two faces. A combination of all of the above factors assure high transmission of the reflected beam and long life of the IRE. There are no known IREM outstanding in all of the above properties. Some of the most successful IREM are listed in table one:

MATERIAL	USEFUL RANGE [microns]	REFRACTIVE INDEX	COMMENTS
AgCl	0.4-20	2.0	Very soft, can be molded but difficult to main surface finish.
AgBr	0.45-30	2.2	Soft [Slightly harder than AgCl], otherwise attractive material for IRS.
KRS-5	0.6-40	2.4	Toxic, relatively soft, has convenient index and useful over wide wave length range.
GaAs	1.0-17	3.3	Good beyond 15 microns. Properties to Ge. Very expensive.
Ge	2-12	4.0	Good and relatively inexpensive.

Table 1: Some Infrared Element Materials.

ATR REFLECTOR PLATE HOLDER FOR SLAB SAMPLES

The purpose of the ATR reflector plate holder for slab samples is to hold the sample under the proper conditions for maximum transmission of the IR beam and for maximum absorption bands of the sample. To accomplish this purpose, the holder is positioned rigidly on the designated positioning pins of the ATR attachment; the plate is placed in a permanent slot to keep the polished faces in a vertical position, to keep the length of the plate in a horizontal position, and to keep the plate at the proper height for the beam to enter the eenter of the end-edge and exit from the center of the opposite edge. The position of the plate can be adjusted horizontally in the slot to achieve maximum beam transmission through reflector plates of slightly different thickness or length. The holder is provided with pressure plates to assure intimate contact of the sample throughout a large area of both faces of the plate. The reference plate holder does not need pressure plates. The faces of the reference plate are in contact only with air.

In the sample plate holder of Figure E the sample is held in place by two separable interlocking steel sections. A flat section holds the sample against one face of the plate. The other section has a rectangular prism steel projection from a flat steel base which ensures contact with the sample on the second face of the reflector plate through a rectangular hole in the holder [The holder is made of Teflon and is approximately $^1/_4$ inch thick]. The ultimate size [length and width] of a slab sample is limited to the contact area of the reflector plate faces. The size is limited further by the size of the hole in the holder. The steel plates can be connected and pressure applied via a thumbscrew to draw them close together and thereby apply pressure on the sample in contact with both faces of the reflector plate. The maximum thickness of the slabs is limited by the length of the connecting posts on the pressure plate.

The sample plate holder for slabs is also quite adaquate for powders.

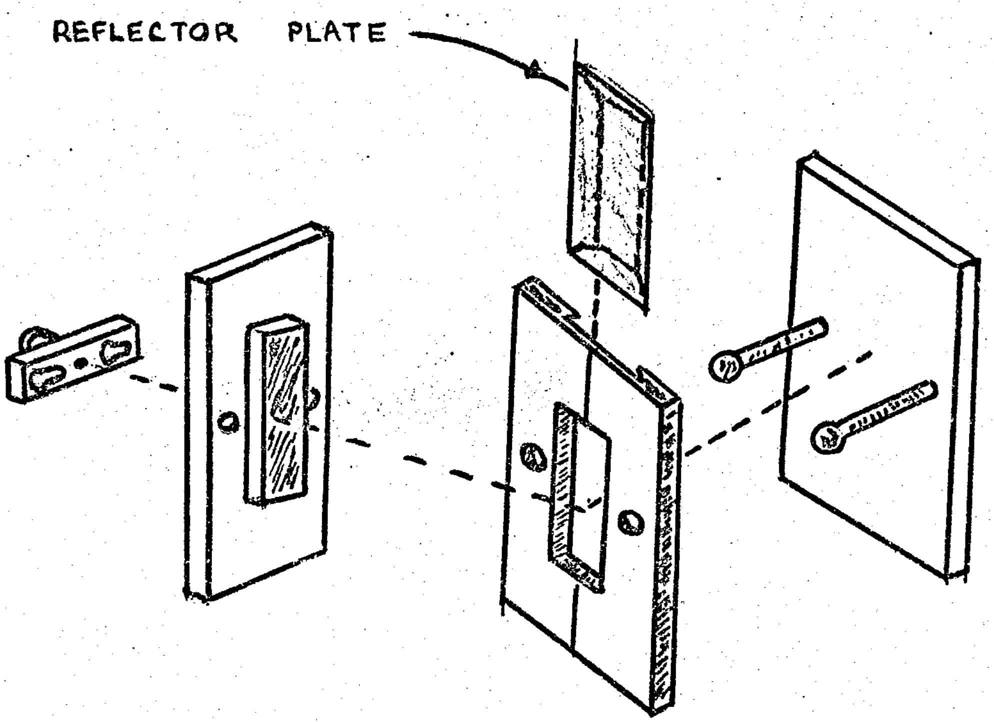

Figure E. ATR Slab Sample Holder Assembly.

Chapter 7

EXPERIMENTAL PROCEDURES

Experimental procedures consist of four steps: beam balancing, sampling, spectrum recording, reflector plate reconditioning.

BEAM BALANCING

Balancing the signal from the IR source using a double beam instrument involves three stages: balancing the instrument, rough adjustment of the ATR attachment before attaching it to the instrument, fine adjustment of the attachment on the instrument.

The stabilized IR spectrophotometer must have its sample and reference beams balanced without the attachment in precisely the same manner and frequency as if ordinary transmission spectra were being recorded.

Rough adjustment of the ATR attachment is accomplished in the following order:

1. A clean KRS-5 reflector plate is held at its edges, not touching its faces nor the end-edges. It is inserted into the slot of the holder with its sloping sides facing away from the holder; the design of the holder should make this directive obvious. The sample reflector plate's horizontal positioning in the slot is adjusted to a predetermined position from experience or from a guide pin, or in the absence of both aids it is placed midway between vertical sides of the holder; the plate is anchored with a tightening screw. The reference reflector plate is

adjusted in the same manner in its holder.

2. Both plate holders are inserted on the designated positioning pins [In this use, the pins marked 45°] with the reflector plates facing their respective mirrors. The sample side of the ATR attachment is the side nearest the operator; it is the same as in ordinary transmission.

3. The image of each end of each plate is centered in the entrance or exit slit [or slot] of the ATR attachment by adjusting [rotating] each pair of mirrors closest to the respective slit while looking into the mirror through the slit.

Fine adjustment of the beams to achieve maximum transmission of each is accomplished in the following order:

1. The ATR attachment is placed on the stabilized spectrophotometer by matching the guides of the attachment with those of the sample and reference holders of the instrument. The attachment is anchored with the anchoring screws. It is imperative that the attachment be anchored firmly to prevent any shift in the beams.

2. Maximum transmission of the IR beam through the sample plate is achieved before adjusting the reference side. Procedure is as follows:

A. Rotate the metal comb near each exit slit in a direction to eliminate all interference of light between its closest mirror and the exit slit. There are no combs near the entrance slits.

B. If the instrument registers 0% T, rotate the comb on the reference side until the indicator is on the scale [for example at 30%]. If, however, the instrument registers 100%, feather the comb on the sample side until T registers 70-80%. Throughout the procedure keep the % T between 0 and 100% by use of the combs, usually in the 70-90% range.

C. Note the % T; then proceed as follows:

[1] Carefully rotate the mirror directly in line with the entrance slit on the sample side until maximum % T is attained. If 100% T should be reached before maximum value is attained, remove the comb from the reference beam and if necessary feather in the comb at the sample beam.

[2] Repeat the procedure with the mirror that directs the beam into the reflector plate.

[3] Repeat procedures [1] and [2].

[4] Repeat procedure [1] for the mirror that directs the sample beam into the instrument.

[5] Repeat procedure [1] for the mirror that receives the beam from the reflector plate.

[6] Repeat procedures [4] and [5].

3. Adjust the reference side in exactly the same manner as the sample side with one major difference; all adjustments of mirrors are made to give minimum T.

4. If the instrument response is sluggish, it may be necessary to reposition the reflector plates: if so, the entire set of fine adjustment procedures must be repeated.

5. After maximum T on the sample side and minimum T on the reference side is attained, remove any comb that may be in the beam. Operate the instrument it is recording at approximately 5 microns [if not already there]. Adjust the % T to exactly 100% by feathering one of the combs. The instrument is now ready for use.

SAMPLING

Sampling of slabs or powders consists of three stages: sample selection, preparation, application. The procedures of the three stages are as follows:

1. A medial section from a rock can be used. Selection of a rock sample is usually quite simple to make after the slabs have been cut; the operator is often in a position, if he desires, to selectively cut off those portions of a slab that constitute an obvious second phase and then analyze the two phases separately. If the phases are highly mixed, separation may not be practical, and a representative sample involves judicious selection of a portion of a slab that represents the average.

Selection of powered rock samples is similar to selection of slab samples. It is advantageous to first slab the rock if it is sufficiently cohesive to be slabbed. In such cases representative portions of the slab can be used. With slabs of highly mixed phases it is sometimes practicable to powder small portions of each phase and analyze them separately. When rock samples are too brittle to be slabbed, again it may be possible to selectively isolate differing phases. If it is not practicable to isolate the phases, regular classical sampling procedures after pulverization or partial pulverization may be necessary.

2. Preparation of slab samples involves the use of a good lapidarists' slabbing saw. To obtain a representative sample from a rock, a slab can be cut through a section near the center. The cut should be uninterrupted and by a good diamond saw with automatic feed. Any stops in the cutting or any movement of the rock in its vise causes ridges in the slab. After the first cut the carrier containing the section of the

rock remaining in the vise is adjusted to cut a slab of the desired thickness. At no time is the rock allowed to shift in the vise. The slab is made by making the second cut in the same manner as the first. This procedure guarantees smooth slabs of uniform thickness and free of ridges. The slab can be trimmed to the desired length and width with a trim saw. Two slabs of the same dimensions can be made from one slab. All edges of one face of each of the two slabs should be slightly rounded to avoid unneccessary damage to the reflector plate. Intimate contact of soft slabs with the reflector plate is fair without any further preparation; polishing improves the contact. Polishing of hard rock slabs is mandatory to attain sufficient contact for significant absorption bands. The polishing method should keep the slab face perfectly flat; the method employing the lapidarists' dop-stick is unsatisfactory--the slab face does not remain flat and the dopping adhesive contaminates the slab. Slab contamination interferes primarily with powder analysis that may follow slab analysis.

Preparation procedures of powdered-rock samples varies slightly with the hardness of the rock. Any rock too soft to be slabbed can be powdered directly with a mullite or agate mortar and pestle. Harder rocks are first pulverized with a Plattner mortar and pestle. Rocks that are as hard as agate can have the entire powdering operation performed in the Plattner. Almost all hard rocks are brittle, and the Plattner powdering operation is difficult only in determining when every particle is sufficiently small to avoid damage to the surface of the reflector plate.

The amount of sample can be small. When the sample covers the usable surface area of the reflector to a depth of five microns, any excess sample will not further affect the spectrum.

3. To apply the rock slabs to the reflector plate, lift the sample holder out of the ATR attachment; place the flat steel section on a bench; place one slab rounded-edge-up on the section; fit the holder onto the section oriented in such manner as to have the metal touch the reflector plate if the slab weren't present; place the other slab through the hole in the holder with rounded edges toward the face of the reflector. The slab that is placed through the hole in the holder should be of dimensions that nearly fit the hole; the other slab should be of approximately the same dimensions as the first and can be placed almost exactly opposite the first one by estimation. The pressure plates are connected and the thumbscrew turned as tightly as possible with thumb and finger. Increased pressure by tools could damage the soft reflector plate.

To avoid damage to the reflector plate, the application of powder sample to the reflector plate is more difficult. An amount of fine powder is applied to the same area of the flat steel section that a slab would have occupied. The powder is spread and packed with a small metal spatula. If the packed layer is not too thick, the operator can usually detect and remove any particles likely to damage the plate. Without dislodging the packed layer, the holder is fitted onto the steel section. A representative amount of sample is carefully spread through the hole in the holder onto the face of the reflector. Care is used to avoid touching the reflector plate with the metal spatula. The sample is spread on the reflector plate by gently tamping it a few times with the projection of the steel section. Finally, the steel section is fastened to the first one, and thumbscrew pressure is applied as in the case of slabs.

The sample holder is tipped to its upright position. Excess powder that has fallen from the reflector plate is brushed away from the holder with a fine brush. The holder is placed in its proper position on the ATR attachment.

RECORDING SPECTRA

In the preparation of an atlas of spectra it was deemed advisable to use similar conditions for all spectra if practicable. The controls of the Perkin-Elmer Model 21 were adjusted for all spectra as follows: Resolution--9.26 auto; Response--4; Gain--5; Speed--4; Suppression--6.

The previously balanced instrument was set at 0.5 microns, and the pen was allowed to stabilize before being applied to the paper.

The scan was made for the entire range of the chart paper [0.5-15.5 microns]. Wherever the pen bottomed out or went over 100%, attempts were made to make each area more informative by rerunning those areas and one or two microns on each side of the area after feathering one of the combs to keep the scan area on the scale.

When both slab and powder spectra were observed for the same sample, the same chart paper was used. The slab spectrum was identified with an S and the powder with a P.

RECONDITIONING THE SAMPLE REFLECTOR PLATE

The reconditioning process involves three steps [occusionally four]; they are as follows: 1. Removing sample holder from ATR attachment and disassembling it, including the removal of the reflector plate from the holder; 2. Cleaning and drying the holder, pressure plates, and reflector plate; 3. Polishing the reflector plate; 4. Grinding the reflector plate.

Only the reflector plate requires great care in cleaning. Sometimes a fine soft brush is advantageous for removing caked-on powder from the reflector plate. At other times very brief exposure of the plate to a stream of cold tap water accompanied by loosening the mud with thumb or fingers is necessary. Prolonged exposure to the water should be avoided because of the slight solubility of the KRS-5; solubility in warm water is considerably greater, and such exposure must be completely avoided. The plate can be tamped dry with cotton balls.

Polishing the reflector plate was accomplished by lightly making 10-15 figure eights with each face across a stretched out 8 x 10 inch piece of felt. A few light motions across the felt were made with the end-edges. The plate was held at the side edges to avoid fingerprints on the plate faces and ends.

Grinding was typically unnecessary until several samples had been run and it was impossible to otherwise achieve more than 50-60% T with unfeathered combs. The grinding process rapidly thins the plate and increases the probability of uneven surfaces; in both cases diffusion will increase at the expense of regular internal reflection.

Grinding was accomplished by adding less than 1 ml of rouge or other fine grinding agent near one end of a second stretched out felt cloth. 2 or 3 ml of methanol were poured on top of the rouge. Fingercots were placed on the thumb, forefinger, and middlefinger of one hand. 2 or 3 figure eights were performed with the reflector face in the wet rouge, then 2 or 3 in the wet portion containing no originally placed rouge, then 8-10 rapidly on the dry portion. The above action removes considerable KRS-5, which is toxic and corrosive; the fingercots provide protection. After the other face was ground, the beveled ends were checked for freedom from contamination. The ground plate was removed from the grinding cloth and polished on the polishing cloth.

REBALANCING THE SYSTEM

After the plate has been returned to the holder and the unit has been placed in position on the ATR attachment, it is necessary to repeat the entire fine tuning procedure of the sample-side-only before the system is ready for a new sample.

Chapter 8

DATA DISCUSSION AND UNKNOWN DETERMINATION

Slab spectra were not satisfactory except in a few cases of the softest slabs. Fahrenfort [1961] suggested the use of carbon disulfide on the contact surface between solid and reflector plate. CS_2 improves effective contact of solid with reflector; however, the absorption bands of CS_2 at 3.5, 4.5, 7, and 11.8 microns sufficiently interfere with spectra to significantly reduce its value. Carbon disulfide was not used in this project.

Powder spectra by ATR were comparable to powder by T. Unless otherwise indicated in the chapter, all discussions of ATR spectra are of powders. All references to T spectral data are of powders and are from Hunt [1950], unless otherwise indicated. All spectra values are recorded in microns.

This chapter consists of three sections: 1. A discussion of each of seven chemical groups; 2. Table two lists the most significant bands for all the minerals studied in both ATR and T values; 3. A discussion of the spectrum of each mineral studied.

A severe instrument noise has marred all ATR spectra at 9.23 microns.

METALLIC OXIDES AND SULFIDES

The binary compounds of metal with non-metal that were studied are hematite [Fe_2O_3], pyrite [FeS], and galena [PbS].

ATR spectrum of hematite was considerably more sensitive than T. ATR bands at 11.46 and 13.83 microns were completely absent in T. Nakamoto [1963] indicates that the hydroxide ion is characterized by a sharp band in the region of 2.70 - 2.85 microns; the absence of this band indicates a probable absence of hydration of the oxide. The presence of a band near 11.35 microns indicates the possible presence of O-O stretching that would not be O_2^{-2}, because it would be IR inactive. Most metal to oxygen bond stretching occurs in the range 20-25 microns which is beyond the range of our instrument. Fe[III] and O stretching is at 23 microns. A thorough IR study of bonding in binary compounds of metal with non-metal should include the far IR.

ATR spectrum of pyrite was totally devoid of a meaningfull signal. T had a strong twin band at 9.7 microns and 9.9 microns. Nakamoto [1963] lists no bands for Fe-S, and the values listed for H_2S and H_2S_2 [which could have formed during the water settling stage] are sufficiently removed from the above values as to be unlikely. There is strong possibility that the T scan is for another compound.

Galena showed only a very weak peak at 15.05 microns for ATR; T did not show this, but it did show three other weak peaks. Nakamoto [1963] does not list PbS bands, and Nyquist [1971] did not report a PbS spectrum.

METALLIC CARBONATES

The metallic carbonates studied are calcite [$CaCO_3$], aragonite [$CaCO_3$], argillaceous limestone [$CaCO_3$], magnesite [$MgCO_3$], rhodochrosite [$MnCO_3$], cerrusite [$PbCO_3$], and dolomite [CaMg][CO_3]$_2$.

All carbonates, excepting cerrusite, have their most dominant band near 7, a sharp and strong band near 11.5, and a third dominant sharp band near 14. Magnesite has a fourth broad but less dominating band near 10. The fourth band is missing in calcite and aragonite, but in rhodochrosite the band is sharp and has equal dominance with the other three bands. The difference between calcite and aragonite spectra is due to difference in crystalline structure; the third band in aragonite has been split into two sharp dominant bands. Cerrusite has each of the four bands, but they are in quite different appearance. There is excellent correlation of ATR with transmission. Slabs had fair sensitivity.

METALLIC SULFATES

The sulfates studied were gysum [$CaSO_4 \cdot 2H_2O$] and barite [$BaSO_4$].

Both ATR and T had three major bands in closely comparable positions, but the general appearances of the two spectra were considerably different. Barite has the bands displaced approximately o.7 micron toward longer wave lengths.

METALLIC PHOSPHATES

Phosphate rock [$Ca_3[PO_4]_2 + Ca_5[PO_4]_3 \cdot OH$] was the only phosphate spectrum scanned. It showed three obvious bands; one was a strong almost sharp band with two characteristic shoulders centered at 9.66; the

the other two were weak, one at 7 and the other at 11.60. No T data were available.

SILICA

The silica [SiO_2] spectra taken were quartz, chert, opal, agate, and flint; of these, the only pure silica is quartz, and opal is hydrated.

Silica has its most dominating very broad band near 9.5 microns, a second very strong but less broad band near 12.75 microns, and a third sharp, medium to strong band near 14.5 microns. In quartz the second band has two lobes. In opal and chert the third band is absent or weak.

It is interesting that the orthosilicate ion[SiO_4^{-4}] has two vibrational frequencies close to those of the quartz spectrum, 12.50 and 9.52 microns.

As expected, the ATR and T spectra corresponded very closely in quartz, a pure substance, and least in chert, an impure substance. They also corresponded well in opal; giving credence to the possibility that the hydration is probably of a specific type and amount. T spectra of agate and flint were not available, but they were very similar to each other in ATR.

METALLIC SILICATES

The spectra of the metallic silicates are of wollastenite $CaSiO_3$, serpentine $3MgO.2SiO_2.5H_2O$, talc $MgSi_4O_{10}[OH]_2$, augite $CaMg[SiO_3]_2$, tremolite $2CaO.5MgO.8SiO_2H_2O$, olivine $[Mg,Fe]_2SiO_4$, actinolite $CaO \cdot 3[Mg,Fe]O \cdot 4SiO_2$, albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$, nephelite $3[K,Na]_2O \cdot 4Al_2O_3 \cdot 9SiO_2$, feldspar [oligoclase] $[Na_2,Ca]O \cdot Al_2O_3 \cdot 5SiO_2$, and muscovite $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$.

In the simple silicates, such as wollastenite, the broad band of silica remains at 9.5 microns, but band two has disappeared and band three has increased in strength and shifted to 15.5 microns. All complex silicates containing more than one metal, have the broad band shifted to between 10 and 11 microns. The appearance or non-appearance of bands two and three is analytically unmistakable in nearly all cases. For example, in albite band two has spread into four fingers ranging from 12.5 to 13.9 microns, and band three is at 15.5 microns.

UNKNOWNS

Unknown 1, "Petrified Mud" from the Columbia River Basin, has a spectrum almost identical with quartz. The color and general appearance indicate considerable impurity; nevertheless, the percentage of impurity is either very slight, or the impurities are non-absorbing through the range of 7 -15.5 microns. Based on that spectral range, "Petrified Mud" is 98% quartz..

Unknown 2, from Plymouth, California, is a soft crumbling rock that powdered into a golden brown material. It is being mined and exported by the Arabs. The spectrum is like that of kaolinite with no additional absorption bands and containing all of the bands that kaolinite has. There is, however, a lack of detail and therefore a lack of purity. The appearance of no other bands suggests greater than 90% kaolinite.

Unknown 3, a green rock somewhat resembling "green quartz", has the spectrum of glass. It has a stronger band near 7 microns than does laboratory glass; this is the major band for carbonates. Inasmuch as this "rock" has undoubtedly weathered a long time, it is understandable that it would have a higher percentage of carbonate than lab glass.

Unknown 4, the meteorite, somewhat resembles biotite; its spectrum is better defined than biotite's. The slab was full of holes resembling the cross-section of a sponge. It is probable that many impurities were trapped during the meteorite's residual time on the Earth. This could account for the slight carbonate band at 7.

Unknown 5, "Wyoming Jade", has a very strong moderately broad band at 10.25 microns; this band has a wide shoulder at 9.25 microns, a slight shoulder at 9.00 microns, and a characteristic shape near maximum absorption. Of all the ATR spectra nephelite fits this perfectly. Nephelite has a second strong band at 14.6 microns; whereas that band on the unknown would occur at approximately 15.6 microns. Albite differs in detail from the unknown at the major band, but albite has a band similar to the unknown at 15.6 microns. Albite also has a four peaked band near 13.5 microns that the unknown does not. Jadeite has a composition intermediate between that of nepheline and albite; this fact suggests that the unknown is jadeite.

$$\underset{\text{jadeite}}{2NaAlSi_2O_6} = \underset{\text{nepheline}}{NaAlSiO_4} + \underset{\text{albite}}{NaAlSi_3O_8}$$

Equilibrium is shifted to the left at high pressures in the order of 20-30 kilobars. The liquid cooled at 25 kilobars would give pure jadeite [Deer: 1967].

The complete absence of a band at either 14.5 or 13.5 microns casts some doubt that it is jadeite. A third factor, which is the fact that jadeite has a different crystalline structure from the other two minerals, causes even greater indefiniteness, because that difference could affect all bonds. However, such structural difference could eliminate or move some bands but not others. So the fact that jadeite is a chain silicate of the pyroxene group and both nepheline and albite are framework silicates and the fact that jadeite is a natural product from nepheline and albite support the assumption that the sample is jadeite.

Unknown 6, a black rock from the Apache National Forest, has the spectrum of quartz with very few impurities. The main band has broadened somewhat toward the longer wave-length, indicating possible small amount of silicate impurities. The moderate broad band between 6 and 7 microns indicates another possibility of a very small amount of carbonate. The presence, however, of the entire basic spectrum of quartz, including the twin lobes between 12.5 and 13 microns, indicates over 90% quartz.

Unknown 7, submitted as "Green Quartz", has six major bands; three can be attributed to quartz and three to magnesite. With a series of known percentage comparison scans one could accurately determine the percentage composition. However, based on the strength of the band at 11.42 microns coupled with the general appearance of the spectrum, it is probable that the rock is more than 50% magnesite and therefore less than 50% quartz.

Unknown 8, a gray and yellow rock, has a spectrum that is principally quartz but also appreciably dolomitic limestone, possibly 75% quartz and 25% dolomite.

In all eight unknowns only the presence and absence of indicated minerals are definite. In the absence of comparison data of known mixtures, percentage compositions are only estimates.

Table 2. Comparative Spectral Positions of ATR and Transmission Infrared Absorption Bands of Minerals

Wave-length Range, Microns: First Line Values = ATR, Values in parentheses = T [Hunt, 1950]

	2-6	7	8	9	10	11	12	13	14	15
METALLIC OXIDES + SULFIDES										
Ilmenite, $FeTiO_3$					10.48m-vb [10.00m,10.30m]			13.90m-sd		
Hematite, Fe_2O_3		7.00s-b [7.05w]			10.30s-vb [10.20s]	11.46m [illegible]		13.83m		
Pyrite, FeS	NO BANDS									
Calena, PbS										15.05w
METALLIC SULFATES										
Gypsum, $CaSO_4 \cdot 2H_2O$	6.18w-sp [6.15s]			9.04s-vb [7.80s]						15.03s-sp [15.15m]
Barite, $BaSO_4$	[6.80m] 6.97m		[7.55w]8.06m-sd	9.50s-b [9.20s]	10.22w-sp[10.16m]					15.02w;15.70s [15.70m]
METALLIC CARBONATES										
Calcite, $CaCO_3$	5.60w [5.58w]	7.12s-b [6.95s]	8.07w-sd			11.47m-sp 11.81w-sd [11.40m] [11.80w]			14.10m-sp [14.02m]	
Aragonite, $CaCO_3$	6.88s [6.95s]		8.50w-sd			11.72s-sp [11.40m,11.65w]			14.10m-sp,14.35m-sp [14.02m] [14.30w]	
Argillaceous Limestone $CaCO_3$	5.38w-sp 5.76w-sp, 6.13w-b	7.10s-b	8.67w-sd	9.71s-b		11.50s-sp,11.83w-sp	12.53m,12.90m	13.82w-sd	14.11s-sp	
Magnesite, $MgCO_3$		7.05s-b [6.90s]		9.96m-b [9.90m]		11.43s-sp,11.70w-sd [11.25s] [11.70w]		13.44s-sp [13.33m]		
Rhodochrosite, $MnCO_3$	6.35w-sd	7.13s-b [7.00s]		9.92s-sp		11.62s-sp [11.50m]		13.83s-sp [13.72m]		15.03w-b
Cerrusite, $PbCO_3$	6.98w-b [7.10s]		8.70m-sd			12.65m-sd,12.93m [11.10s]			14.54m [14.00w]	15.00w-sd
Dolomitic Limestone $CaMg[CO_3]_2$	5.76wsp,6.92ssp [5.52w],[6.90s]		8.12w	9.56m-b		11.39s-sp [11.30s]		13.78m-sp [13.70m]		
METALLIC PHOSPHATES										
Phosphate Rock $Ca_3[PO_4]_2$ and $Ca_5[PO_4]_3 \cdot OH$	6.90m [7.15m]	7.03m [7.40m]		9.66s-sp [9.35s]	10.42w-sd [10.00m]	11.60w [11.10m]				

Table 2. [continued]

Wave-length Range, Microns: First Line Values = ATR, Values in parentheses = T [Hunt, 1950]

	2-6	7	8	9	10	11	12	13	14	15
SILICA										
Quartz, SiO_2				9.40s-b [9.20s]			12.60s, 12.91s [12.52m][12.82m]		14.46m-sp [14.42m]	15.02w
Chert, SiO_2		7.00w-b		9.50s-b [9.20s]		11.07s-vb	12.58s, 12.90s [12.52m][12.82m]	13.90w-sd	14.60m-sd [14.40m]	
Opal, SiO_2			8.65w-sd	9.50s-b [9.20s]	10.17w-sd		12.80s [12.55m]			15.02w
Agate, SiO_2				9.50s-b			12.78s		14.48s-sp	15.00w
Flint, SiO_2			8.70m-sd	9.70s-vb			12.80s		14.50m-sp	15.00w-sd
METALLIC SILICATES										
Wollastenite, $CaSiO_3$			8.42m-sd	9.50s-b [9.10s], [9.40s]	10.20w [9.75s]					15.50s [15.50m]
Serpentine $3MgO \cdot 2SiO_2 \cdot 5H_2O$			8.56w-sd	9.50m-sd	10.50s-b	11.50w-sd				15.50s
Talc $MgSi_4O_{10}[OH]_2$					10.55s-vb [9.80s]		12.50w-sd			15.07s [14.90m]
Augite $CaMg[SiO_3]_2$				9.50s [9.37s]	10.50s-b [10.38s]	11.59s-vb [11.45s]	12.50w-sd			15.00m [14.95m]
Tremolite $2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$				9.15msd, 9.64msd [9.00s], [9.30s]	10.55svb, 10.9w [10.55s][10.85]		12.67w-sd	13.18m-sp [13.15m]	14.66m-sp [14.60m]	15.05w-sd [14.95m]
Olivine $[Mg,Fe]_2SiO_4$	6.30m-sd, 6.95s-sp				10.25m [10.00s]	11.50s-b, 11.95wsd [11.20s], [11.90m]		13.35w-sd [13.10w]		
Actinolite $CaO \cdot 3[Mg,Fe]O \cdot 4SiO_2$				9.15m-sd, 9.55m [9.00s], [10.10s]	10.60s-b [10.50s]	11.00w [10.85s]		13.26m-sp [13.15m]	14.66m [14.60m]	
Albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$			8.70s [8.70s]	9.18s, 9.80s-sd [9.10s], [9.70s]	10.18s-vb		12.76m-sp [12.68m]	13.19m-sp [13.10m]		15.50m [15.5m]
Nephelite $3[K,Na]_2O \cdot 4Al_2O_3 \cdot 9SiO_2$	6.90m-b		8.12w-sd		10.34s-b [10.10s]				14.11w-sd14.58sb [14.05m][15.00m]	
Feldspar [oligoclase] $[Na_2,Ca]O \cdot Al_2O_3 \cdot 5SiO_2$			8.92s-sd [8.70s]		10.16s-vb [9.90s]			13.07s-sp13.88ssp [13.70m][13.80m]		15.6s [15.6m]
Muscovite $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	2.79m-sp, 5.5m-b, 6.08mb]	7.00w			10.30m-vb [9.70s]			13.50w-vb		15.04w

Table 2. [continued]

Wave-length Range, Microns: First Line Values = ATR Values in parentheses = T [Hunt, 1950]

	2-6	7	8	9	10	11	12	13	14	15
METALLIC SILICATES [continued]										
Topaz $Al_2O_3\cdot[OH,F]\cdot SiO_2$			8.61m-sp		10.10m-sd	11.50s-vb			14.19m-sp	15.6s
Biotite $[K,H]_2O\cdot 2[Mg,Fe]O\cdot[Al,Fe]_2O_3\cdot 3SiO_2$				9.75,msd	10.18s-vb [10.00s]			13.50w-vb		15.04w
Hornblende $RO\cdot[Na2,K_2,H_2]O\cdot R_2O_3\cdot 2SiO_2$	6.96m-sp				10.96s-vb [9.80s]		12.63w-sd [12.75w]	13.80w-b		
Kaolinite $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$				9.04s-sd,9.74s-sd [8.93s] [9.65s]	10.05s-b [9.90s]	11.00s-b [10.95s]	12.74m [12.50m]	13.94m [13.30m]	14.85m-vb [14.50m]	
Howlite $4CaO\cdot 5B_2O_3\cdot 2SiO_2\cdot 5H_2O$	6.97s-m					11.34s-sp,11.73wsd		13.40s-sp		
Pyrex glass $Na_2O\cdot CaO\cdot 6SiO_2+K+B$	6.5w-b				10.50s-vb			13.15m-vb		
UNKNOWNS										
Petrified Mud Columbia River Basin	6.10m,6.58w,6.93w		8.70m-sd	9.35s-b			12.63s,12.90s		14.45m-sp	
Plymouth, CA Arab Export	6.98m-sp		8.65m-sd	9.35s-sd	10.00s-b	11.06m-b	12.77m-b		14.60m-b	
Gemmell	6.97m-sp				10.00s-vb,10.75s-b		12.77m-vb			
Meteorite	6.90m-vb		8.98wsd		10.60s-vb	11.50w-sd				
Wyoming Jade	6.50m-vb		8.38m-b	9.45m-sd	10.40s-b					15.7s
Apache Nat'l. Forest	6.27m-vb		8.70,msd	9.45s-vb			12.65s,12.90s		14.48m-sp	
Green Quartz	6.92s-m		8.67w-sd	9.45s-vb		11.36s-sp	12.89m-sp	13.43s-sp	14.45m-sp	
Drake	6.95m-sp		8.15m-sd	9.26s-b		11.40m-sp	12.59ssp,12.90ssp	13.68w-sd	14.08w,14.47msp	15.02w

In the discussion of the following individual minerals, all T values listed by Hunt [1950] are compared to all values determined by ATR. ATR powder spectral values are listed on the top line; T values are on the next line; ATR slab values, when listed are on the third line. Spectral values at the same position are corresponding absorption bands for the different methods; those values that have no counterpart in the other method are on separate positions. Letters immediately following the numbers indicate the amount of absorption [s = strong, m = moderate, w = weak, v = very]; those following a hyphen describe appearance of band [sp = sharp, sd = shoulder, b = broad]. All spectral values are in microns.

HEMATITE Fe_2O_3

ATR slab spectrum was totally without definite absorption band 5. Only by comparing slab and powder spectra can the indications of absorption bands be identified in slabs. ATR was considerably more sensitive than T. ATR bands at 11.46 and 13.83 were completely absent in T. The hydroxide ion is characterized by a sharp band in the region 2.70-2.85. The absence of this band indicates a probable absence of hydration of the oxide. The presence of a band near 11.35 indicates the possible presence of O-O stretching that would not be O_2^{-2} nor O_2^{-1}, because both would be IR inactive. Most metal to oxygen bond stretching occurs in the range 20-25, which is beyond the range of the Model 21. Fe[III] and O stretching frequency is 23. A thorough study of bonding in binary compounds of metal with non-metal should include the far IR.

7.00s	10.30s	11.46m	13.83m
7.05w	10.20s		

PYRITE FeS_2

Pyrite was totally devoid of ATR meaningfull signal in the powder; no attempt was made on the slab. T had a strong twin band at 9.7 and 9.9. Nakamoto [1963] lists no value for Fe-S. The T values listed for H_2S and H_2S_2, which could have formed during the water settling stage in the T procedure, are sufficiently removed from the spectral values as to be unlikely. Nyquist [1971] has no spectrum for FeS_2. There is strong possibility that the T spectrum is mislabeled for another compound. Only T bands are listed.

9.7s 9.9s 10.95w 12.6w

GALENA PbS

Galena showed only a very weak peak at 15.05; this was just as evident in the slab as in ATR powder; T did not show this. The only correlation with T was the absence of all moderate or strong bands. Nakamoto does not quote Pb-S, and Nyquist has no spectrum for PbS.

6.9w 9.50w 11.50w 15.05w

QUARTZ SiO_2

Excepting for the absence of weak peaks at less than 9, ATR powder resembles T very closely. It is interesting that SiO_4^{-4} has two vibrational frequencies close to those in the quartz spectrum, 12.50 and 9.52.

9.40s 12.60s
5.1w 5.38w 5.6w 5.95w 6.2w 8.6w 9.20s 10.95w 12.52m

12.91s 14.46m 15.02w
12.82m 14.42m

CHERT SiO_2 [impure]

The general resemblance of ATR powder spectra for chert is fair, but not as good as for quartz. This is to be expected; quartz is pure and chert can vary in its impurities.

					7.00w		9.50s	11.07s-b
5.1w	5.38w	5.6w	5.95w	6.2w		8.6w	9.20s	

12.58s	12.90s	13.90w-b	14.60w
12.52m	12.82m		14.42w

OPAL $SiO_2 \cdot nH_2O$

ATR and T powder spectra are quite similar, indicating a probable specific type and amount of hydration. The twin peaks near 12-13 in quartz and chert have blended into one, and the band at 14.6 has disappeared.

	8.65w	9.50s	10.17w-sd	12.80m	15.02w
6.1w		9.20s	10.50w	12.55m	

AGATE SiO_2 [impure]

Agate, or banded chalcedony, has extraordinarily strong ATR bands ranging from over-balanced above 100% to bottoming-out at 0% at two positions. One band of such strength is not unusual, but two such bands occur with no other spectrum. T spectra were not available.

9.50s-b	12.78s	14.48s-sp	15.00w

FLINT SiO_2 [impure]

Flint and agate have exceptionally similar spectra; the only fundamental difference is the failure of flint to have total transparency between the three major bands. No T spectra were available.

8.70m-sd 9.70s-b 12.80s 14.50m-sp 15.00w

CALCITE $CaCO_3$

The spectrum of calcite was one of the very few with any ATR sensitivity at 0.5-7. Slabs had greater than average response, but not throughout the spectrum. Correlation with T is very good, with ATR powder having the greater sensitivity in the middle range.

5.60w	6.85w	7.12s-	7.68w	8.07w	10.50w	11.47m	11.81w	14.10m-sp	14.50w	15.03w
5.58w		6.95s				11.40s	11.80w	14.02m		

ARAGONITE $CaCO_3$

Many of the soft and brittle minerals cannot successfully be slabbed; aragonite is one of them.

The differences between calcite and aragonite spectra are due to differences in crystalline structure.

	5.63w	6.88s	11.72s	14.10m-sp	14.35m-sp
4.02w	5.58w	6.95s	11.40m	14.02m	14.30w

ARGILLACEOUS LIMESTONE $CaCO_3$

"Argillaceous Limestone Standard Reference Material" powder from the National Bureau of Standards has very fine particle size. There is some indication that fine particle size increases the signal, especially at short wave-lengths.

No T values were available.

2.91w-sd, 3.43w-sd, 3.99w-sd, 4.37w-sd, 5.05w-sd, 5.58w-sp, 5.76w-sp, 6.13w 7.10s-b, 8.00w-sd, 8.67w.sd, 9.25m-sd, 9.71s-b, 11.50s-sp, 11.83w-sp, 12.58m, 12.90m. 13.82w-sd, 14.11s-sp, 14.40w-sd.

MAGNESITE $MgCO_3$

There is very close correlation between ATR and T.

		7.05s-b	9.96m-b	11.43s-sp	11.70w-sd	13.44s-sp
4.00w	5.52w	6.90s	9.9m	11.25s	11.70w	13.33m

RHODOCHROSITE $MnCO_3$

ATR and T spectra are similar with one major exception; the dominant band at 9.92 with ATR is totally missing with T.

		6.35w-sd	7.13s-b	7.50w-sd	9.44w-sd	9.63w-sd
4.05w	5.58w		7.0s			

9.92s-sp	11.62s-sp		13.83m-sp	15.93w
	11.50m	11.95w	13.72m	

CERRUSITE $PbCO_3$

Cerrusite yields a considerably different spectrum from reagent grade lead carbonate examined via T by Miller [1952] in the form of a Nujol mull.

6.10w-b	6.98w-b	8.70m-sd	9.45s-b	12.65m-sd	12.93m	14.54m
	7.1vs					13.6w
15.00w-sd	15.18w-sd					

DOLOMITE $CaMg[CO_3]_2$

"Dolomitic Limestone Standard Reference Material No. 88A" powder from NBS had virtually the same ATR spectrum as that of dolomite powdered by the writer. One notable addition by NBS sample was the sharp band at 5.76. Comparison of spectra gave less distortion of ATR from T with NBS sample than with other dolomitic samples.

	5.76w-sp	6.15w	6.92s-sp	7.50w-sd	8.12w	9.56m-b
4.0w	5.52w		6.9s	7.5w		9.8w
11.39s-sp	11.75w-sd		12.30w-sd	13.25w-sd	13.78m-sp	
11.30s	11.70w				13.70m	

GYPSUM $CaSO_4 \cdot 2H_2O$

Although the three major bands in ATR and T were comparable, the general agreement of the spectra were not really close. T spectrum for $CaSO_4$ anhydrous was also available. Comparing the two T with ATR suggested that the drying process in T sample preparation caused partial dehydration of the gypsum.

BARITE $BaSO_4$

ATR and T were quite comparable, but T showed more detail. T listed a moderate band at 15.70; at the end of the ATR spectrum [15.50] there was definite indication that there would be strong band in the vicinity of 15.70.

6.97m	7.14w-sd	8.06w-sd	9.50s-b	10.22w	
6.80m		7.55w	9.2s	10.16m	11.30w

	15.02w	
12.75w		15.70m

<u>ILMENITE</u> $FeTiO_3$

Ilmenite has only one broad absorption band in the 7-15.5.

Correlation of ATR with T is fair.

10.48m-b
10.0m

Chapter 9

CONCLUSION

The spectra of films and of powder were excellent. They were often more sensitive in the 7-15.5 micron range than transmission spectra; the reverse was true in the 0.5-7 micron range.

All but one of eight unknowns were positively identified and semi-quantitatively analyzed; the eighth was tentatively identified.

Because inorganic compounds typically have bonding between heavier atoms than organic compounds, a better fingerprint of inorganic spectra would be at longer wave-lengths. Inasmuch as KRS-5 plates are transparent to 25 microns, an excellent ATR spectrum range for minerals would be 6-25 microns.

The attainment of significant slab spectra was essentially a failure. There were sufficient successes, however, to cause optimism for some future project. It is believed that some combination---with very flat, polished slabs of uniform thickness, with a redesign of the sample holder to allow uniform and increased pressure, with an insoluble IR transparent liquid on the surface of the slab and of the same refractive index as the plate, with a simple system for melting and recasting plates to obtain high polish, or with reflector plates of harder material---the system could be successful.

The future of ATR is bright. It is a simple system that gives highly reliable results with no chemical complications. Use would be considerably more extensive if the system were easily balanced and if the plates were of more durable material.

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APPENDIX

LIST OF SPECTRA OF MINERALS BY ATR

NAME OF MINERAL [S = slab, P = powder]	SPECTRUM NO.
Hematite	1
Pyrite	2
Galena	3
Quartz	4
Chert	5
Opal	6
Agate	7
Flint	8
Calcite	9
Aragonite	10
Argillaceous Limestone	11
Magnesite	12
Rhodochrosite	13
Cerrusite	14
Dolomitic Limestone	15
Gypsum	16
Barite	17
Ilmenite	18
Wollastenite	19
Phosphate Rock	20
Serpentine	21

NAME OF MINERAL	SPECTRUM NO.
Talc	22
Augite	23
Tremolite	24
Olivine	25
Actinolite	26
Albite	27
Nephelite	28
Feldspar	29
Muscovite	30
Muscovite	31
Topaz	32
Biotite	33
Hornblende	34
Kaolinite	35
Howlite	36
Borosilicate Glass	37
Unknown No. 1, "Petrified Mud"	38
Unknown No. 2, "Plymouth Rock"	39
Unknown No. 3, "Green Rock"	40
Unknown No. 4, "Meteorite"	41
Unknown No. 5, "Wyoming Jade"	42
Unknown No. 6, "Apache Rock"	43
Unknown No. 7, "Green Quartz"	44
Unknown No. 8, "Gray and Yellow Rock"	45

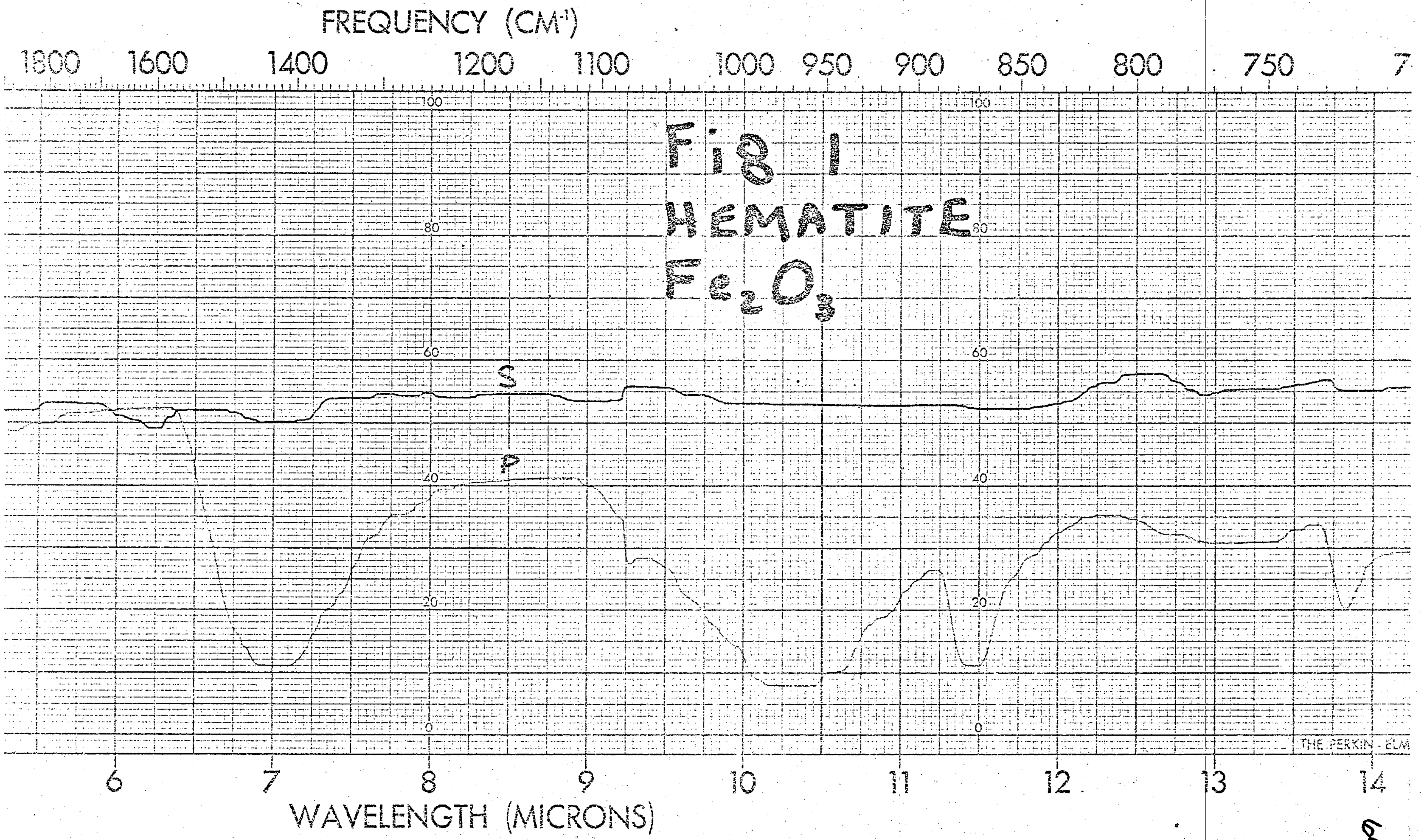


Fig 1
HEMATITE
Fe_2O_3

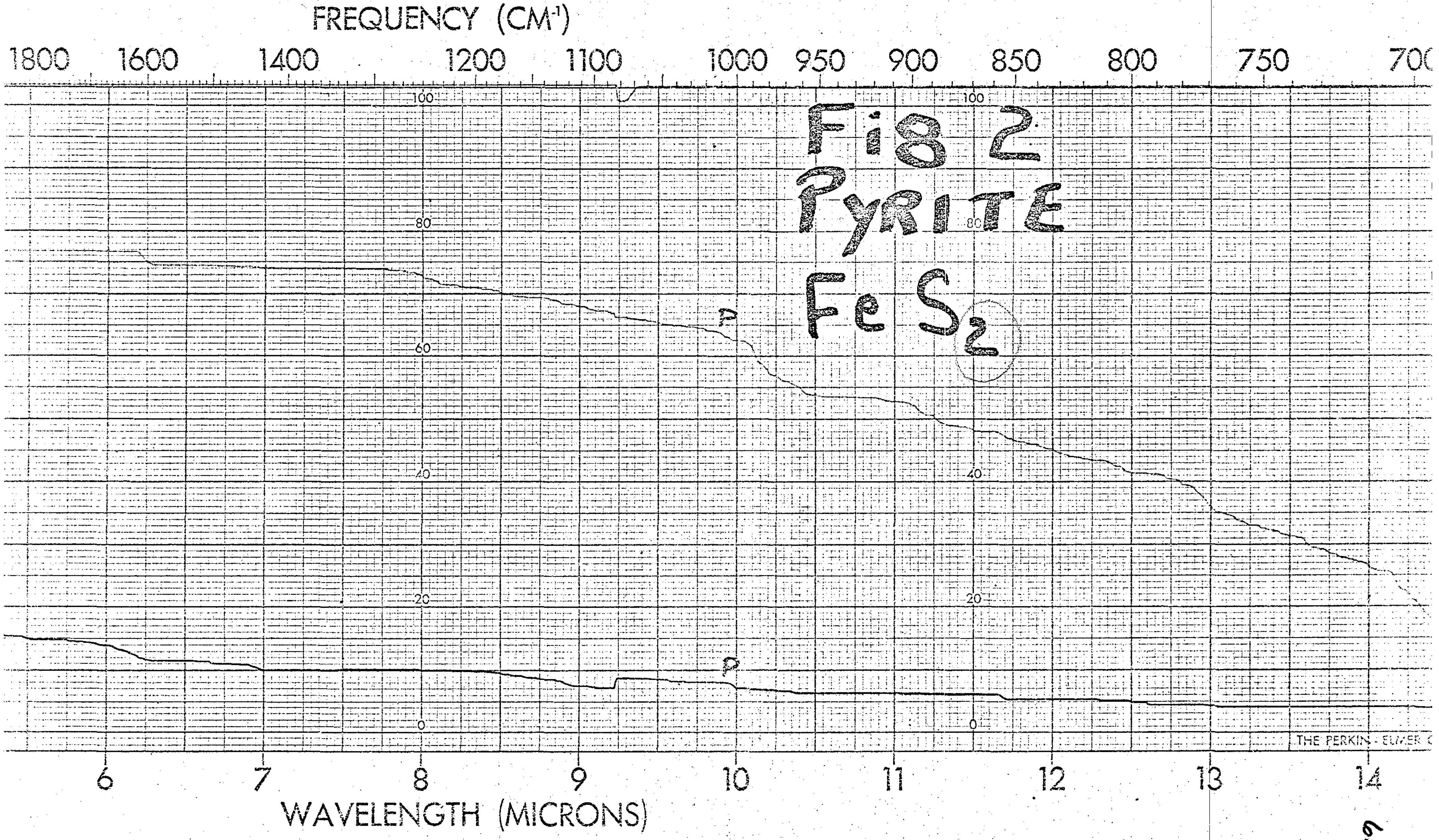


Fig 2
PYRITE
FeS$_2$

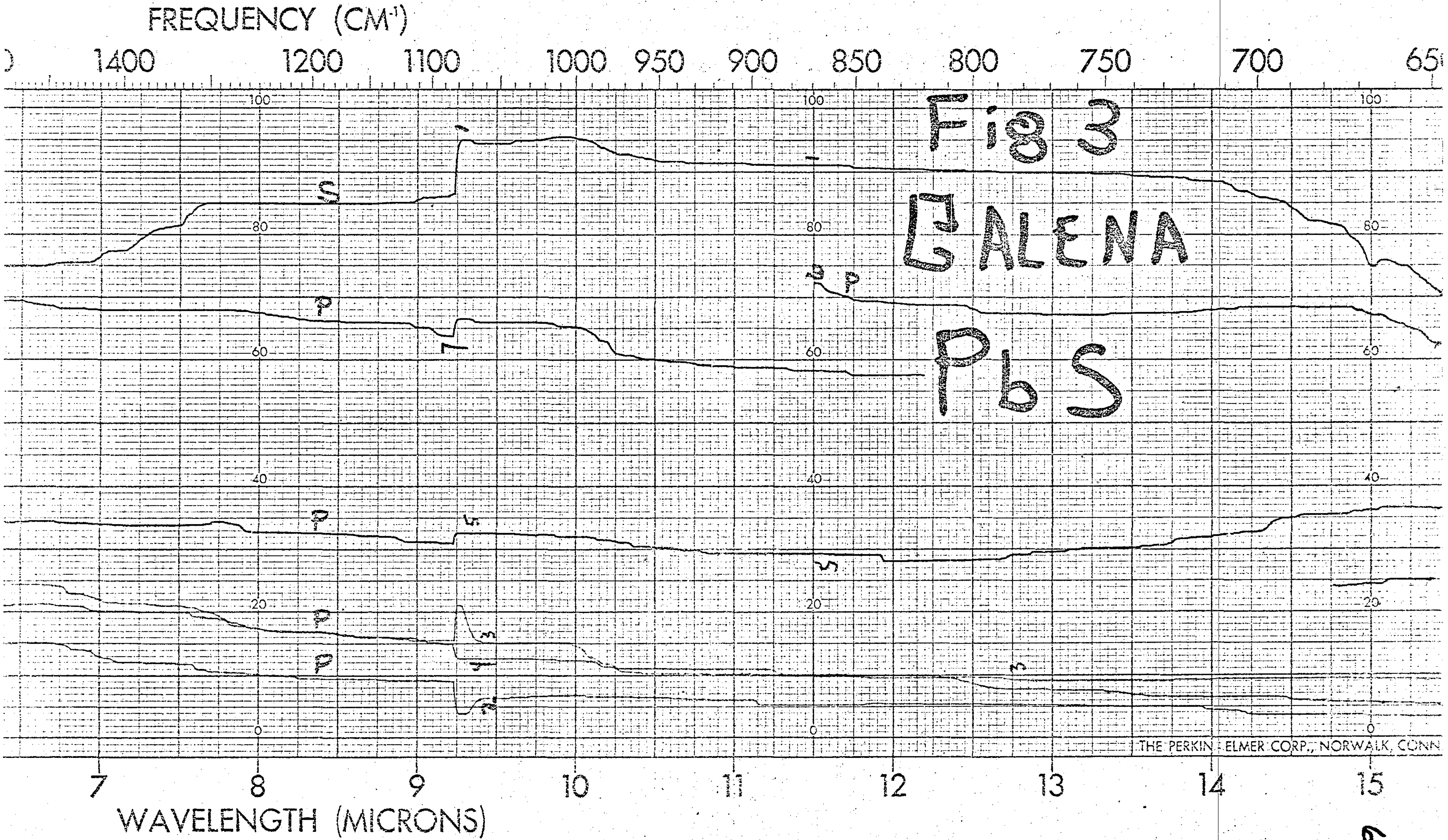


Fig 3
GALENA
PbS

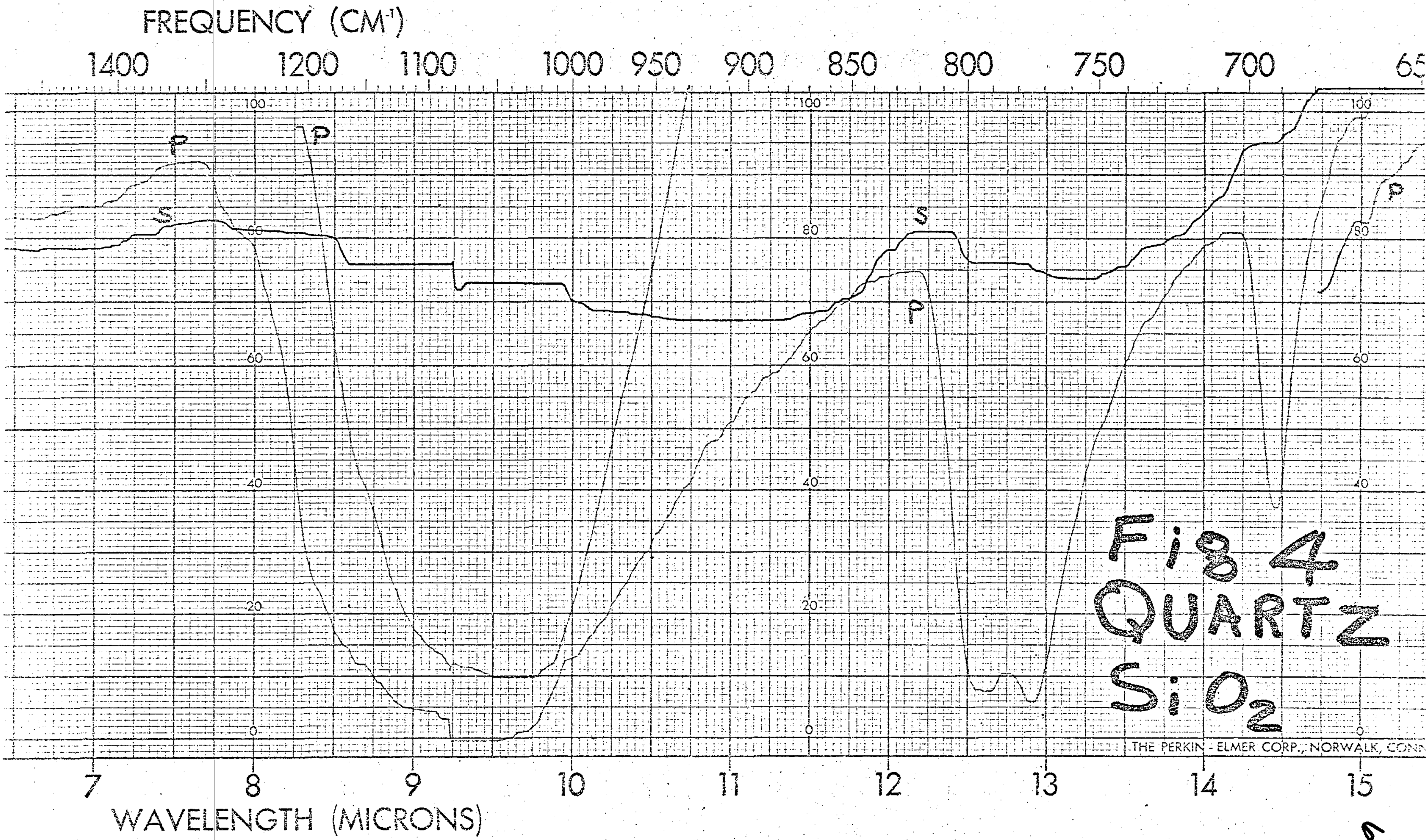


Fig 4
QUARTZ
SiO_2

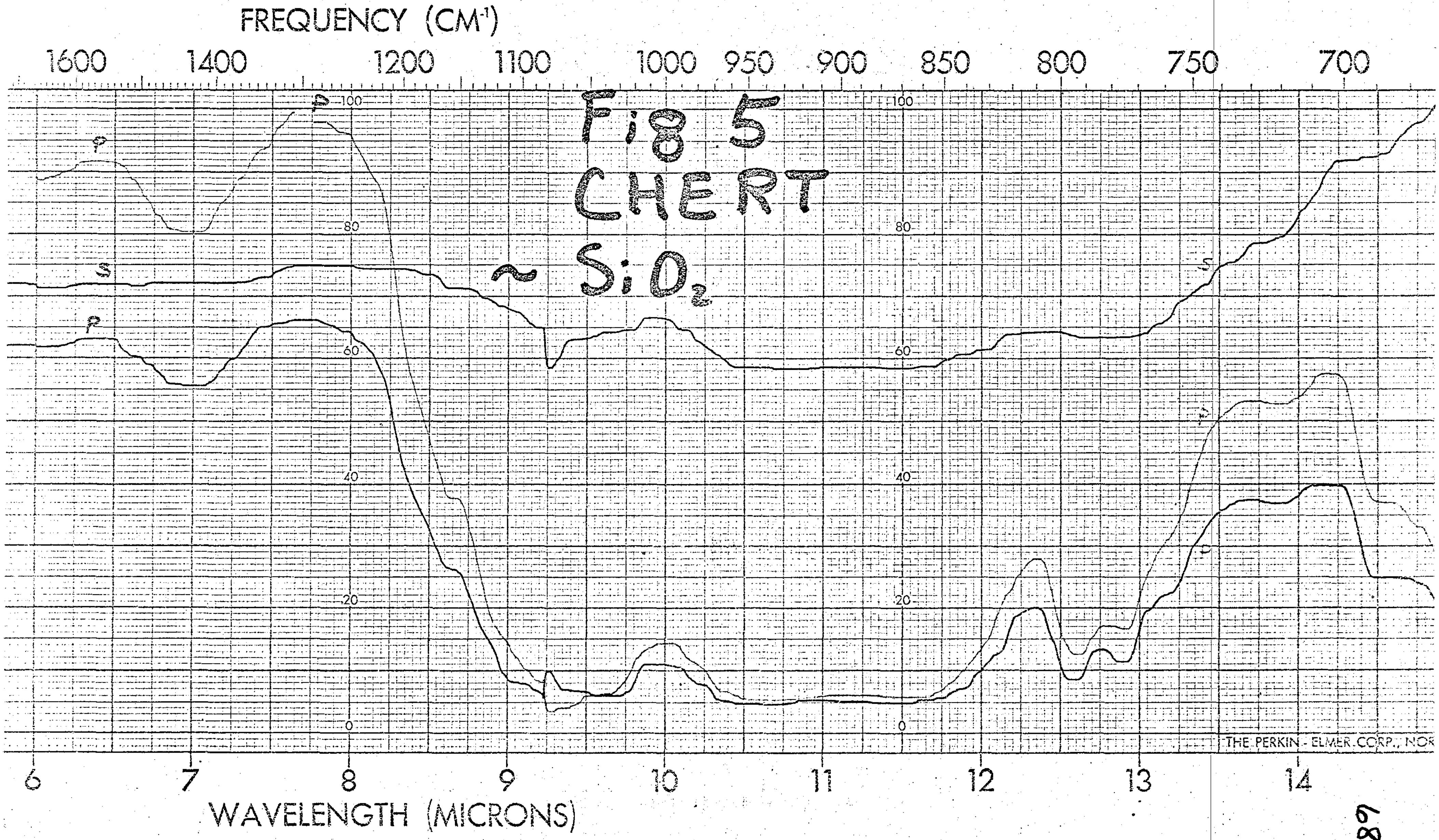


Fig 5
CHERT
~ SiO_2

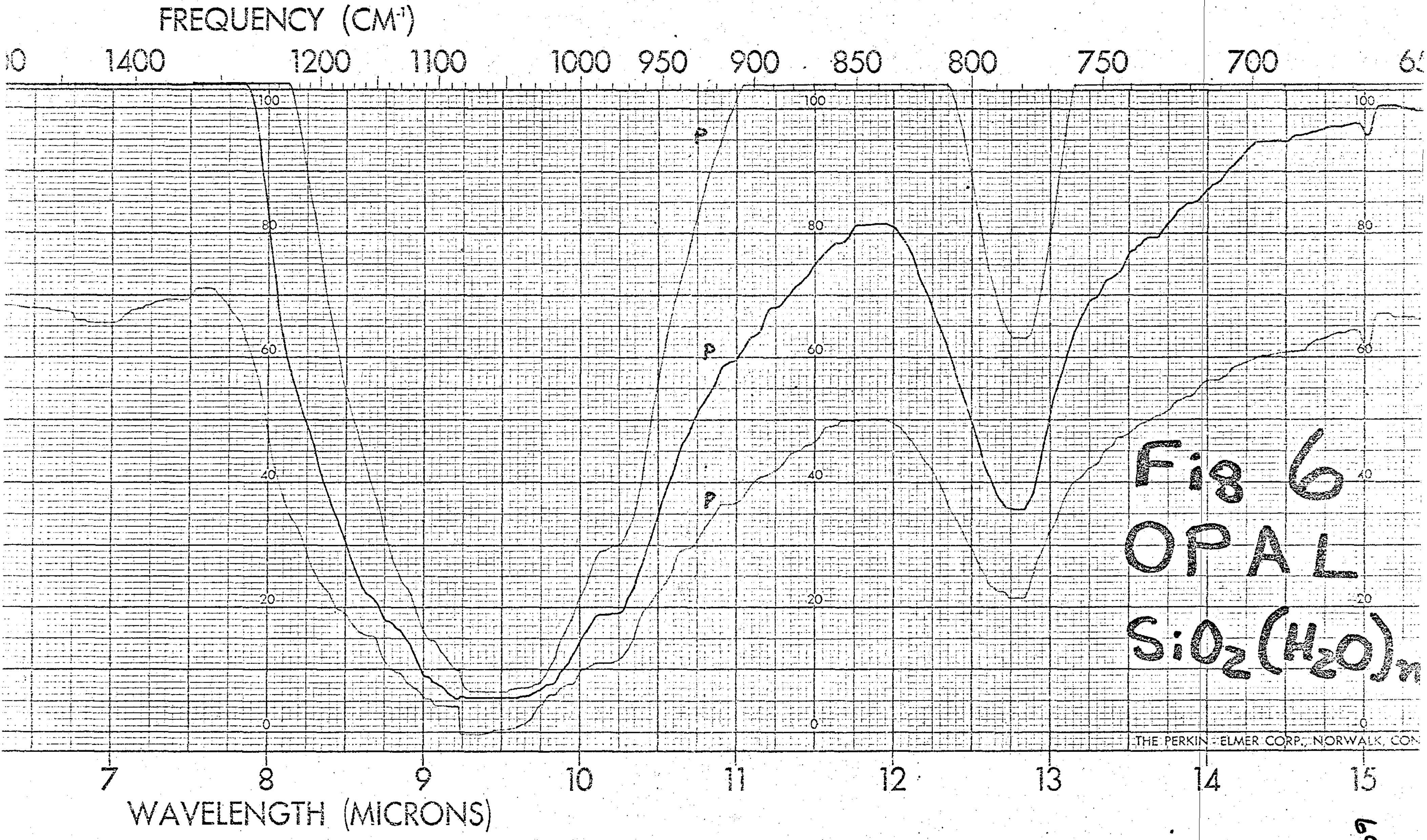


Fig 6
OPAL
$SiO_2(H_2O)_n$

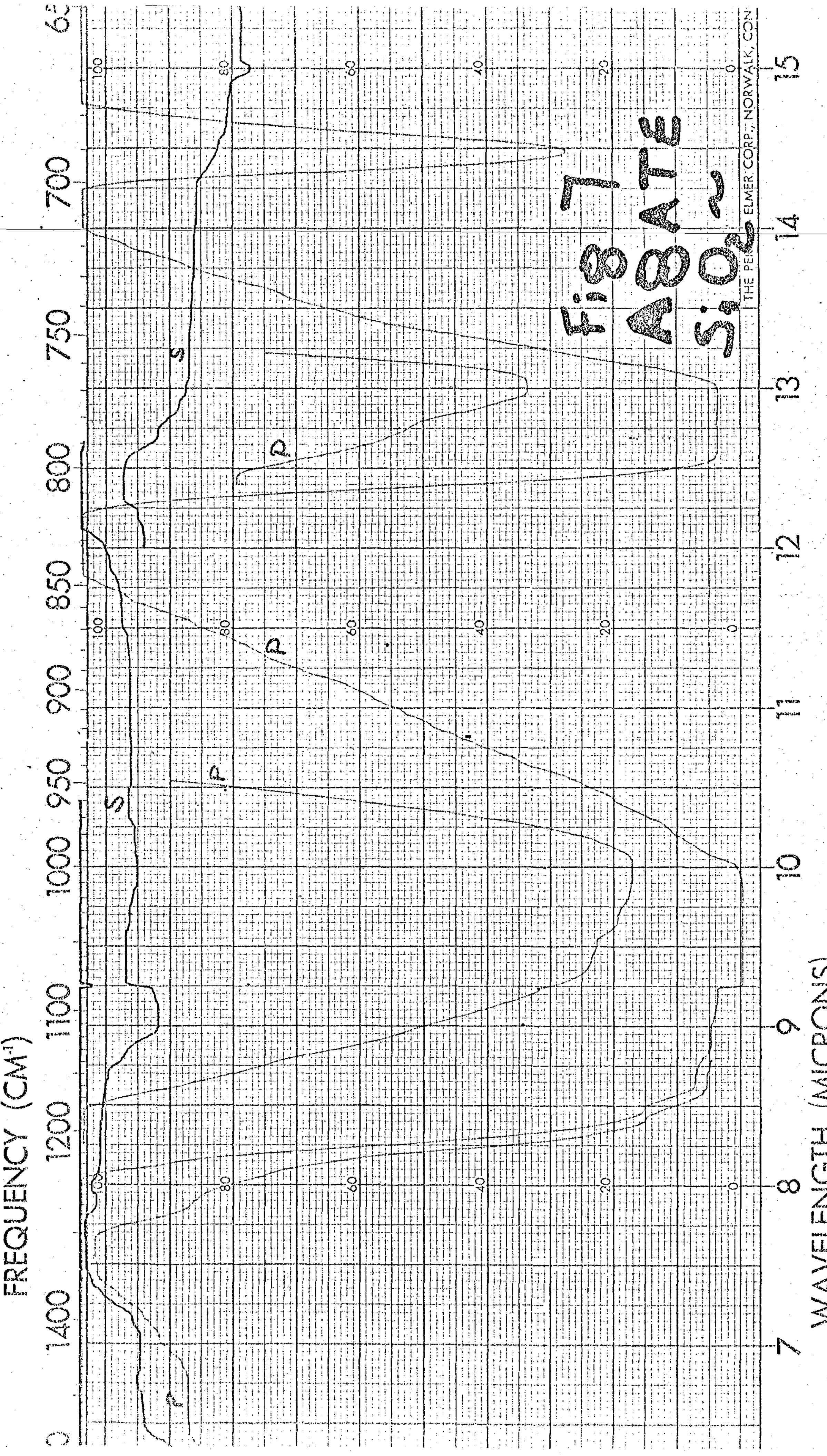
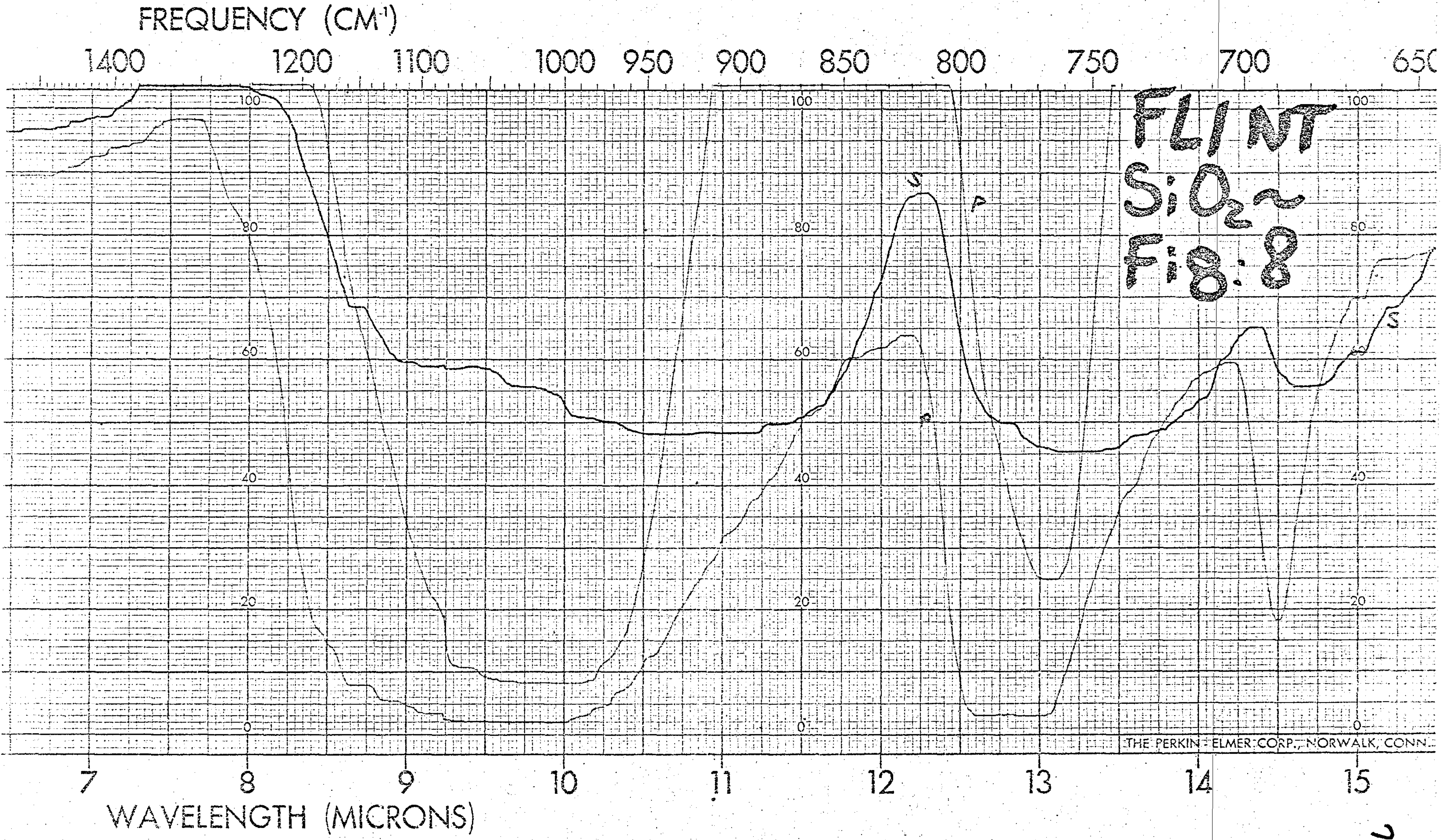


Fig 8 A8ATE SiO2



FLINT
SiO_2~
Fig. 8

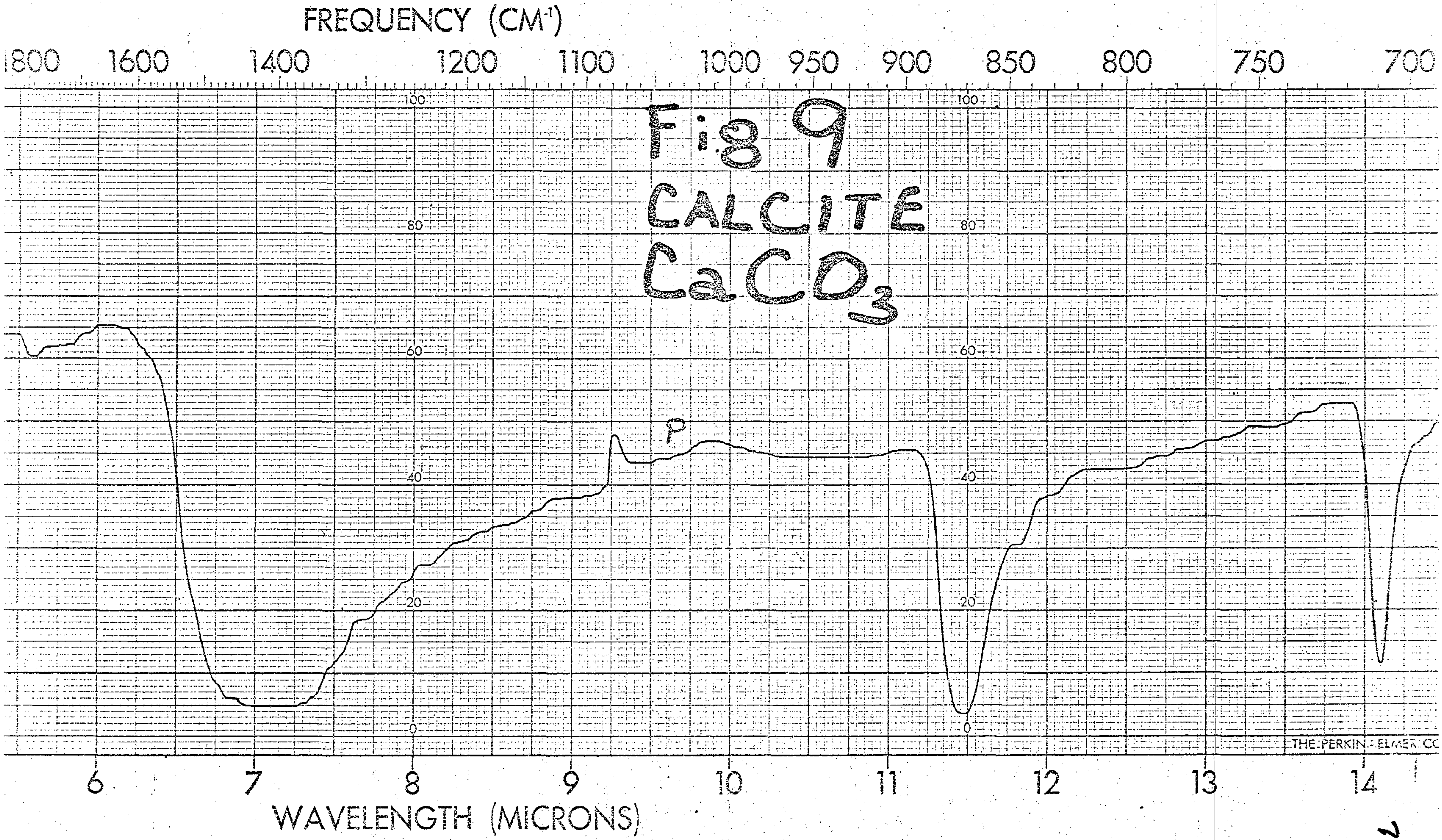


Fig 9
CALCITE
$CaCO_3$

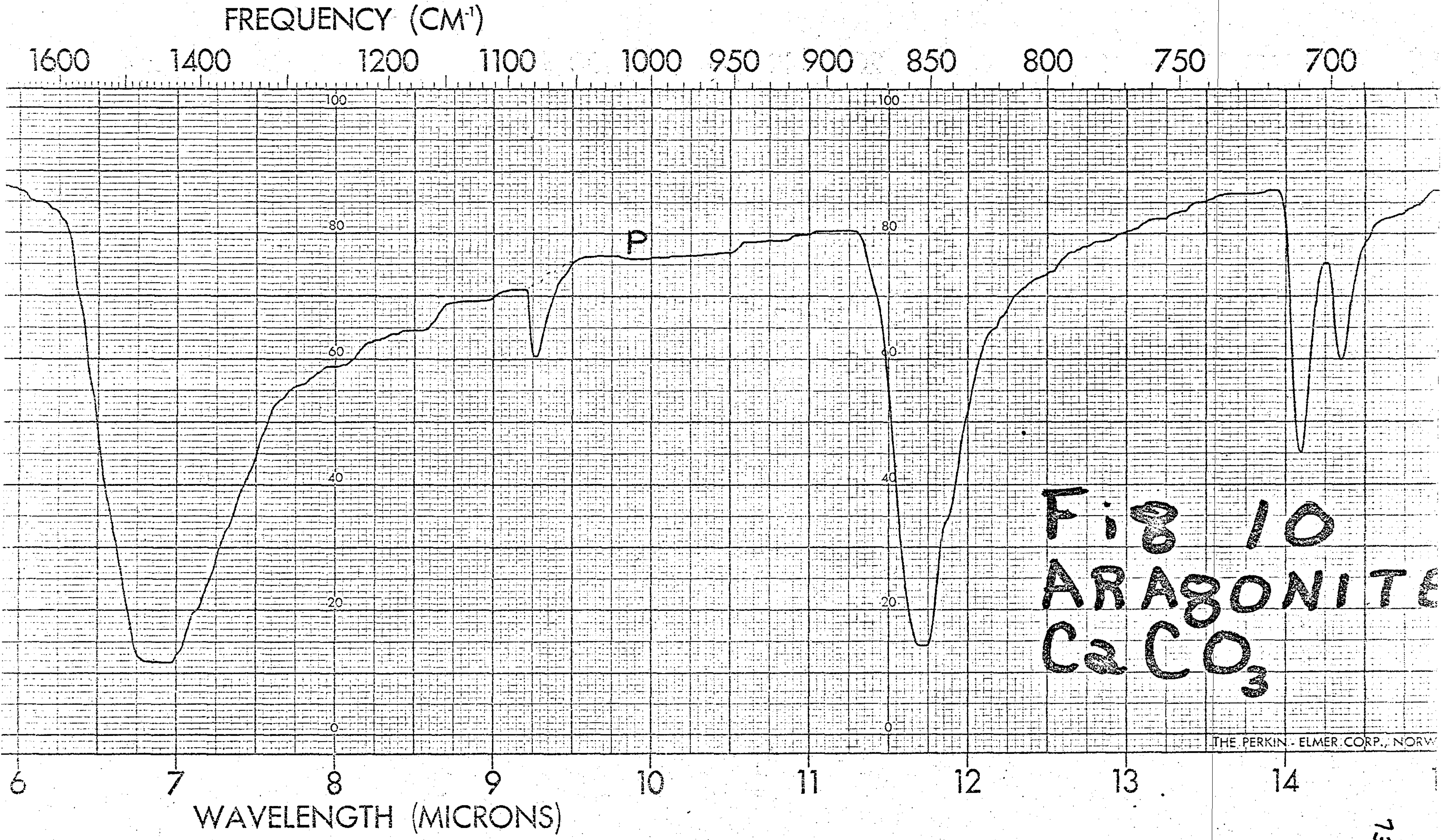


Fig 10
ARAGONITE
$CaCO_3$

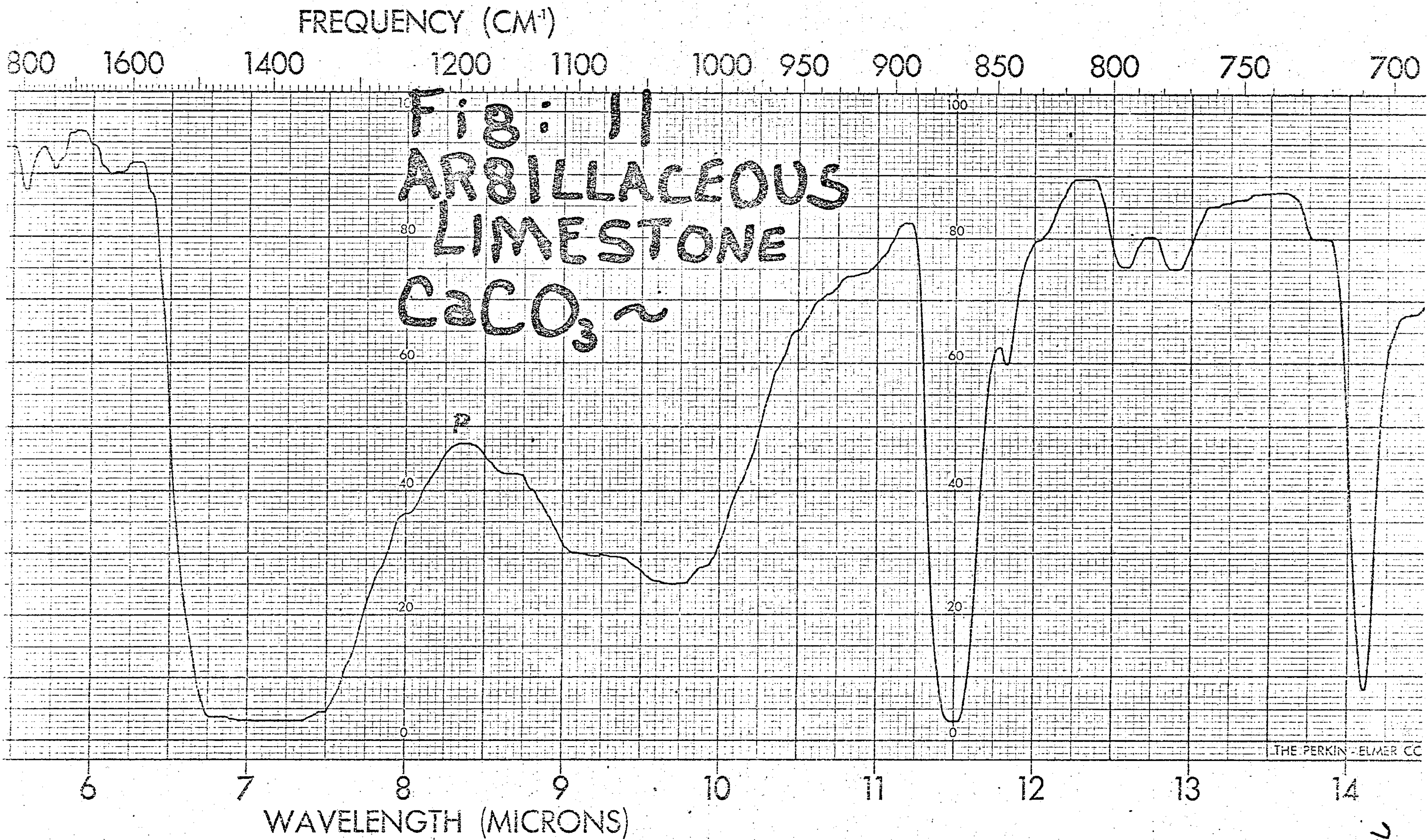


Fig: 11
ARGILLACEOUS
LIMESTONE
$CaCO_3$ ~

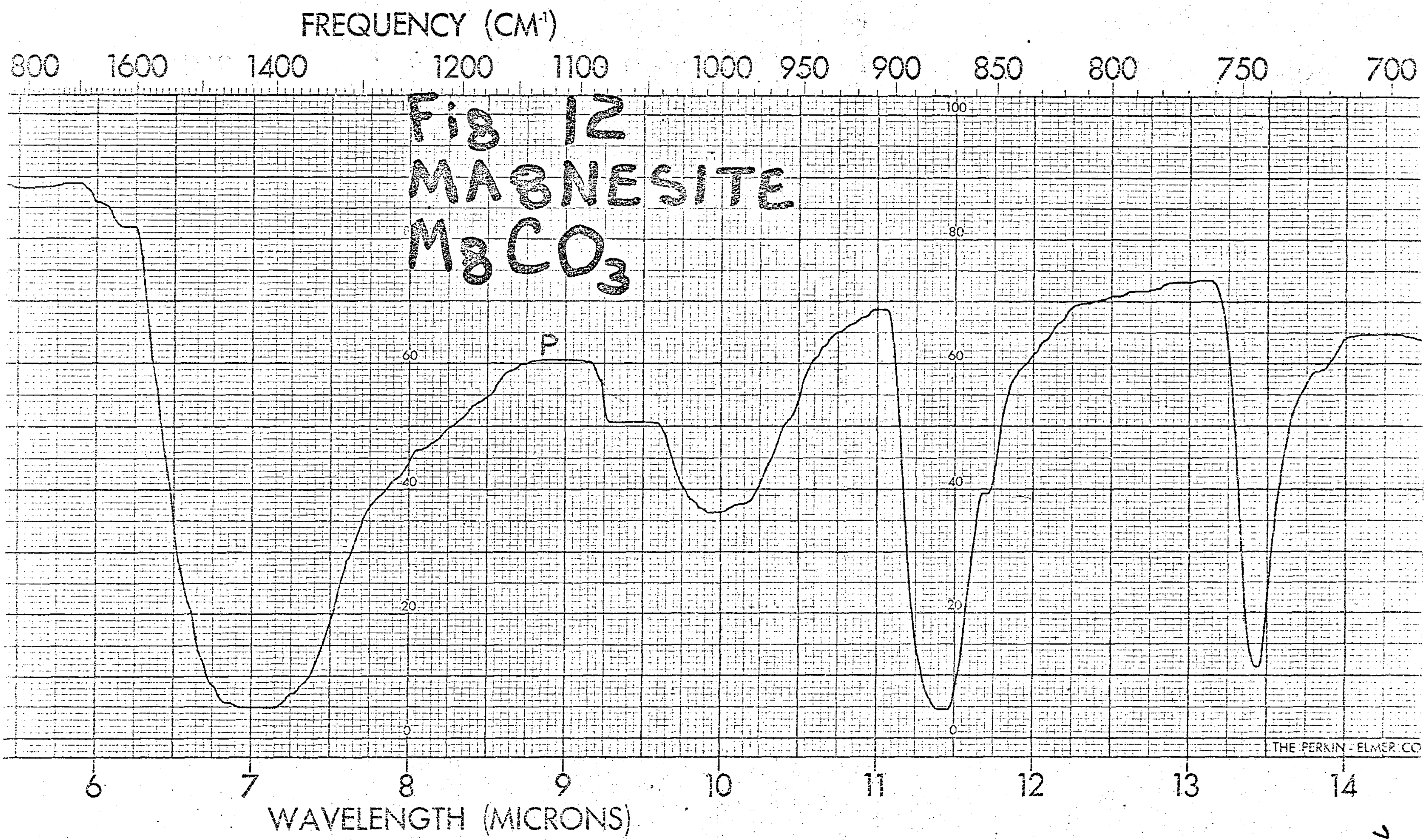


Fig 12
MAGNESITE
$MgCO_3$

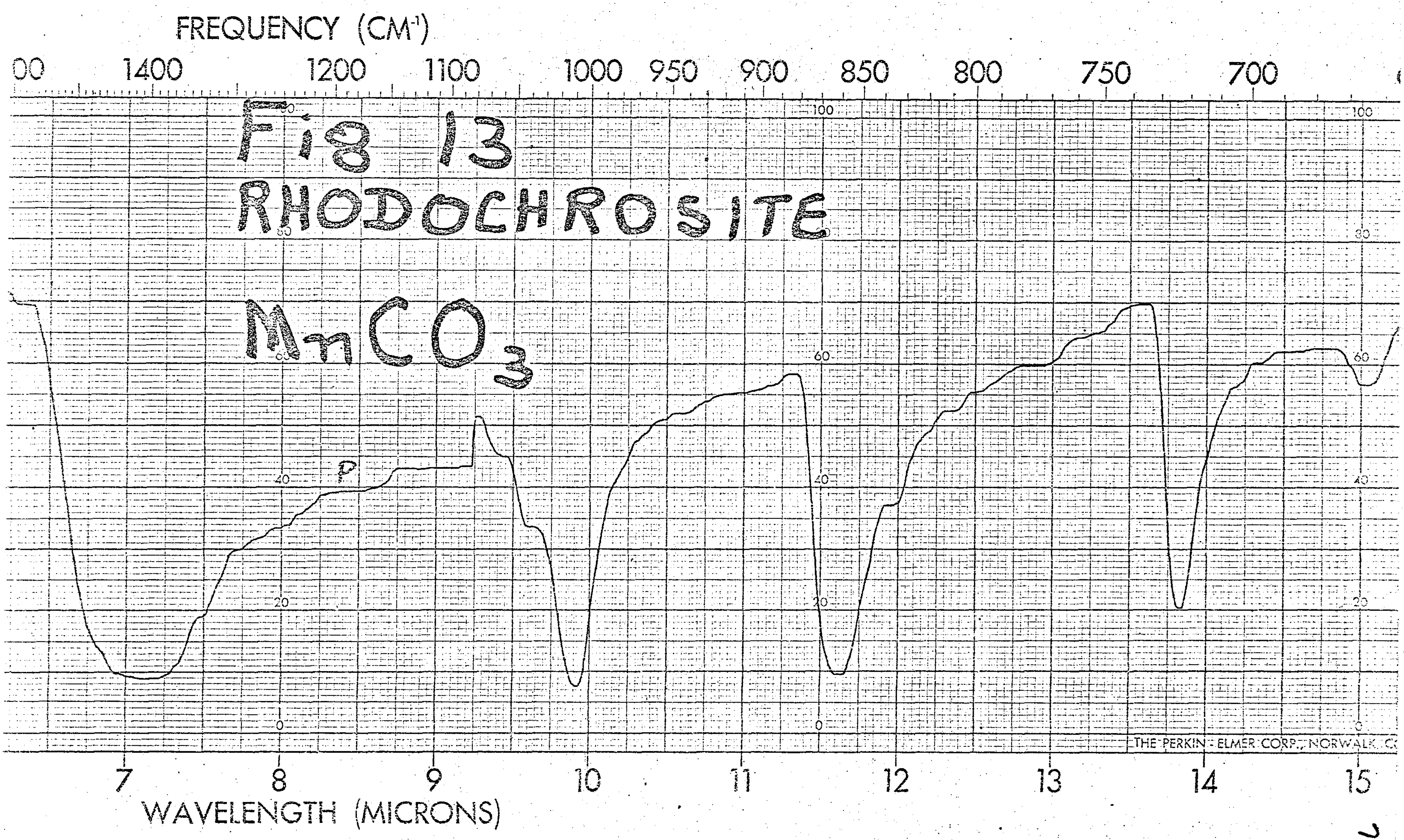


Fig 13
RHODOCHROSITE
MnCO$_3$

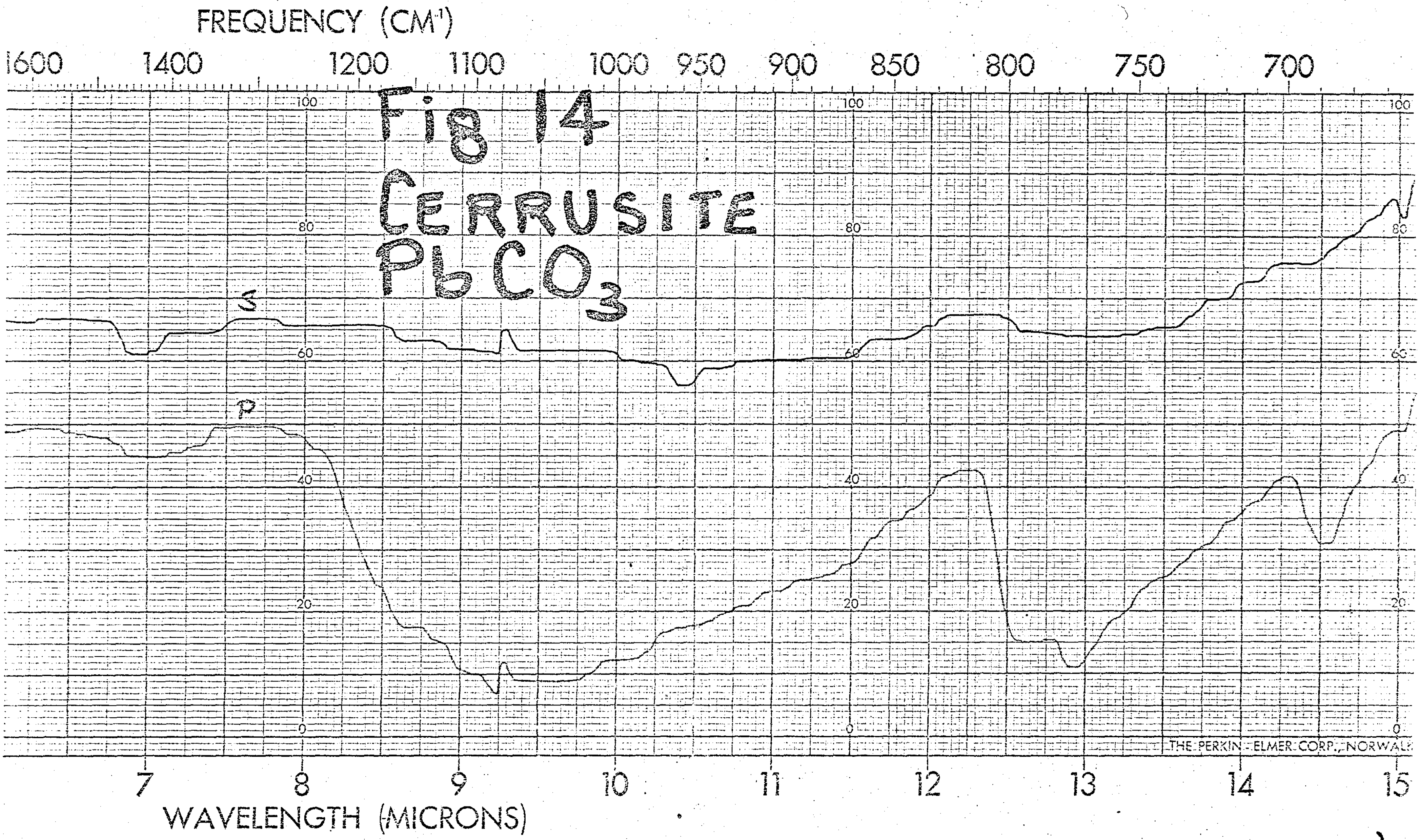


Fig 14
CERRUSITE
$PbCO_3$

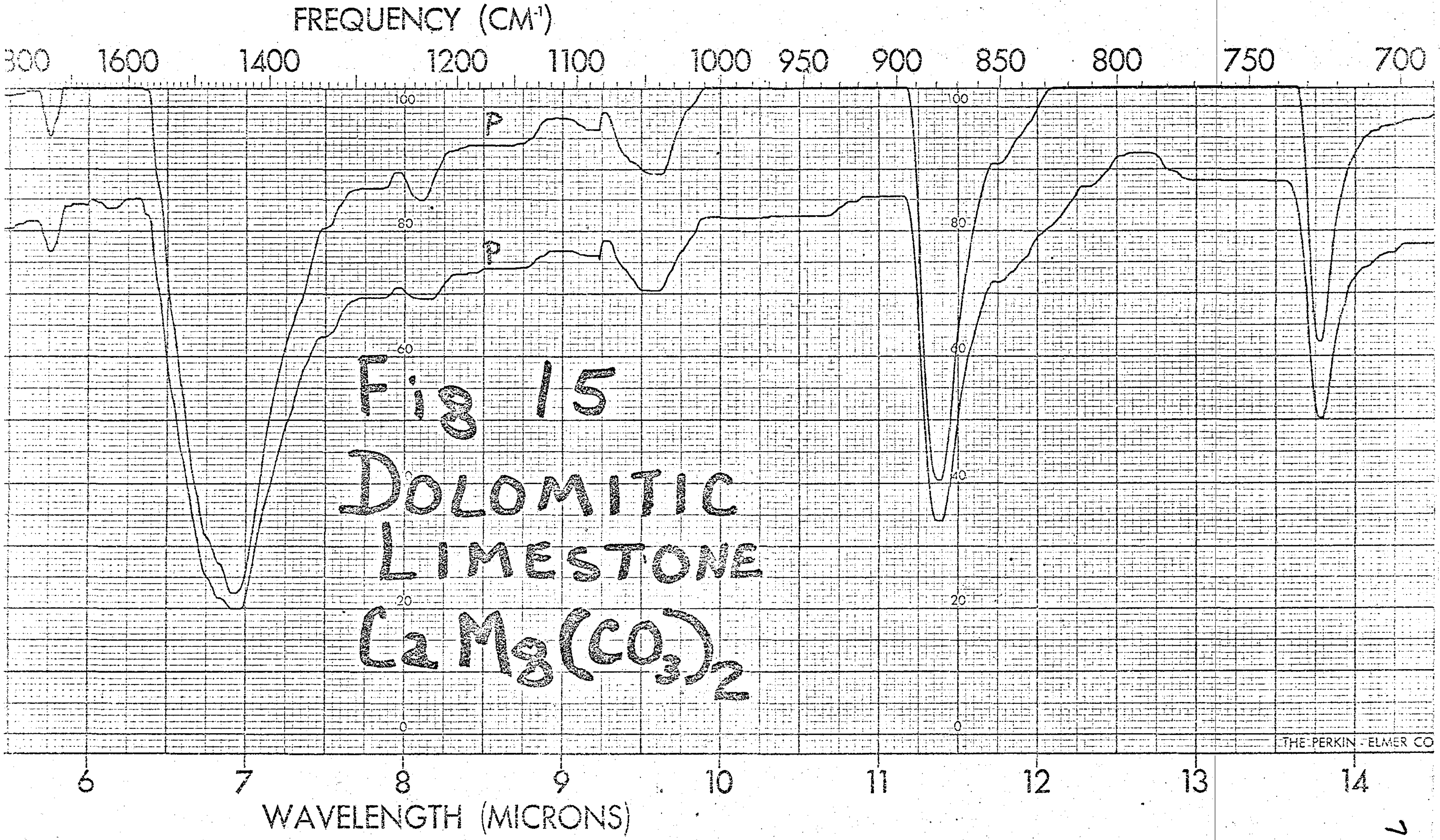


Fig 15

DOLOMITIC LIMESTONE

$CaMg(CO_3)_2$

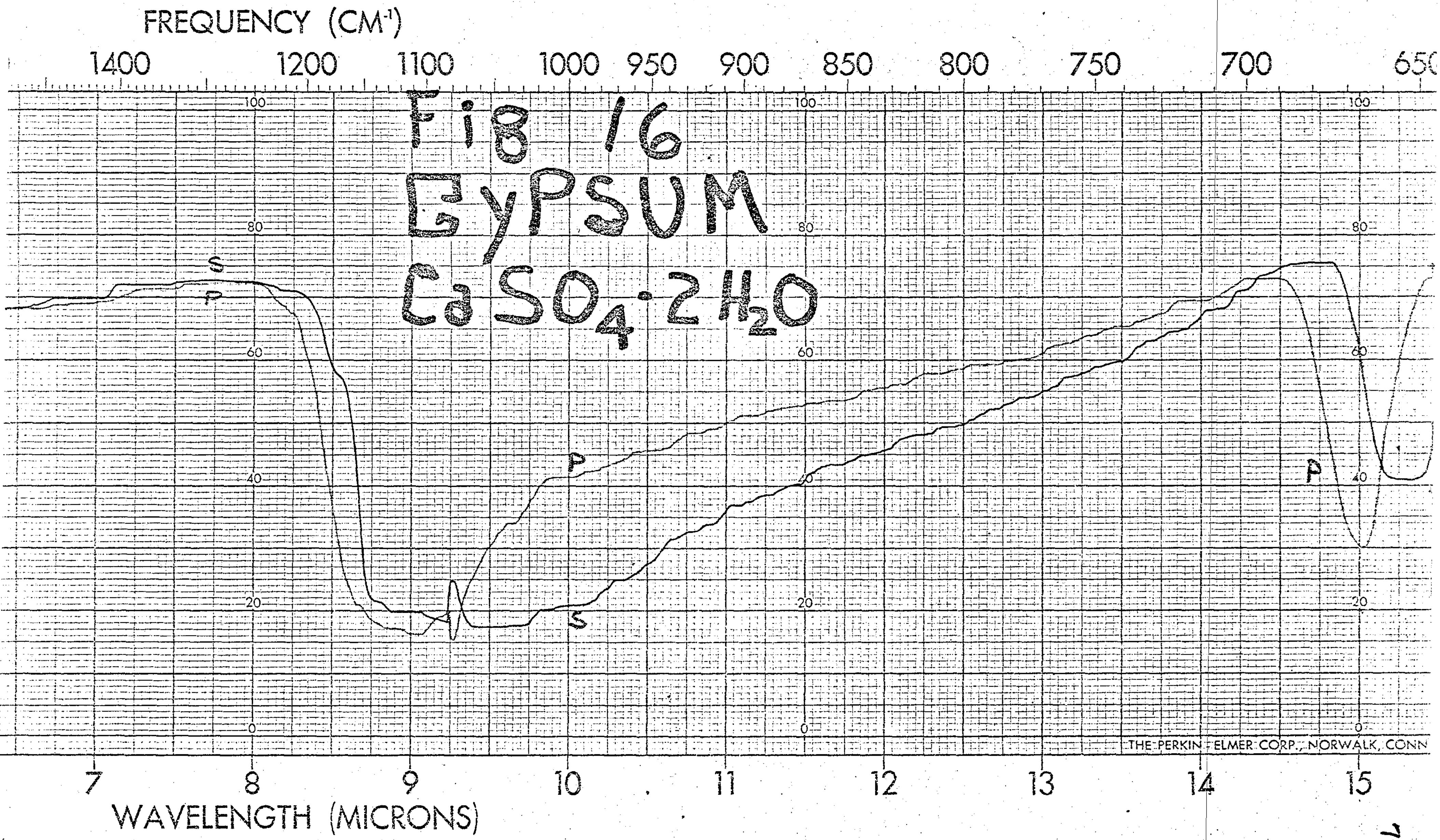


Fig 16

GYPSUM

$CaSO_4 \cdot 2H_2O$

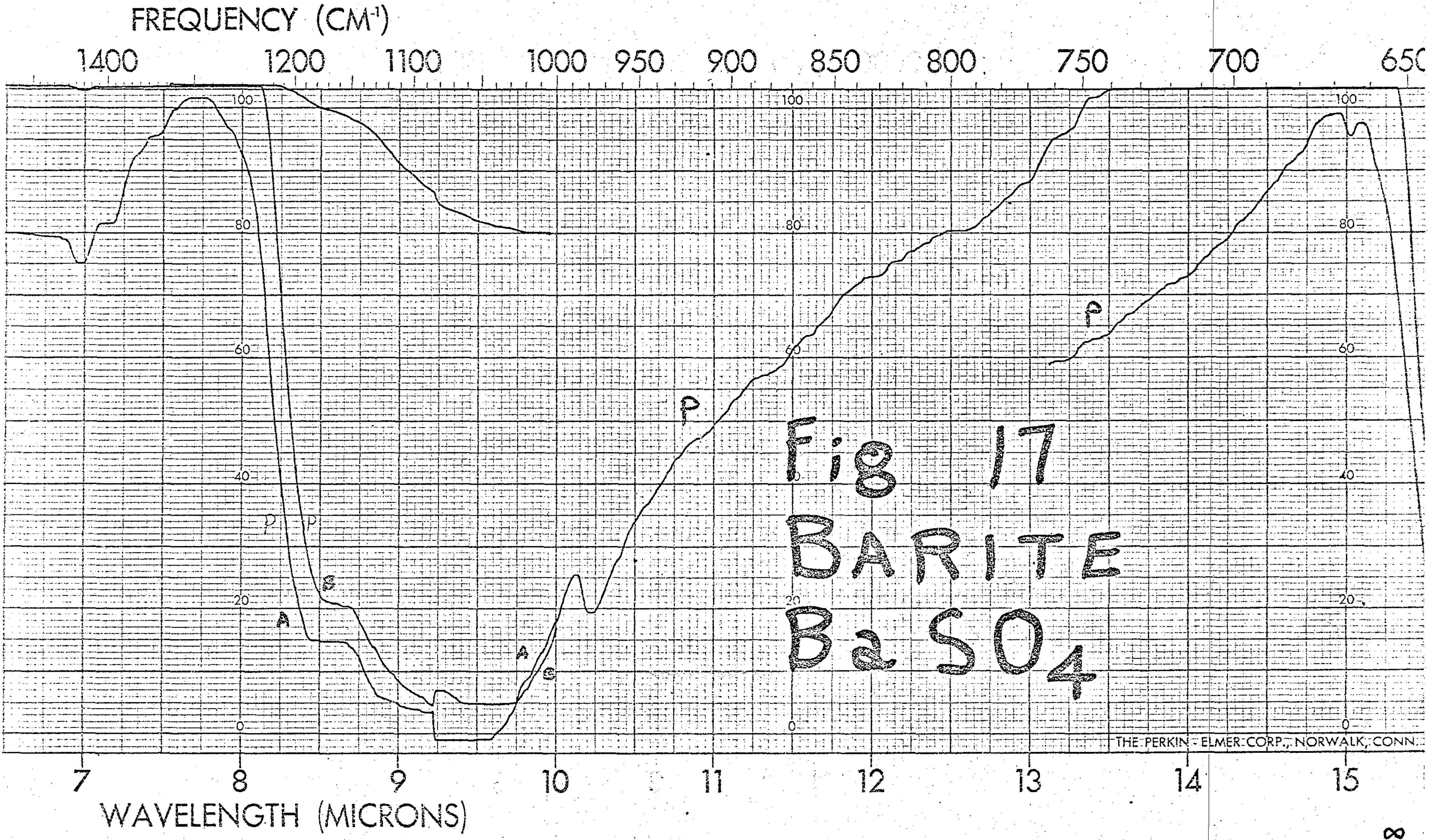


Fig 17
BARITE
$BaSO_4$

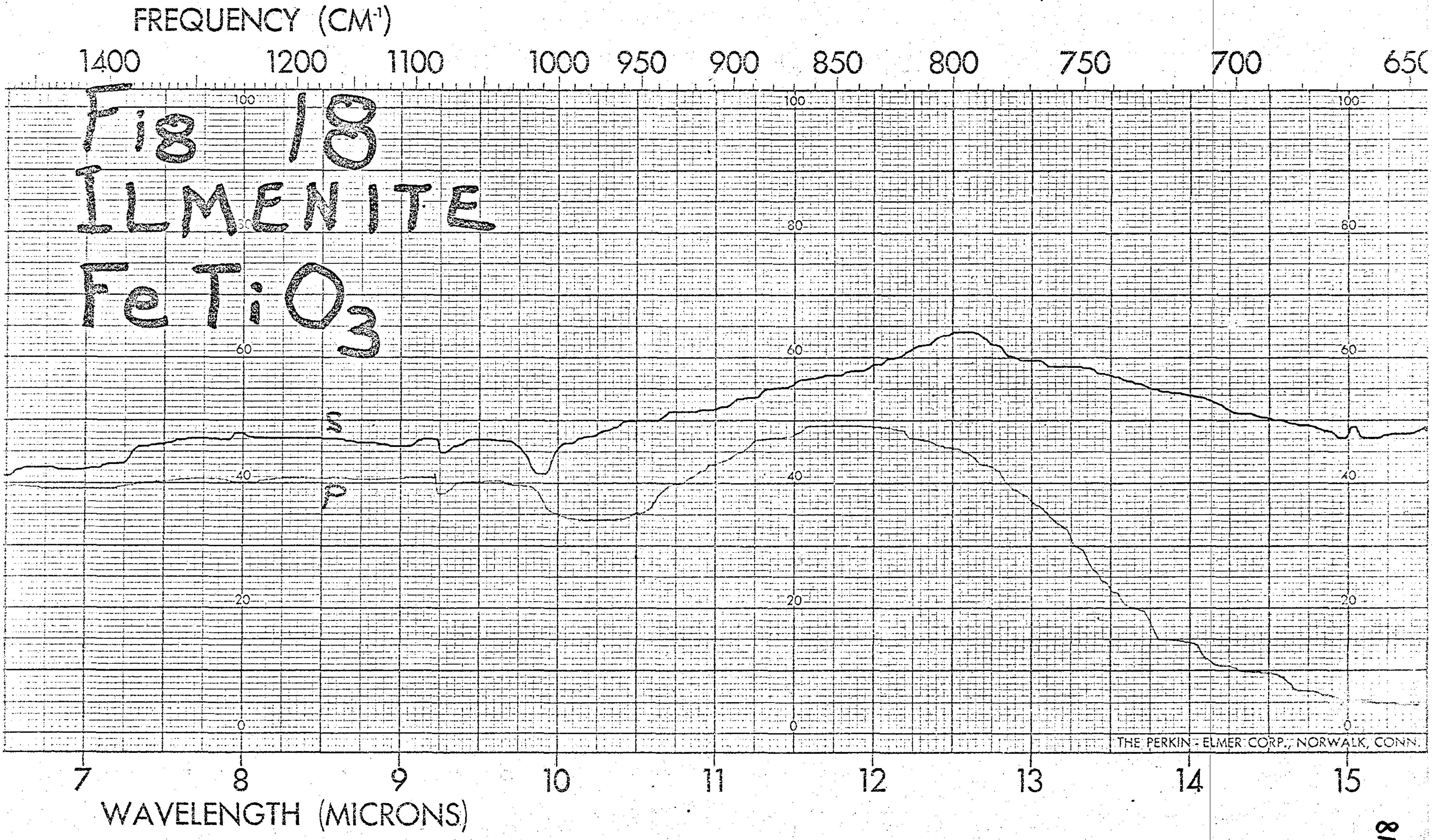


Fig 18
ILMENITE
$FeTiO_3$

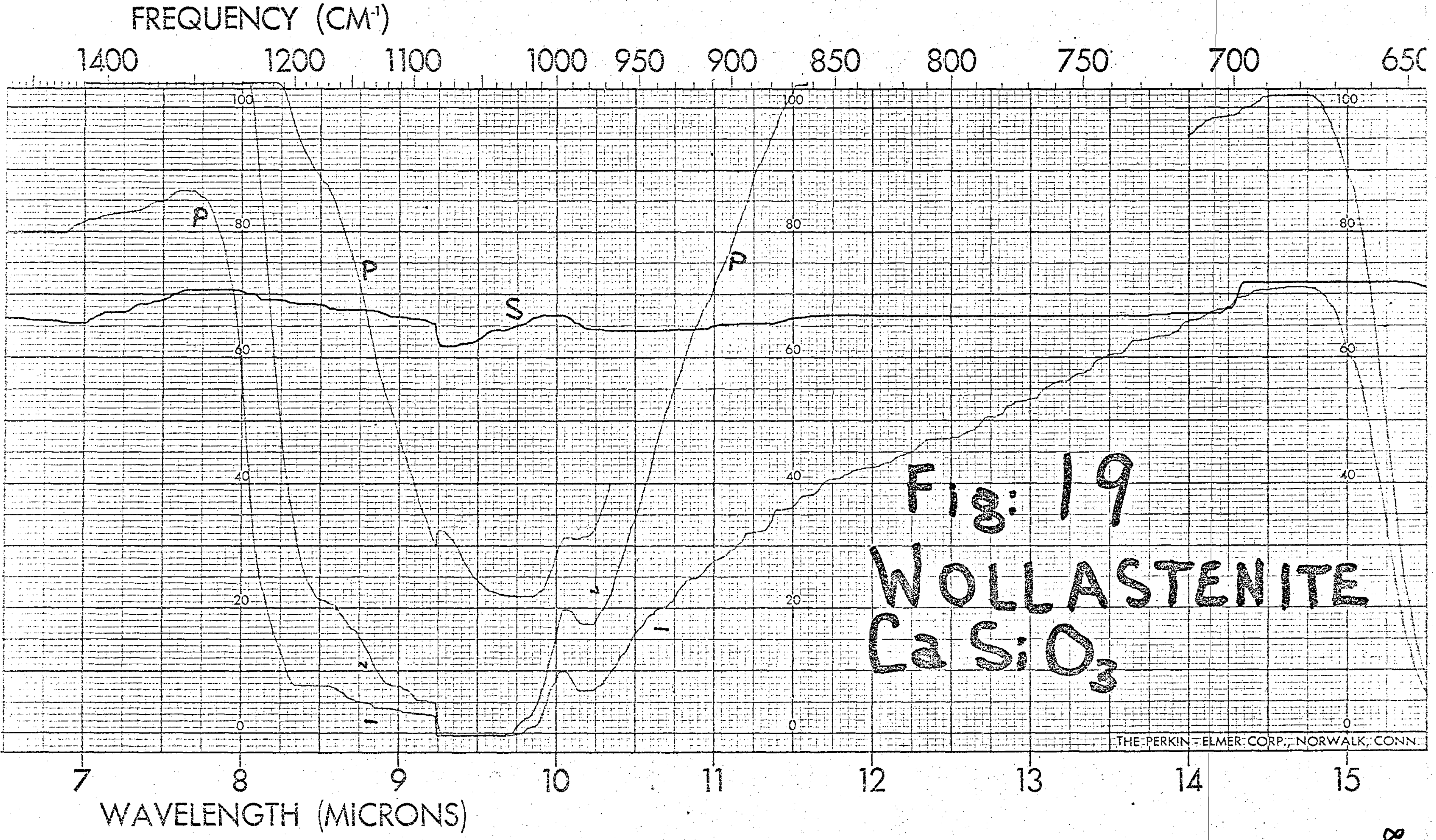


Fig: 19
WOLLASTENITE
$CaSiO_3$

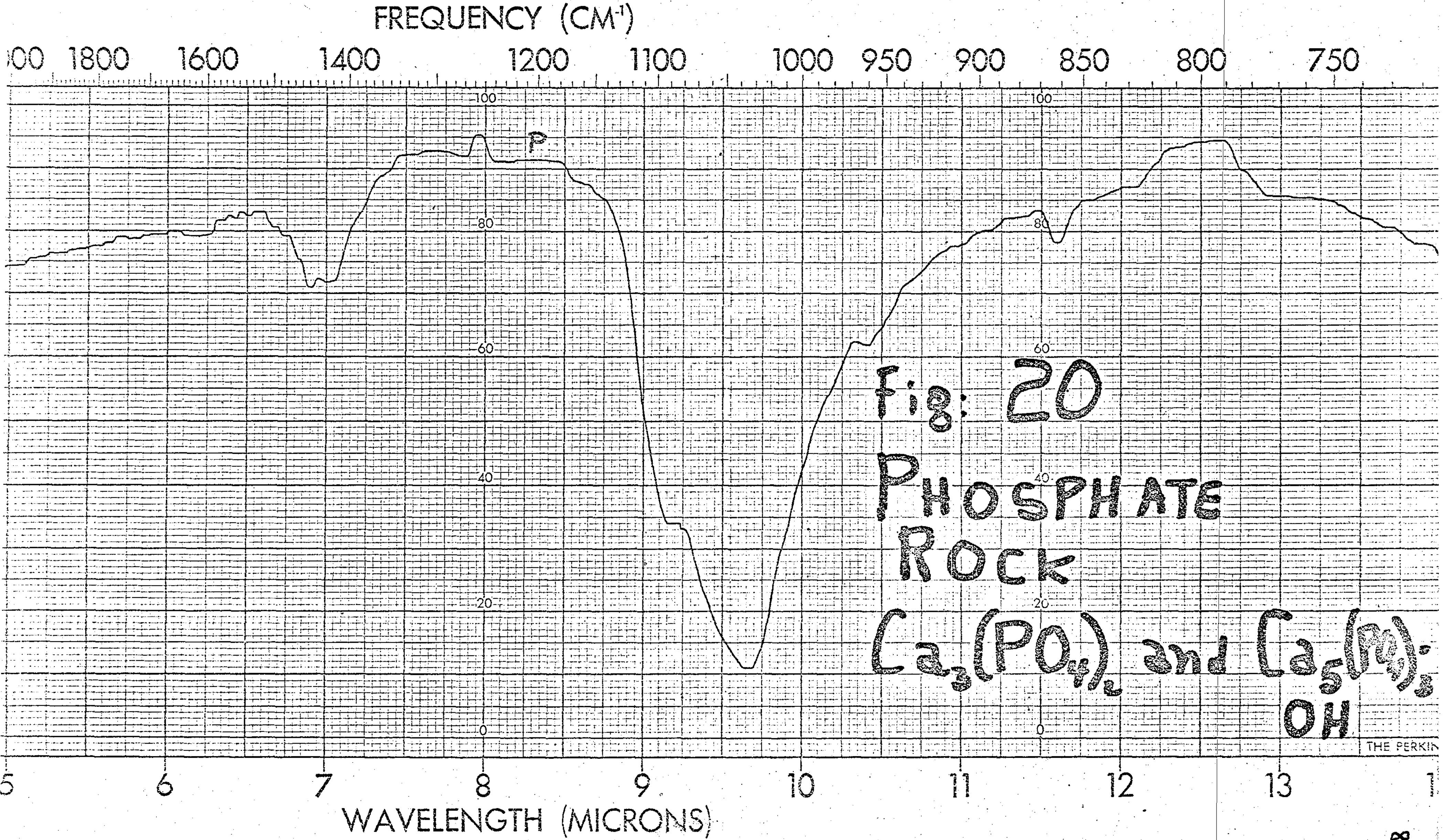


Fig: 20 PHOSPHATE ROCK $Ca_3(PO_4)_2$ and $Ca_5(PO_4)_3OH$

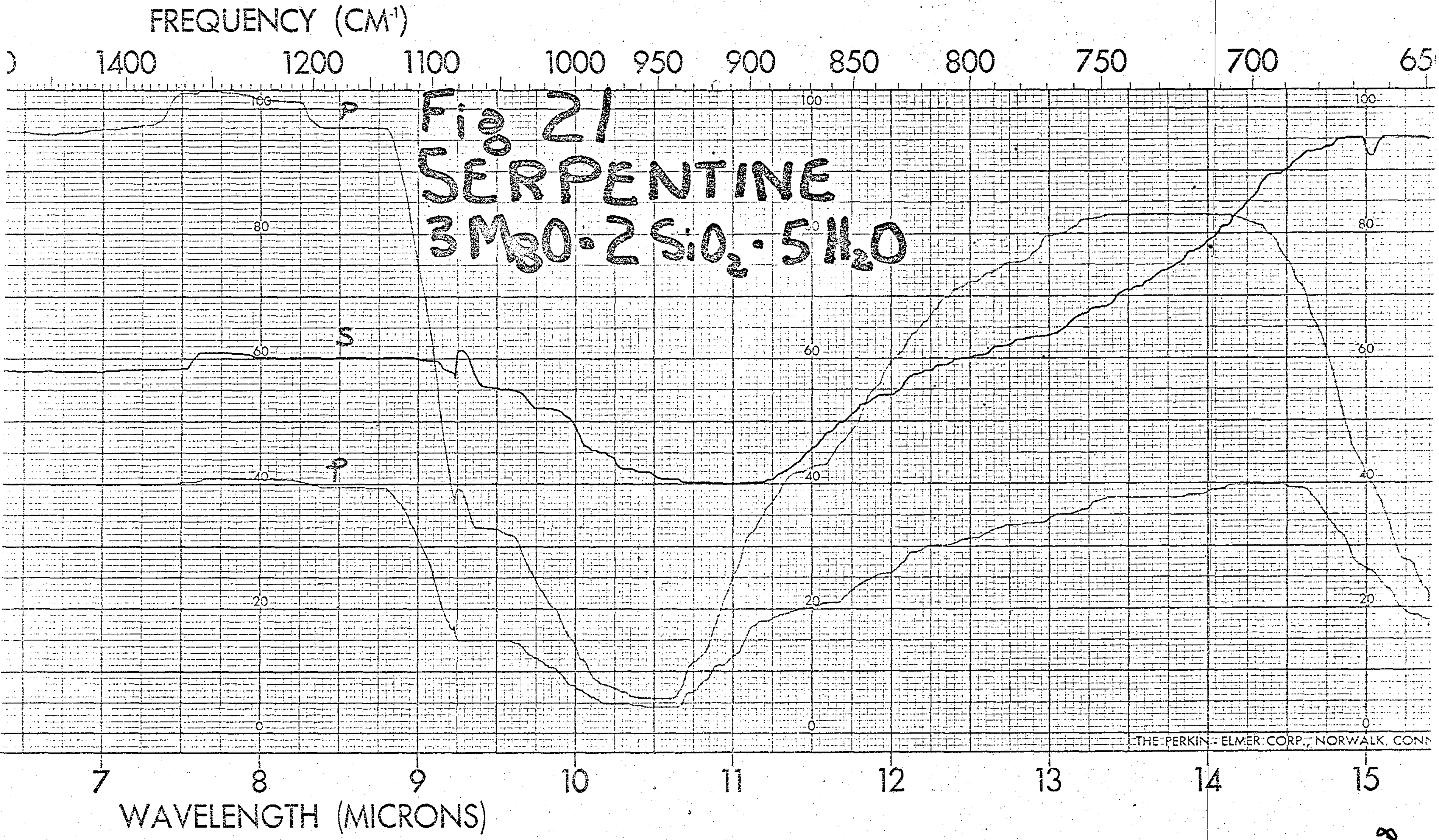


Fig 21
SERPENTINE
$3MgO \cdot 2SiO_2 \cdot 5H_2O$

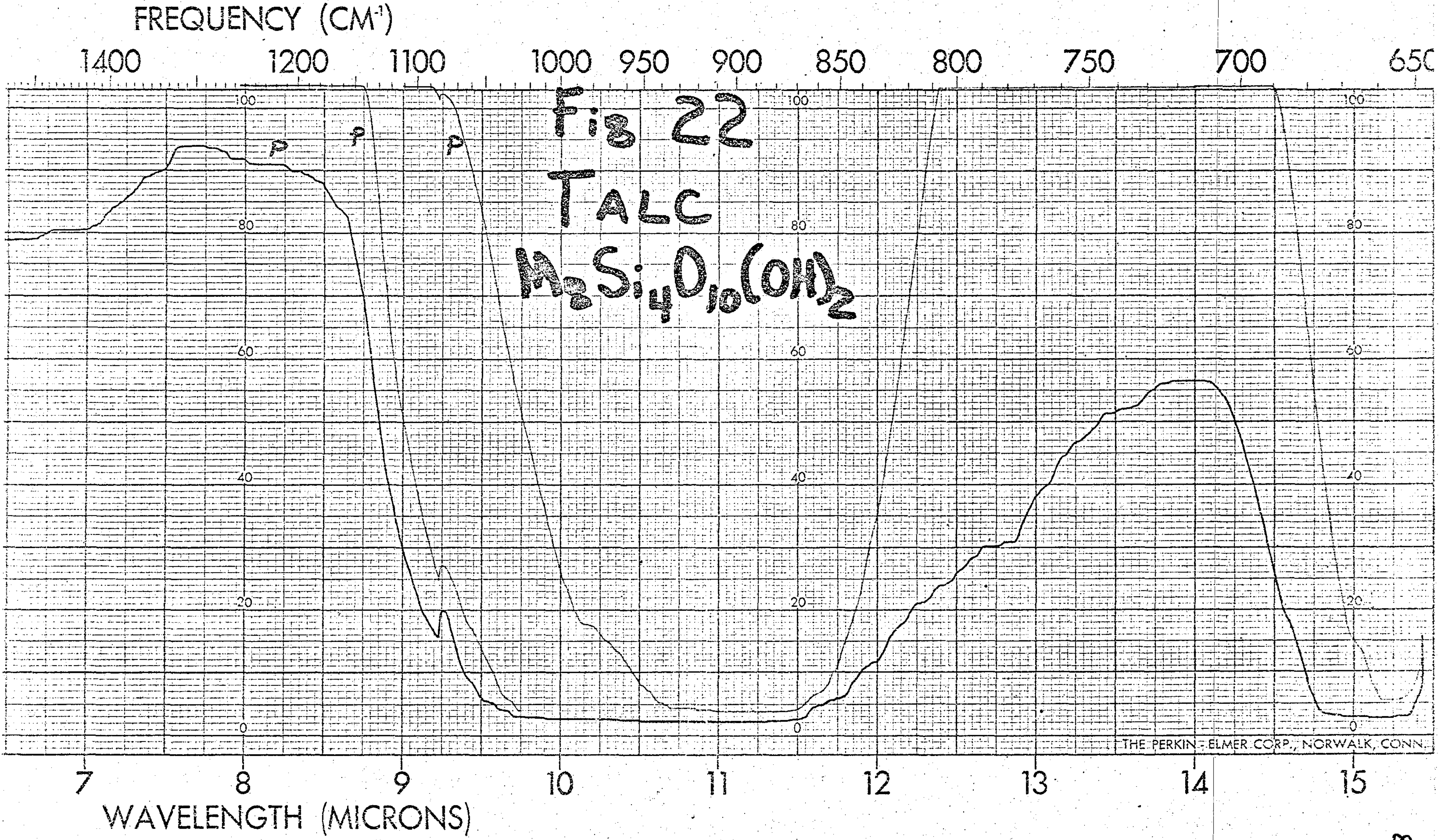


Fig 22

TALC

$Mg_3Si_4O_{10}(OH)_2$

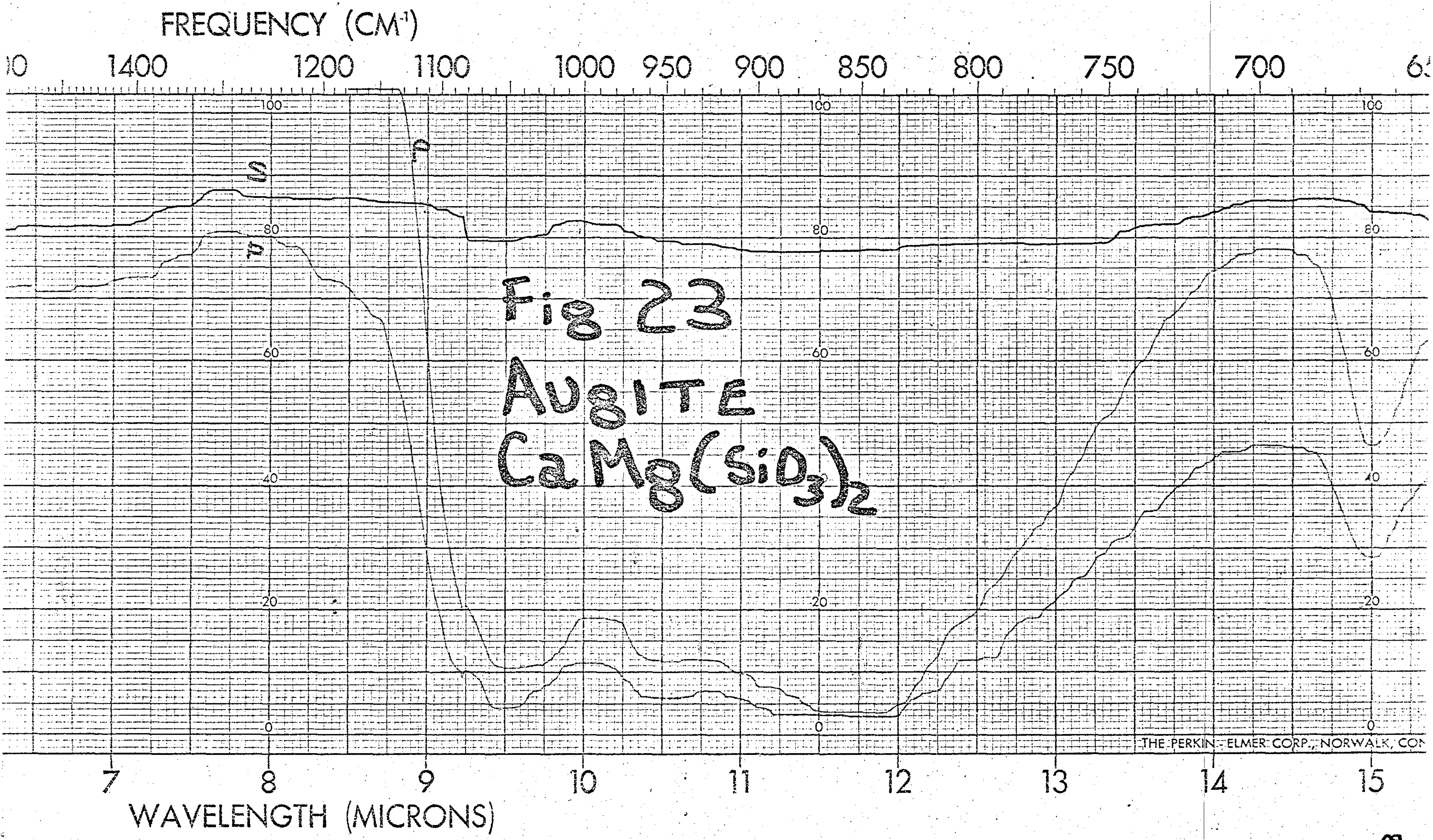
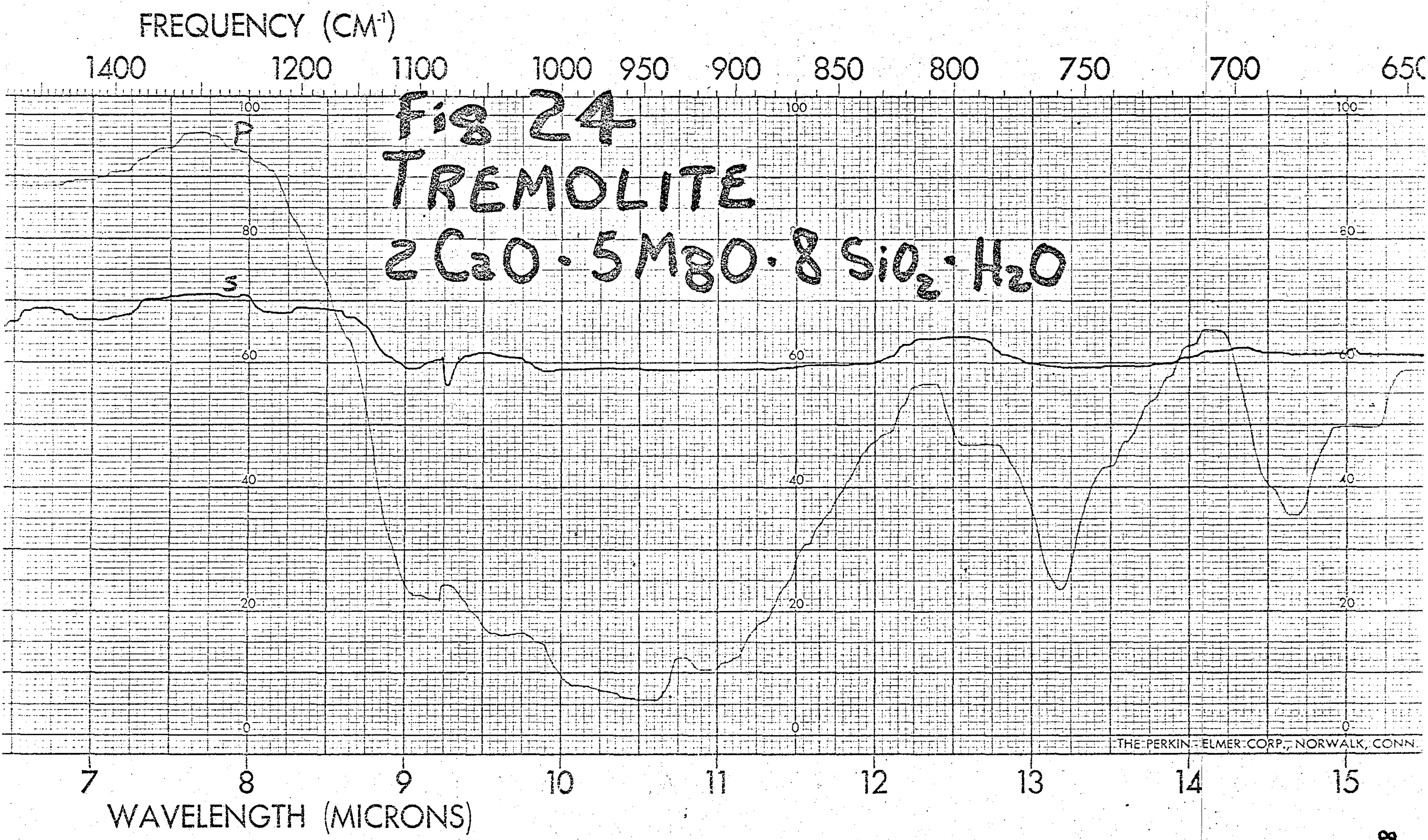


Fig 23
AUGITE
$CaMg(SiO_3)_2$

Fig 24
TREMOLITE
$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$



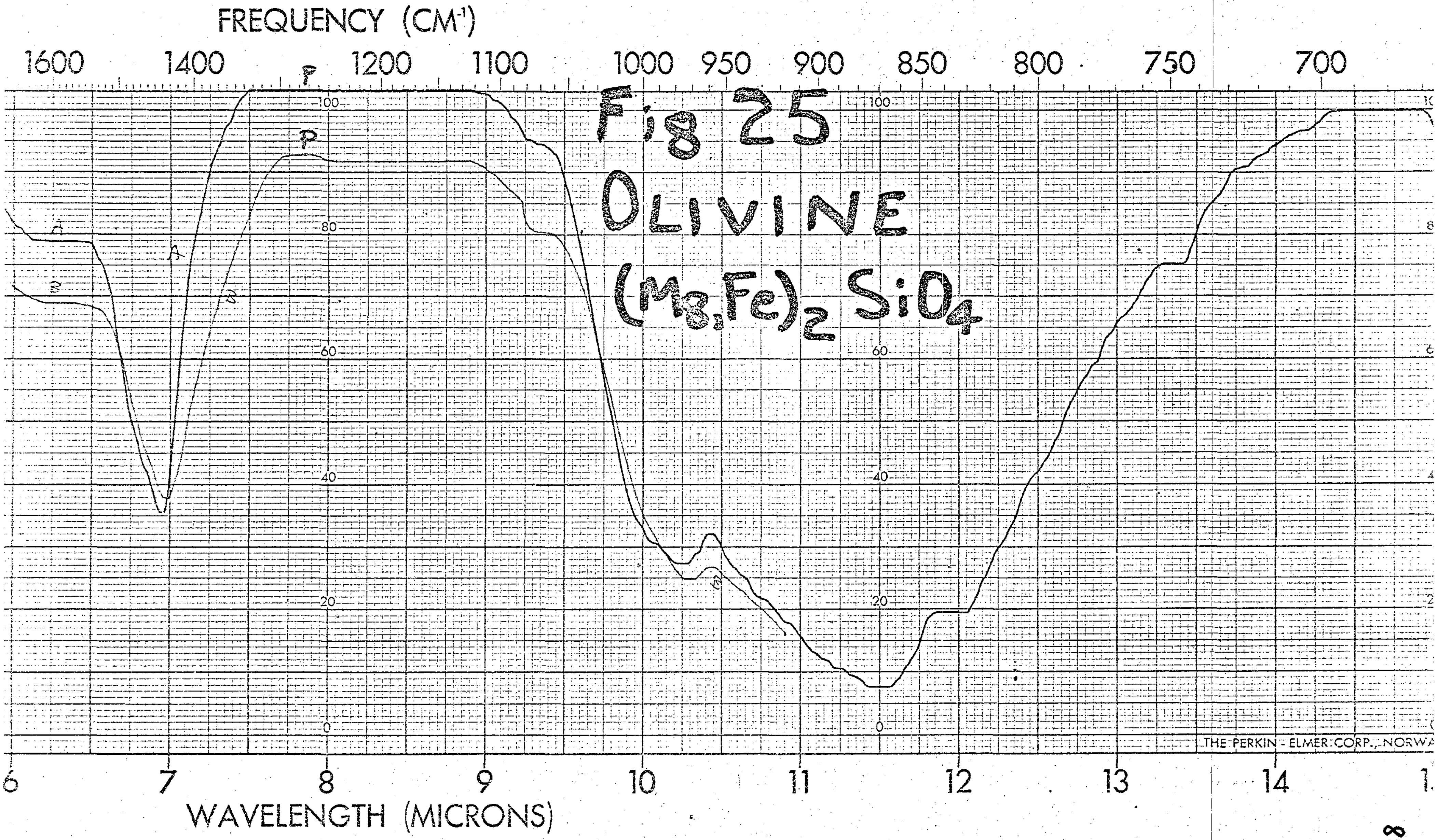


Fig 25

OLIVINE

$(Mg,Fe)_2 SiO_4$

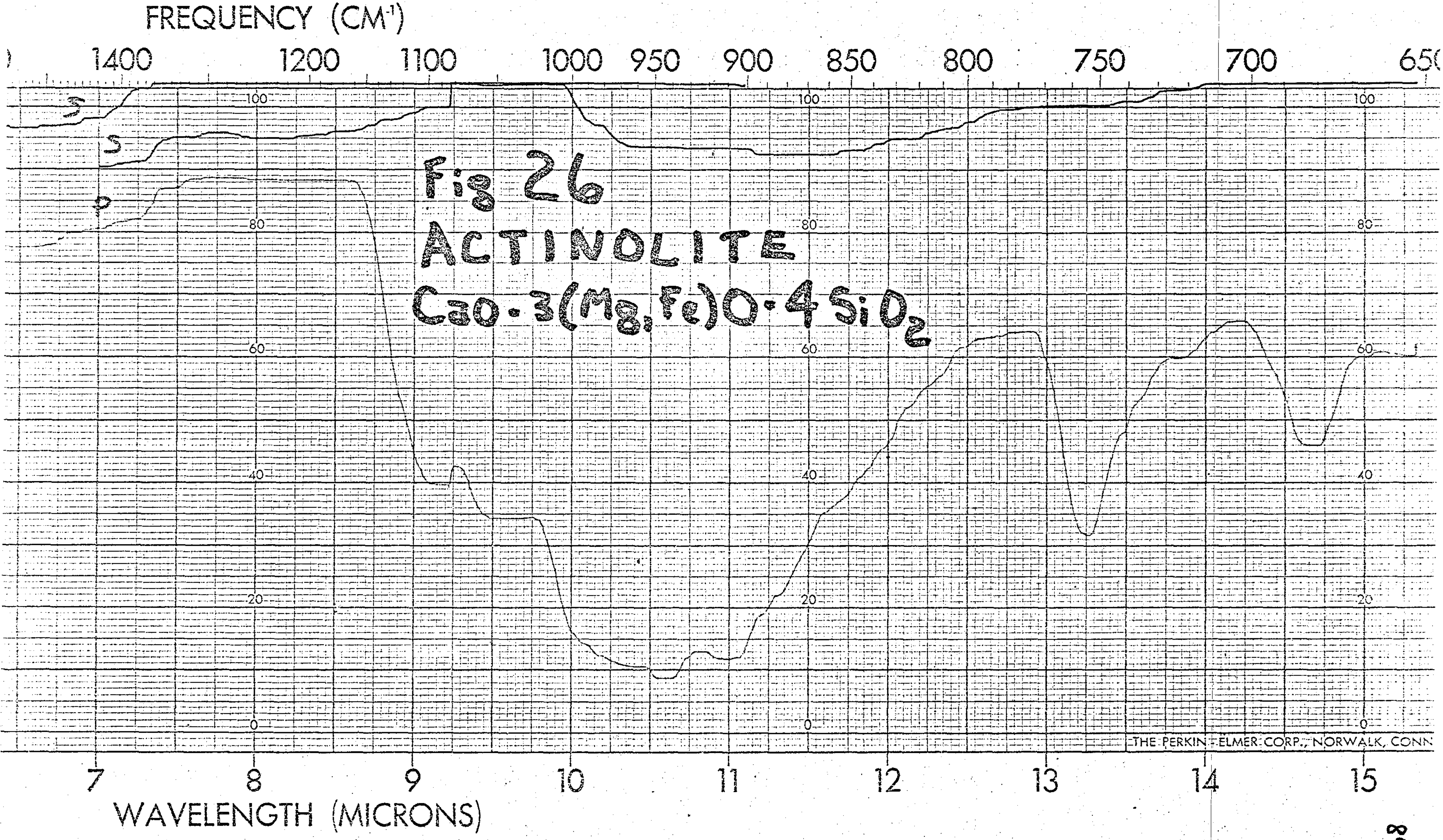
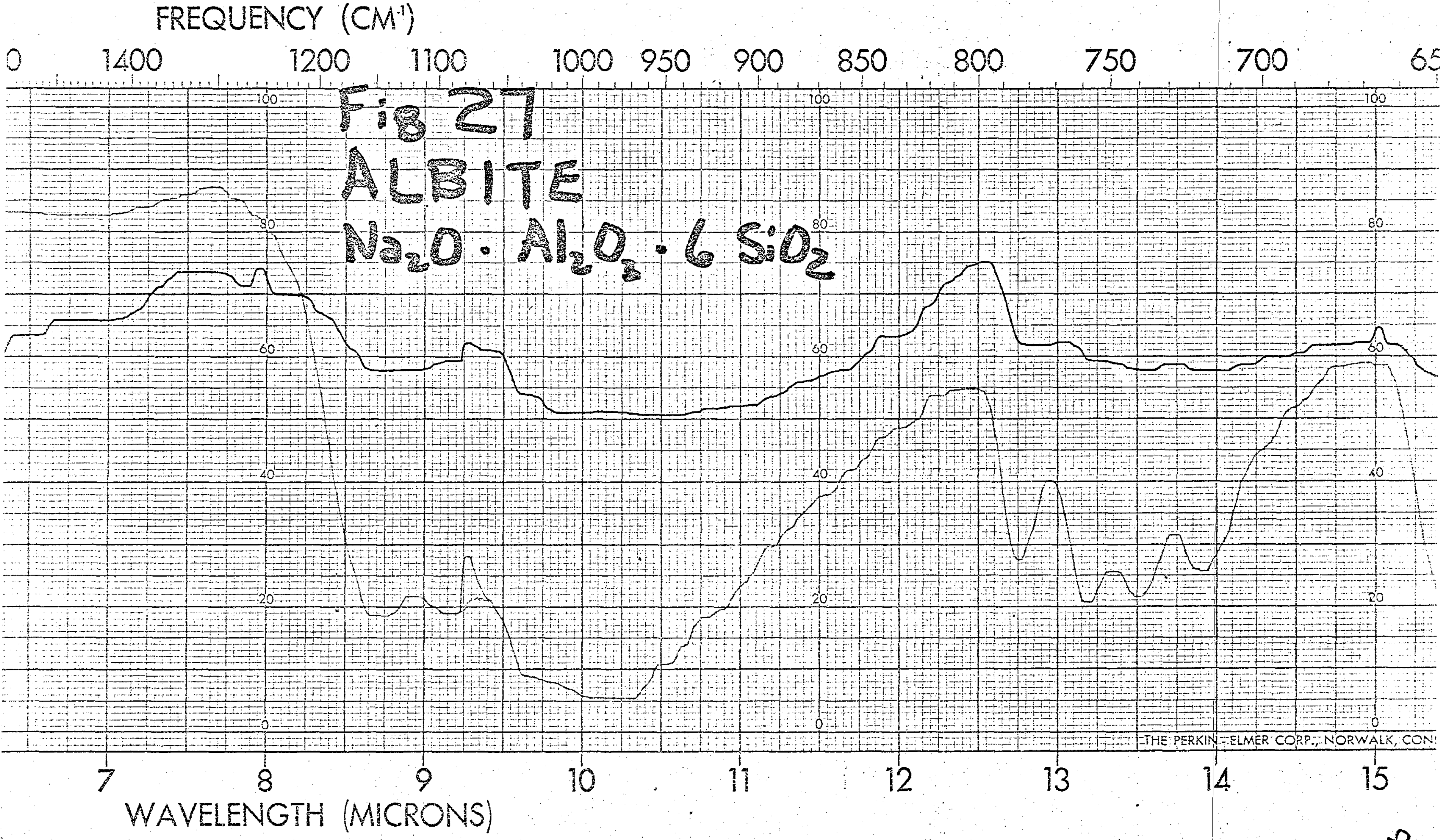


Fig 26
ACTINOLITE
$CaO \cdot 3(Mg,Fe)O \cdot 4SiO_2$

Fig 27

ALBITE

$Na_2O \cdot Al_2O_3 \cdot 6 SiO_2$



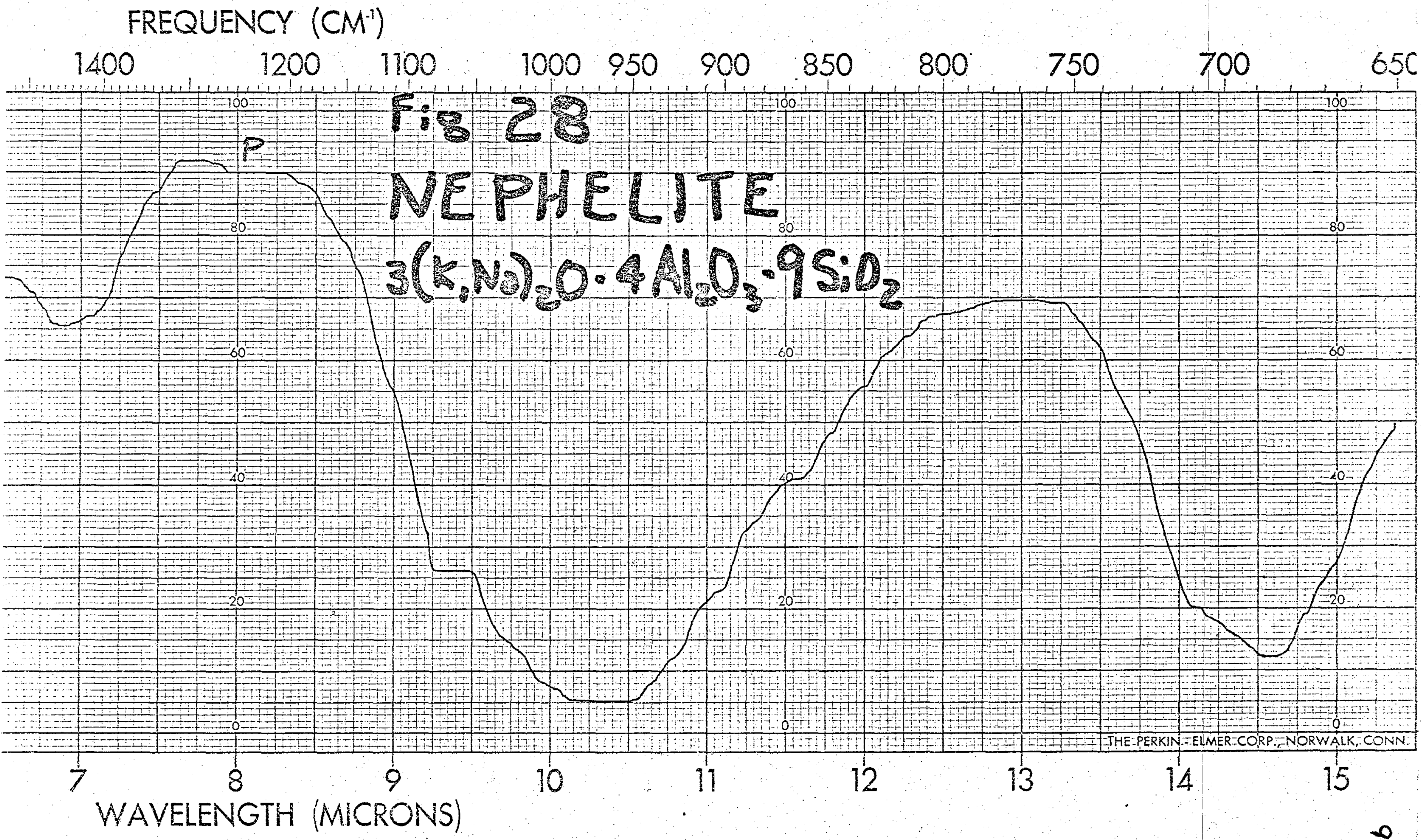


Fig 28

NEPHELITE

$3(K,Na)_2O \cdot 4Al_2O_3 \cdot 9SiO_2$

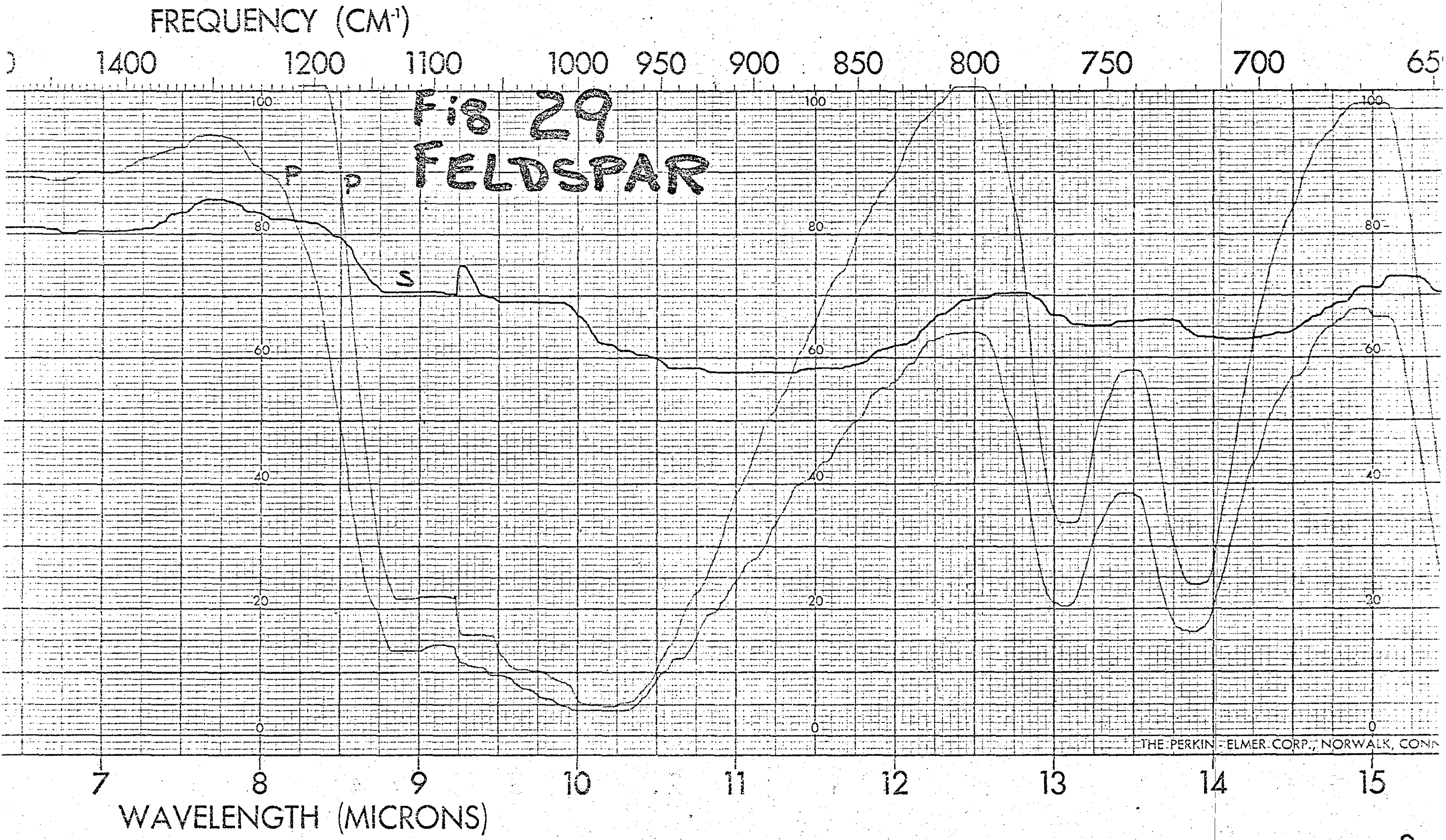


Fig 29 FELDSPAR

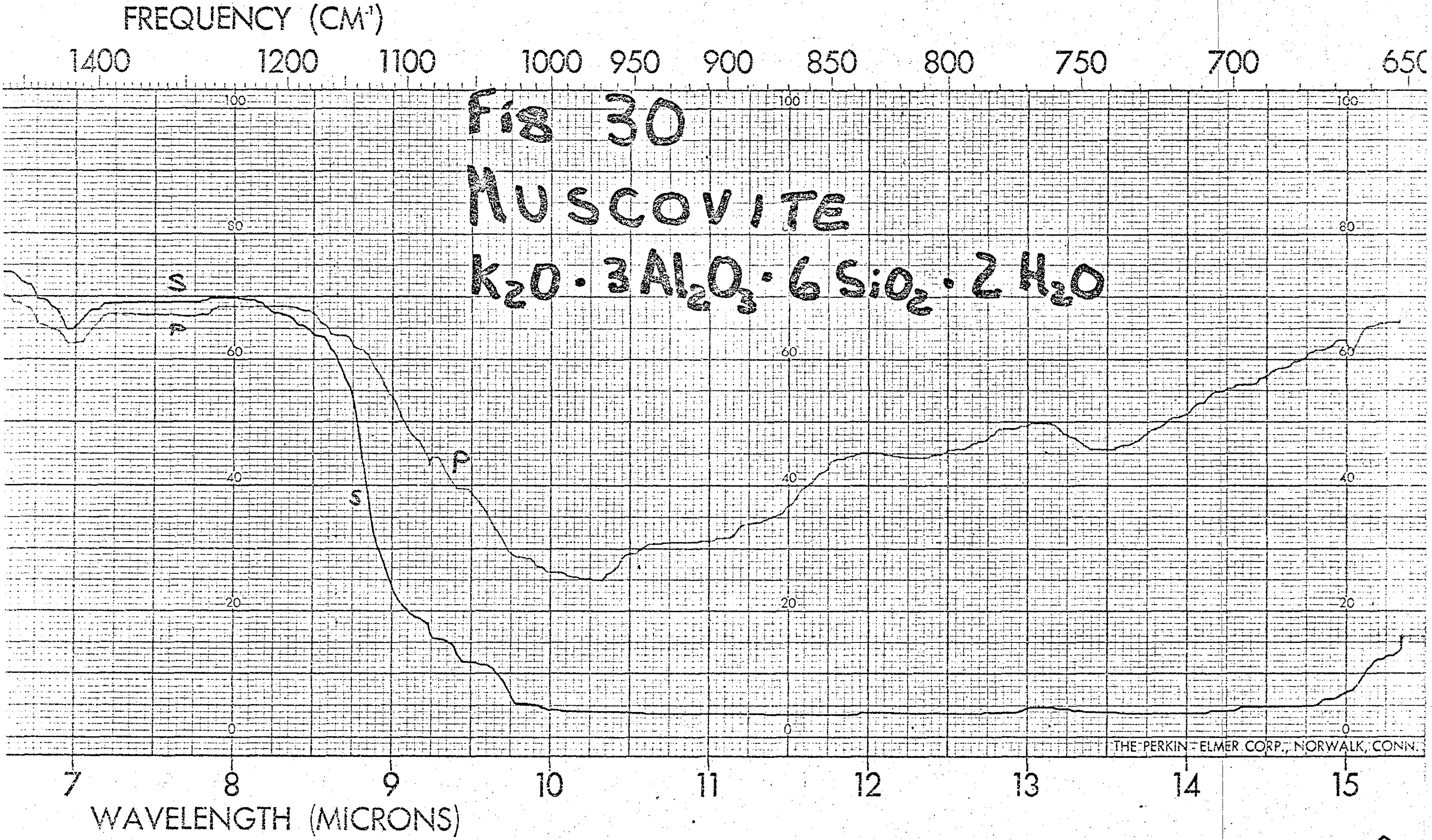


Fig 30
MUSCOVITE
$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$

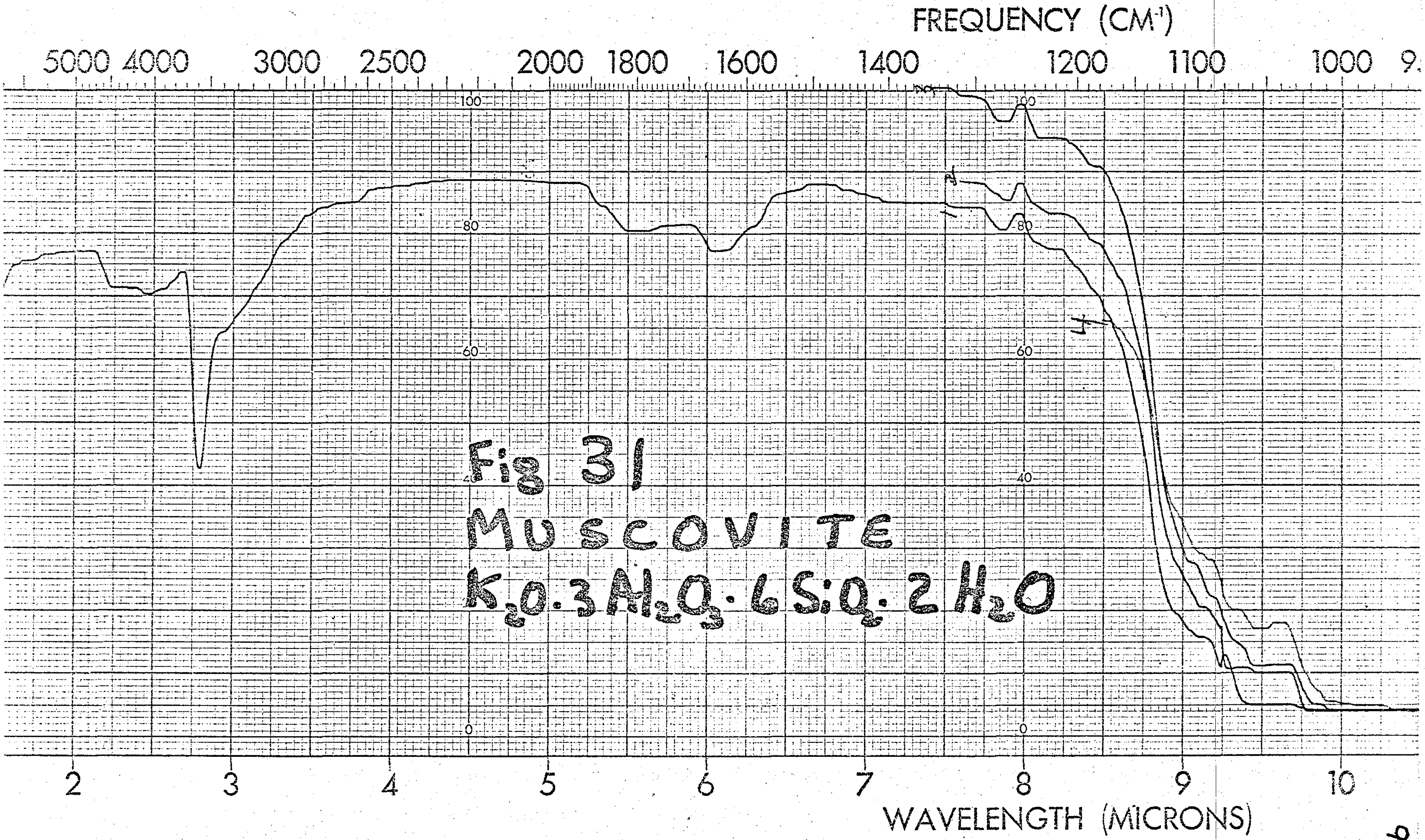


Fig 31

MUSCOVITE

$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$

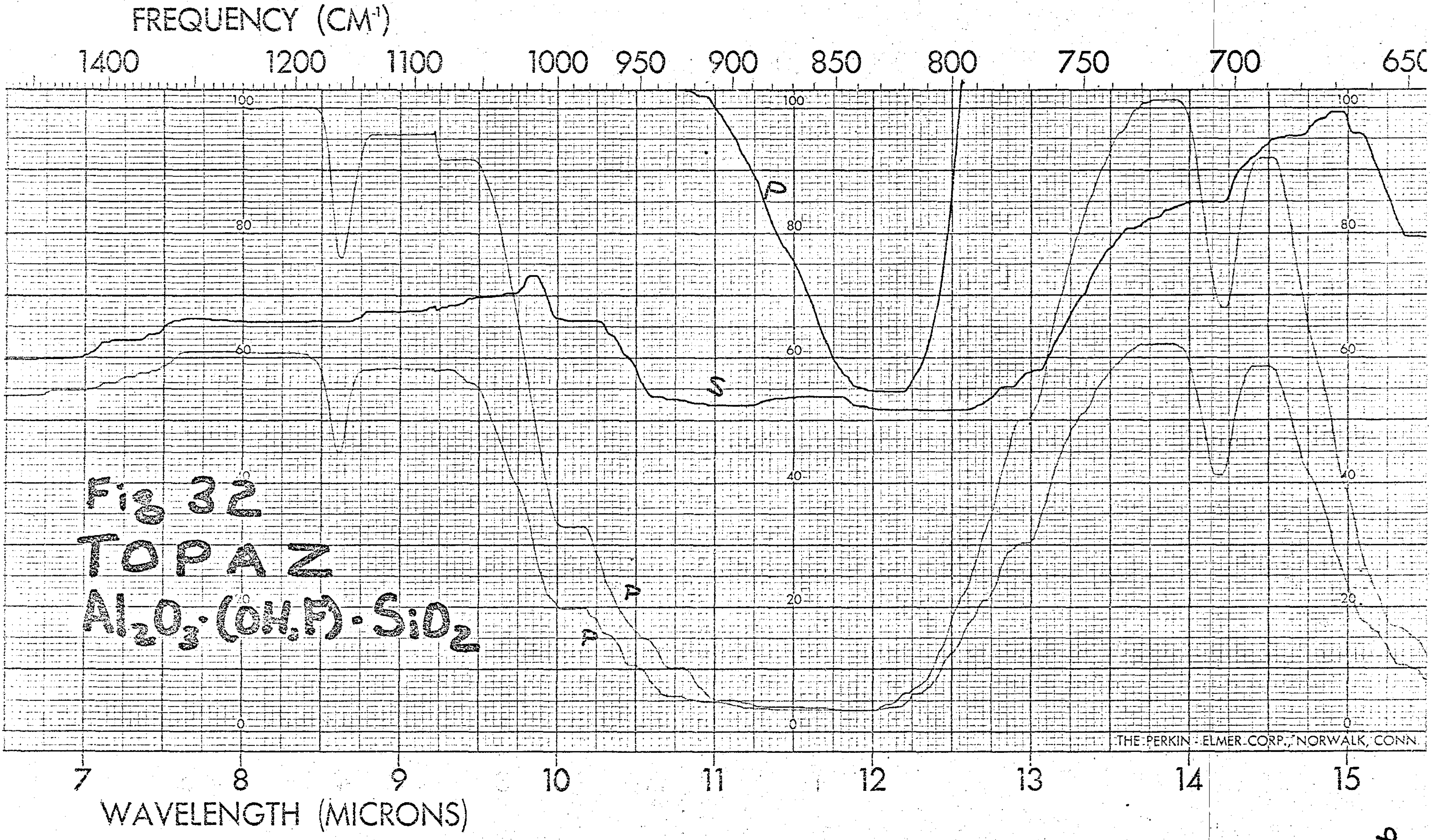


Fig 32
TOPAZ
$Al_2O_3 \cdot (OH,F) \cdot SiO_2$

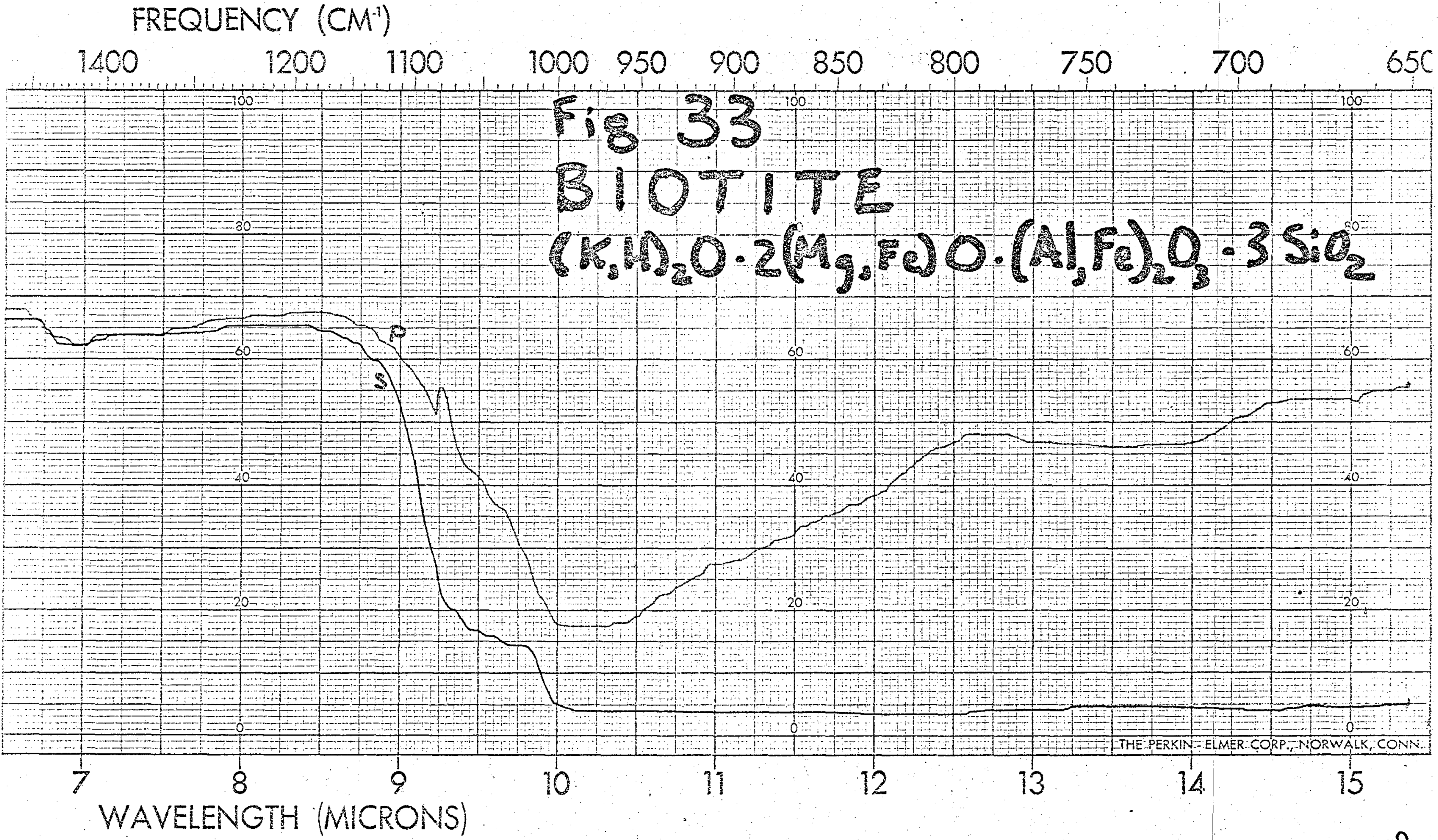


Fig 33

BIOTITE

$(K,H)_2O \cdot 2(Mg,Fe)O \cdot (Al,Fe)_2O_3 \cdot 3SiO_2$

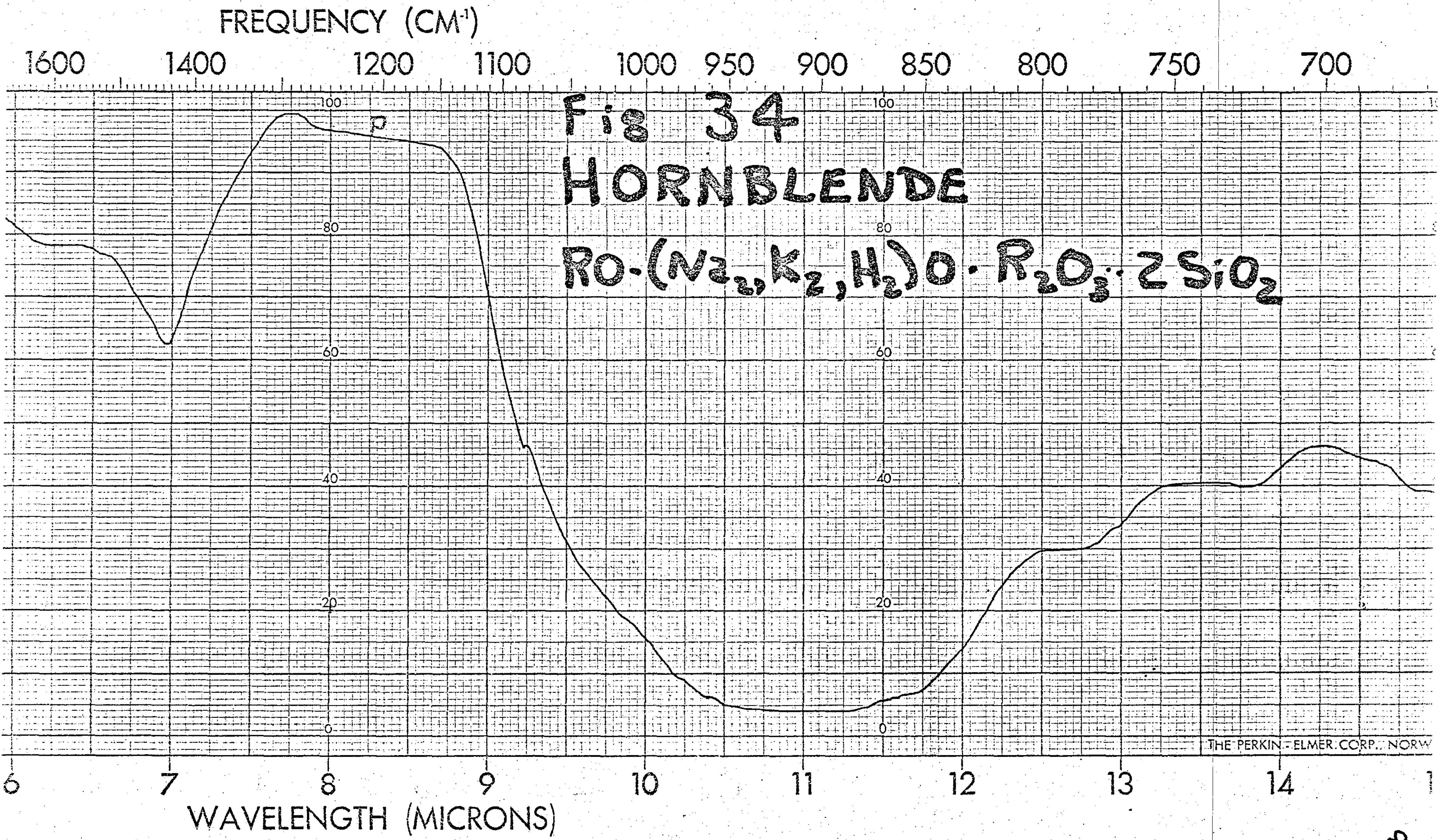


Fig 34
HORNBLENDE
$RO \cdot (Na_2, K_2, H_2)O \cdot R_2O_3 \cdot 2SiO_2$

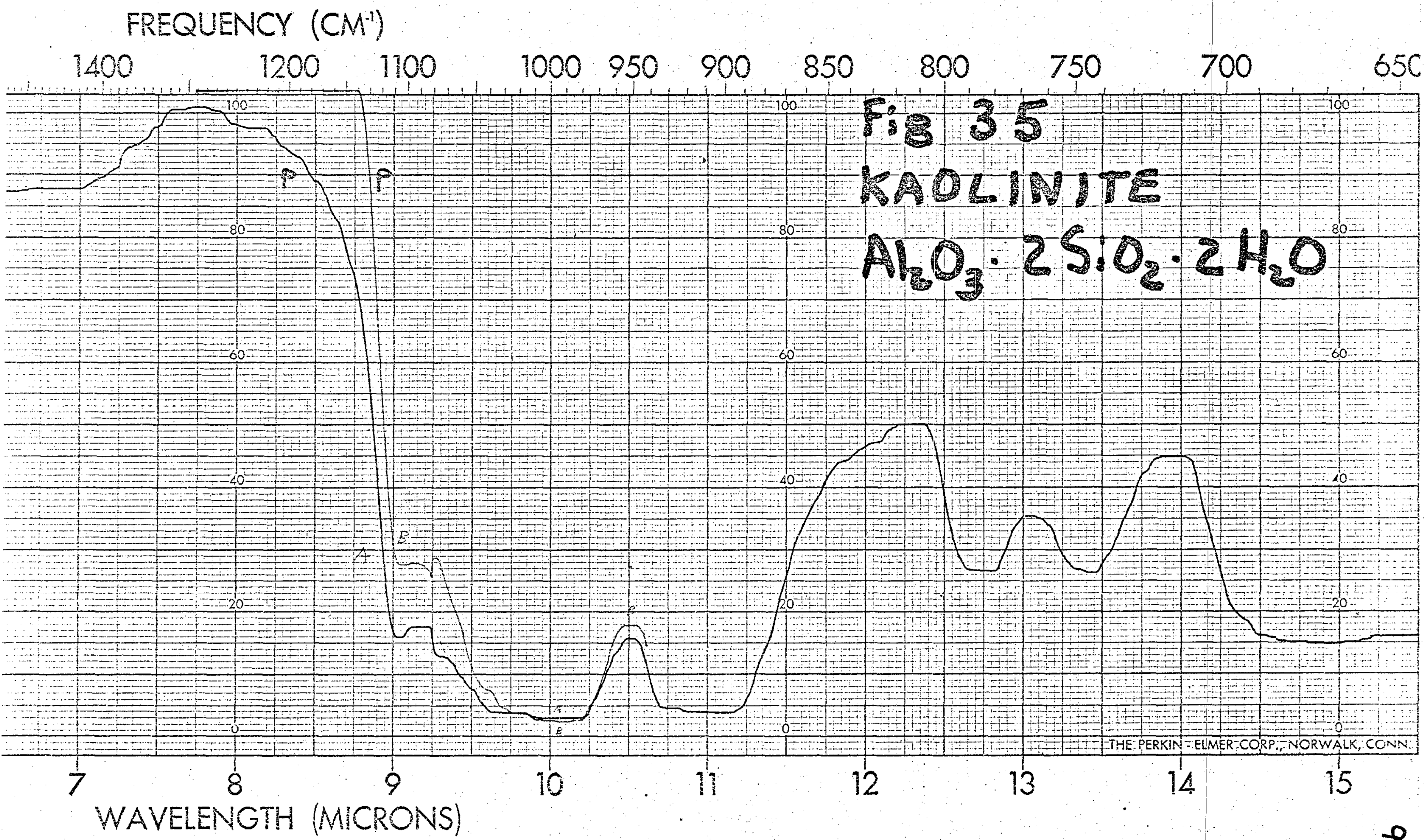


Fig 35

KAOLINITE

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$

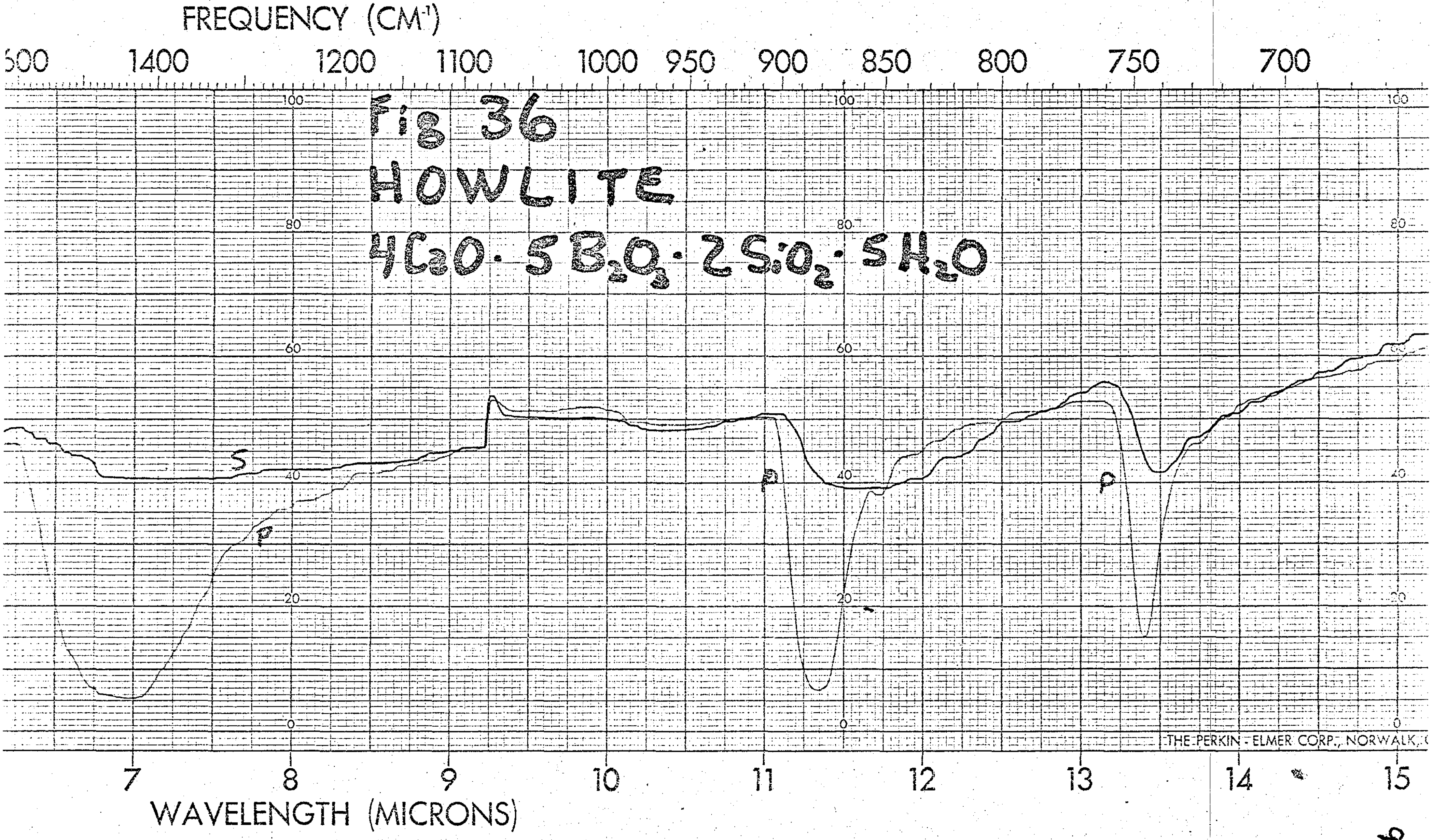


Fig 36
HOWLITE
$4CaO \cdot 5B_2O_3 \cdot 2SiO_2 \cdot 5H_2O$

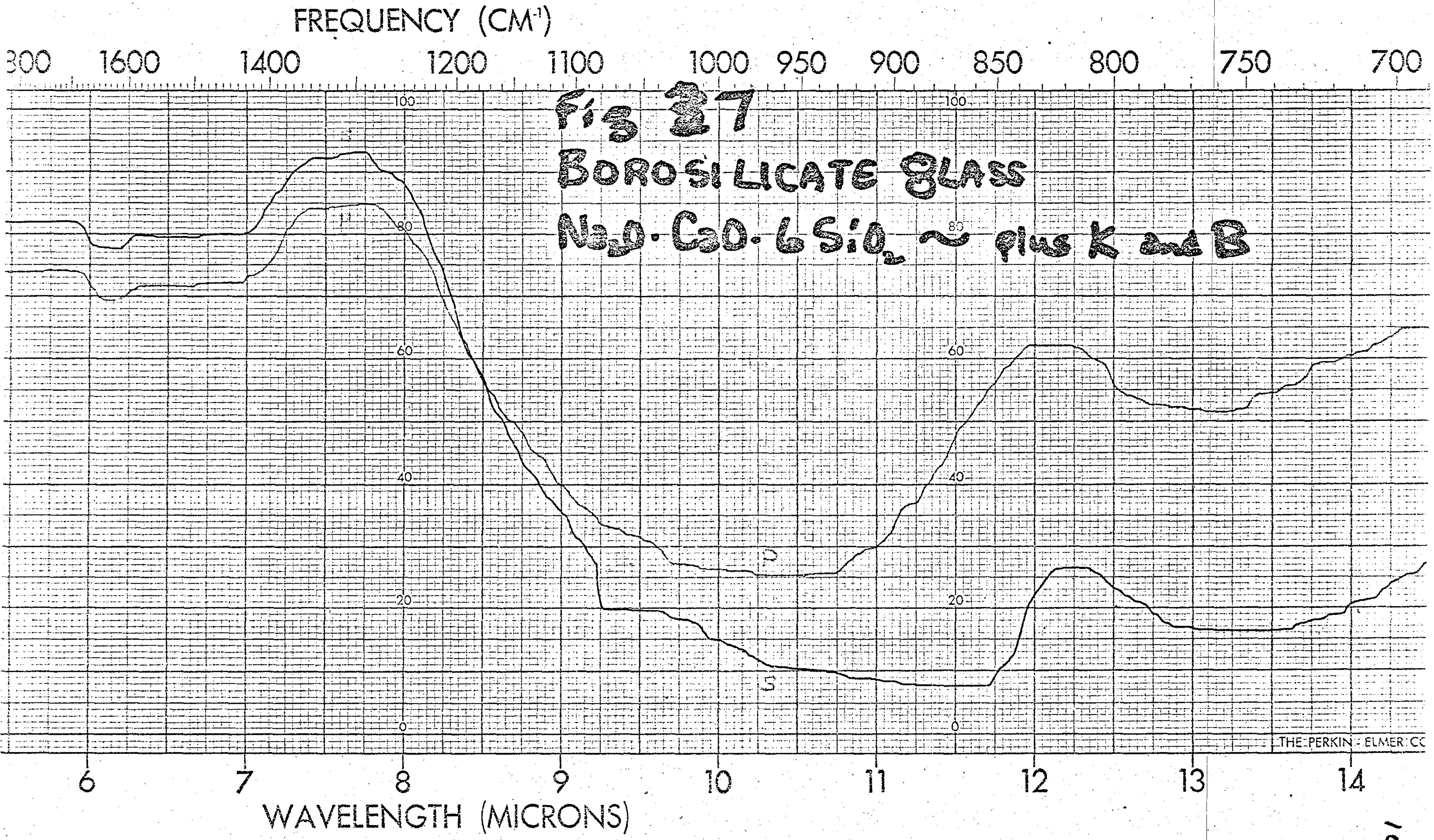


Fig 37

Borosilicate glass

$Na_2O \cdot CaO \cdot 6SiO_2$ ~ plus K and B

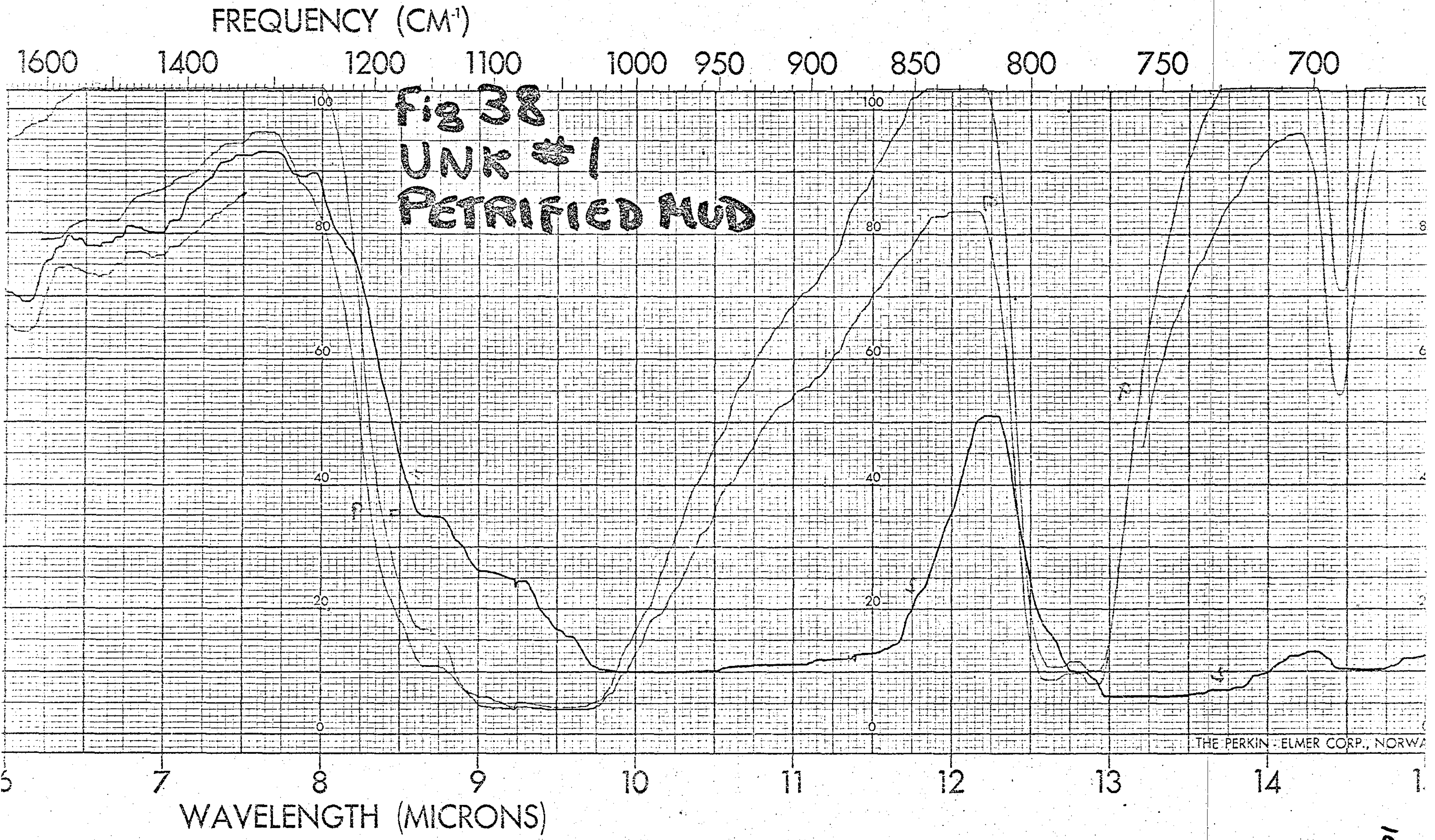


Fig 38
UNK #1
PETRIFIED MUD

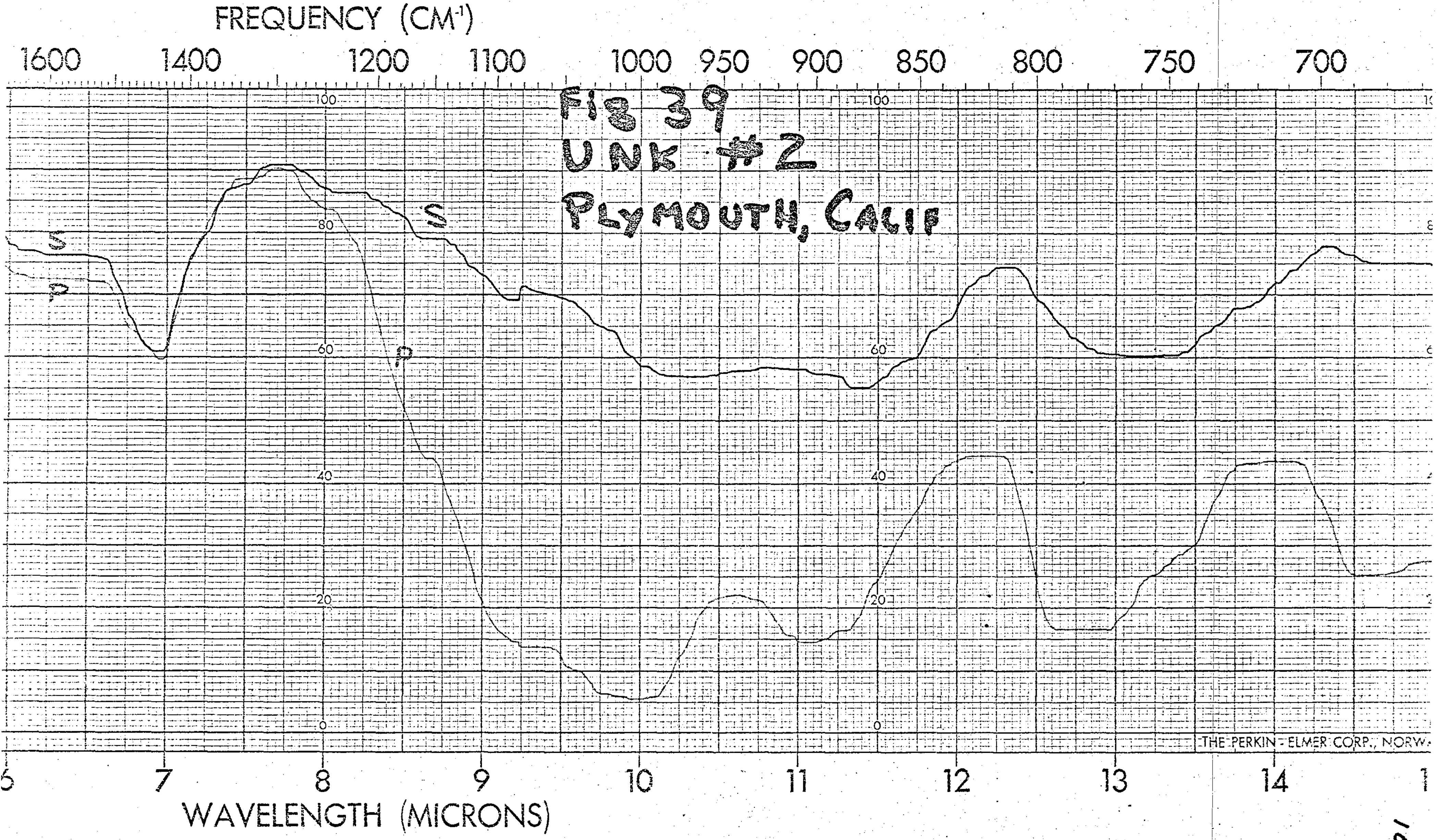
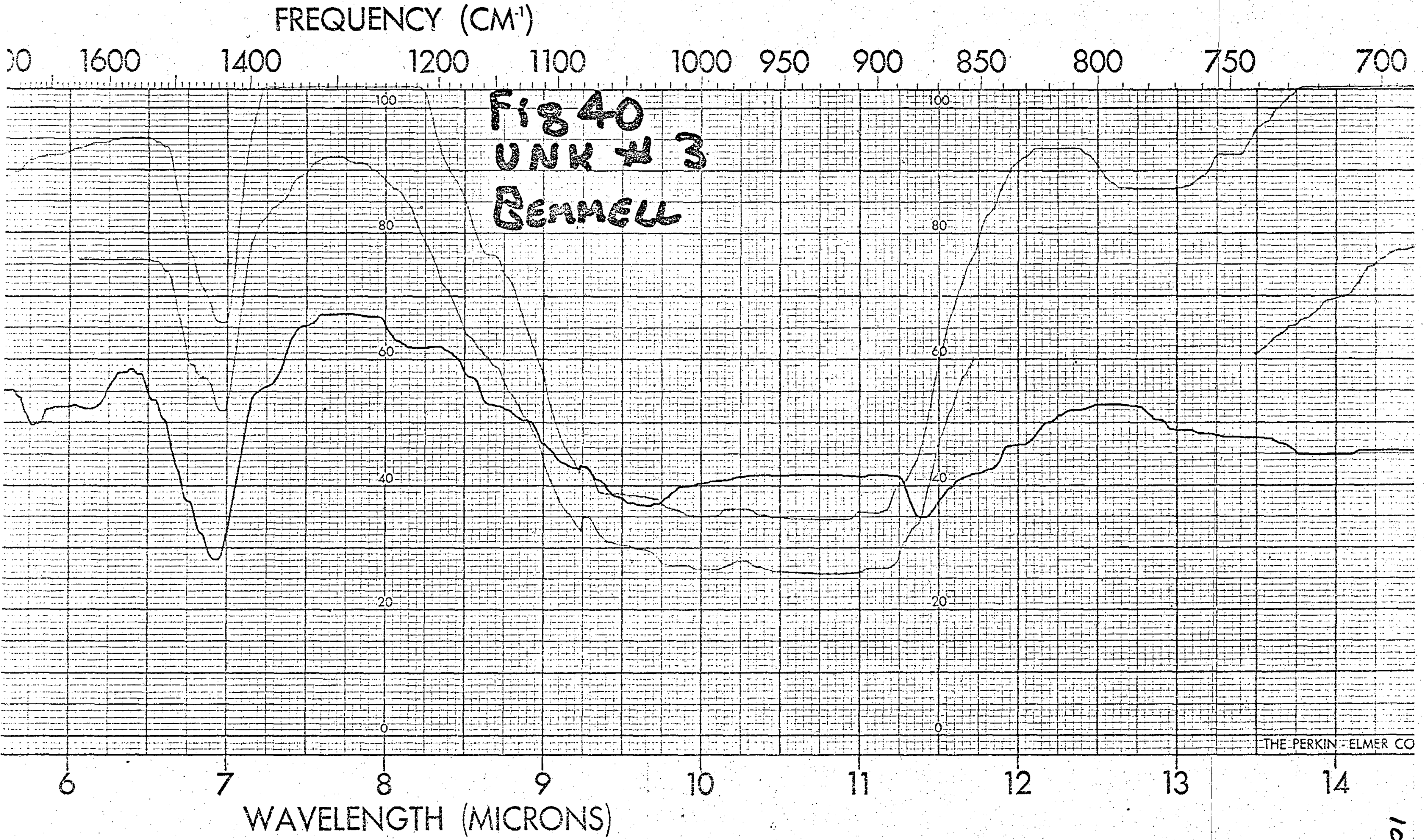


Fig 39
UNK #2
PLYMOUTH, CALIF

Fig 40
UNK #3
BENNELL



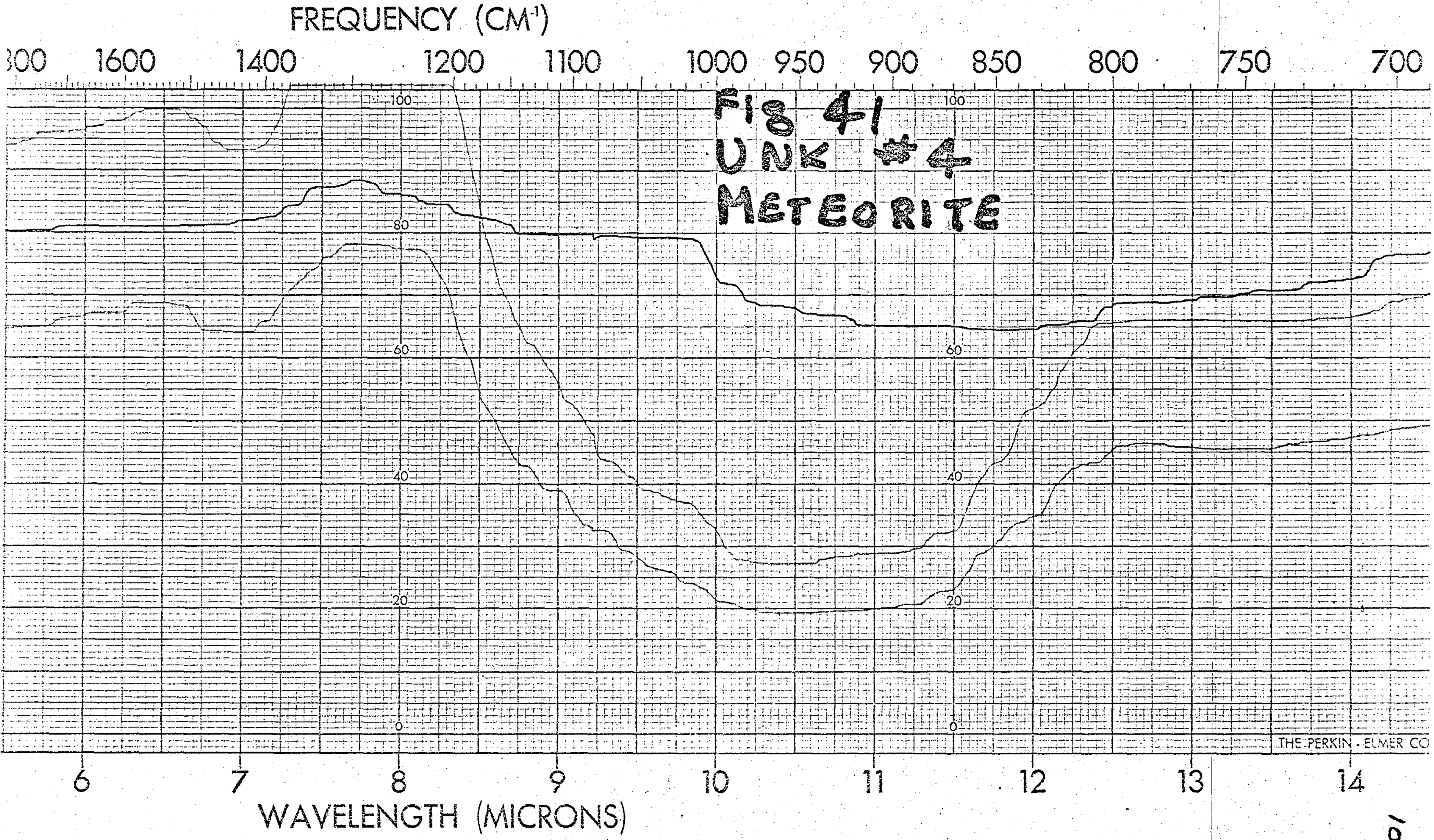


Fig 41
UNK #4
METEORITE

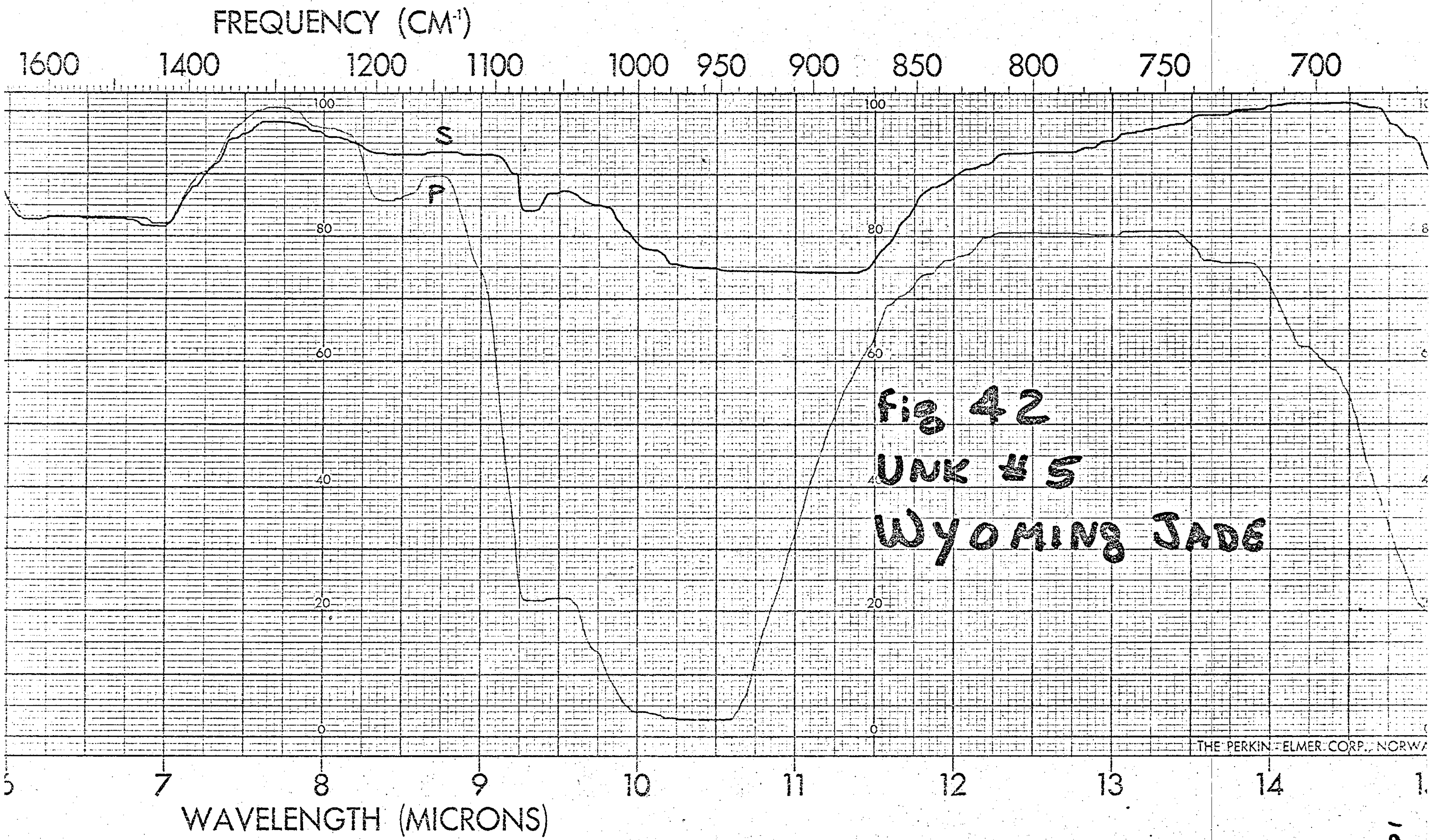


Fig 42
UNK #5
Wyoming Jade

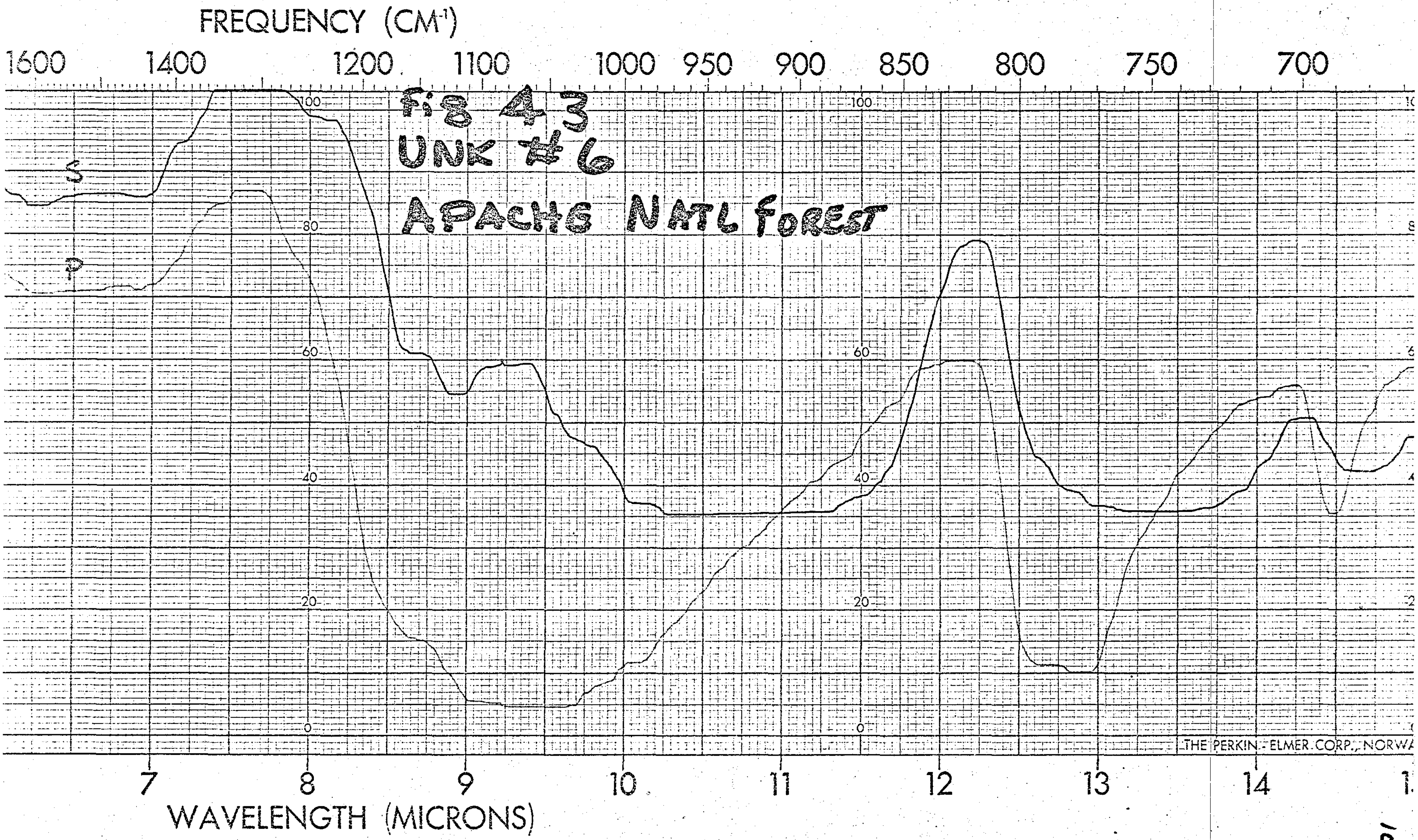


fig 43
UNK #6
APACHE NATL FOREST

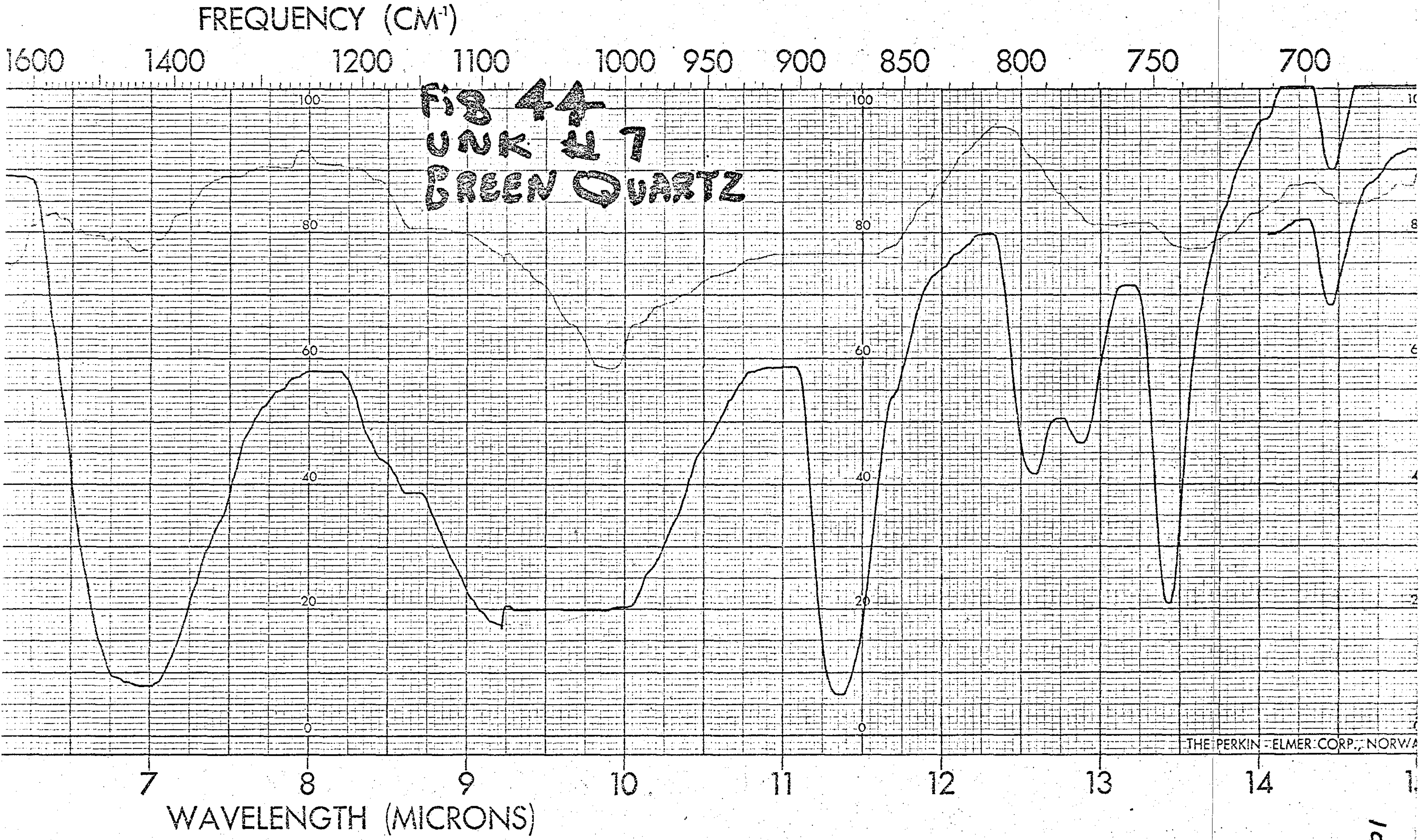


Fig 44
UNK 47
GREEN QUARTZ

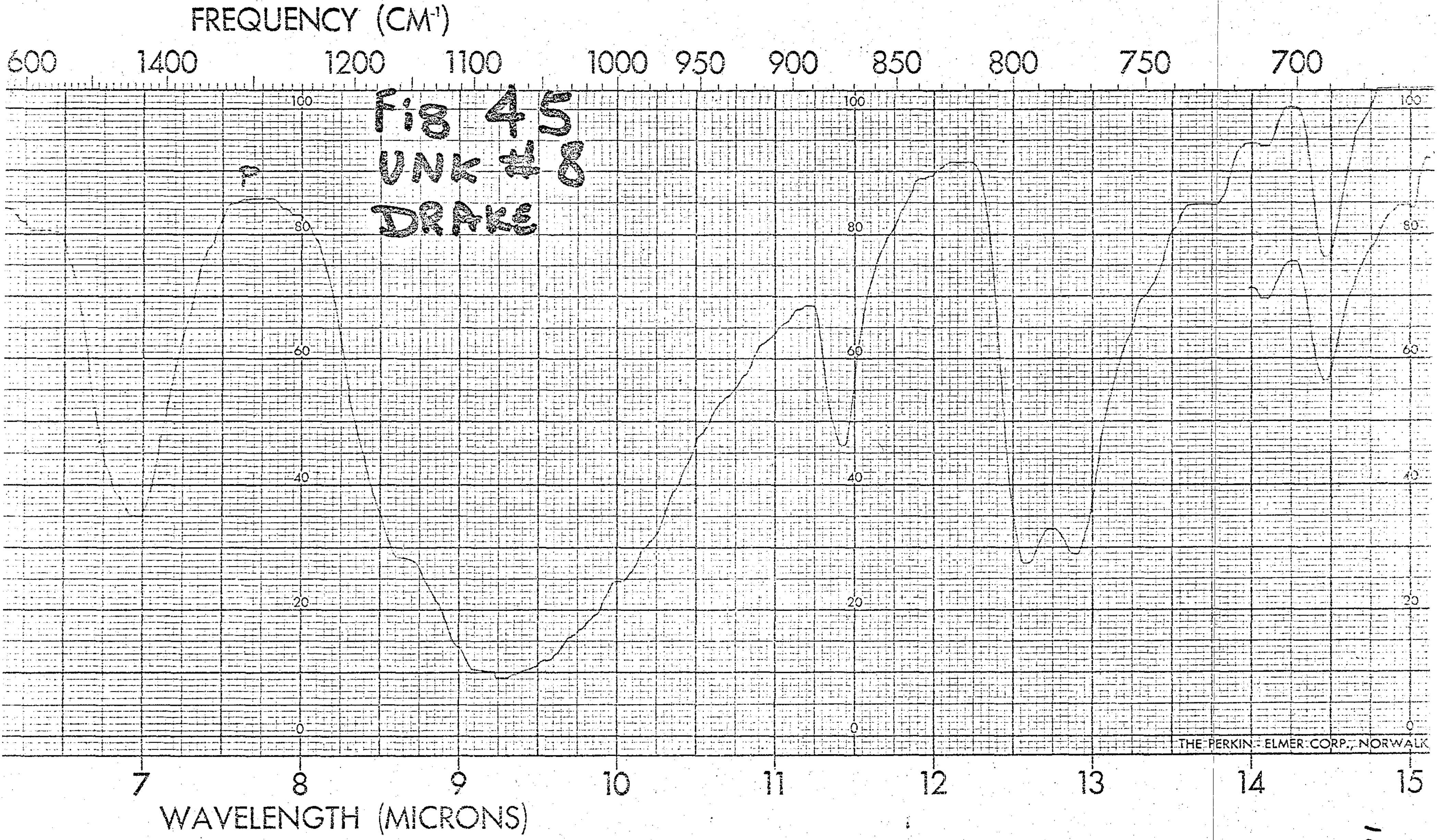


Fig 45
UNK #8
DRAKE