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THE DETERMINATION OF QUARTZ IN DUSTS BY INFRARED SPECTROSCOPY

by

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MINERAL SCIENCES DIVISION

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ABSTRACT

Alpha-quartz has been determined down to one tenth of a milligram when collected on a polyvinylidene chloride ("Saran") filter, by the absorption of its characteristic peak at a wavelength of 12.5 microns. It was estimated that the limit of detection under the conditions used, was one twentieth of a milligram. Possible interferences from feldspar, mica and pyrite have been examined. According to the spectra recorded in the literature, hornblende, kaolinite and montmorillonite might also interfere. By the use of a selective infrared detector and composite filters of polyvinylidene chloride and "Irtran 2" (zinc sulphide) it is suggested that a simple non-dispersion infrared analyser for the determination of alpha-quartz in dusts might be devised.

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INTRODUCTION

In February 1967 a number of air sampler filters were examined by infrared spectroscopy at the request of Mr. G. Knight, Mining Research Division, to determine whether any of the filter materials had adequate transparency at 12.5 microns, the wavelength of the characteristic peak of alpha-quartz. One filter, made of polyvinylidene chloride ("Saran") had the required transparency. Known weights of quartz were deposited on a number of these Saran filters, and the infrared spectra of these filters were recorded on a Beckman IR-12 spectrometer. A composite of the resulting spectra in the wavelength neighbourhood of 12.5 microns is shown in Figure 8 and a plot of the absorption of the 12.5 quartz peak versus weight of quartz on the filter is shown in Figure 9. The data from which the absorption-weight graph was constructed are listed in Table 1.

TABLE 1

Absorption of Alpha-Quartz (12.5 peak) vs Weight of Quartz on Filter

(FIGURE 1)

Sample No.	3	4	9	2	10	12	14	15	17
Wt. quartz (mg)	0.10	0.11	0.12	0.18	0.23	0.42	0.58	0.79	1.10
Peak (%T)	82.0	80.0	84.0	76.7	71.8	70.6	62.7	51.5	39.5
Bkgd-(%T)	90.3	87.7	90.4	86.0	84.0	94.0	84.2	82.7	79.9
Quartz absorption	0.042	0.040	0.032	0.50	0.068	0.124	0.128	0.206	0.306

The best straight line fitting the values in the table is:

Absorption = 0.25 (mg of quartz) + 0.00665 and the estimated limit of detection is 0.05 mg of quartz.

NON-DISPERSIVE INFRARED ANALYSIS FOR QUARTZ

The brief preliminary investigation described indicated that it was feasible to determine α-quartz on polyvinylidene filters down to an amount of 0.05 mg.

In March 1969, the question was put whether a relatively inexpensive simple analytical method for quartz determination by infrared were feasible and it was suggested that might be possible by non-dispersive infrared analysis.

Gas analysers based on this principle have been commercially available for 25 years. . In essence, they consist of an infrared source, a rotating "chopping disc", a sample and reference chamber, and a double-celled detector. The infrared radiation from the source is passed alternately through the sample and the reference chambers and into the "sample" detector cell or into the "reference" cell. The detector cells contain an equal and appropriate amount of the gas to be determined, and are divided by an airtight diaphragm. One side of the diaphragm is metallized and forms, with a fixed plate mounted close to it, a variable-capacity condenser which forms part of the electronic measuring circuit.

If the sample and reference chambers contain no gas or equal amounts of the same gas present in the detector cells, the amount of infrared radiation falling alternately on the cells is equal, the absorption of the radiation in the two cells and the resultant heating of the gas in the two detector cells are of the same amount, and there is neither difference of pressure on the two sides of the flexible diaphragm, nor movement of the diaphragm altering the capacity in the electronic circuit.

If, for example, the sample chamber contains more of the gas to be measured than the reference chamber, then more of the infrared radiation will be absorbed in the sample chamber, and less will be

absorbed by the gas in the corresponding detector cell. The gas pressure in the "sample" detector cell will be lower than that in the "reference" detector cell, and the diaphragm will move toward the "sample" detector.

Because the gas in the detector cell absorbs at only the wavelengths at which it emits radiation, it is a selective detector for these specific wavelengths. Even if other gases absorb at some of these wavelengths provided that their amount remains fixed, their absorption can be compensated for by introducing the same concentration into the reference chamber.

Since no radiation is wasted by grating dispersion or prism absorption, and because of the very simple optics a minimum is lost by absorption in lenses or windows, these non-dispersive infrared gas analysers are relatively sensitive. The sensitivity is also improved by the fact that they absorb at all the wavelengths at which the gas absorbs, and not at one selected wavelength as is the case in dispersive analysis. These robust, simple and sensitive gas analysers have over years of use proved the validity and reliability of the method.

Although the quartz is not a gas, it was considered that non-dispersive infrared analysis might be feasible if there were available a detector selective only for the wavelengths for which quartz absorbs. Ideally, the best detector would be alpha-quartz itself.

This goal is possible if use is made of the temperature coefficient of the piezo-electric effect. When a sheet made from a quartz crystal forms the dielectric in a capacitor, and such a capacitor forms part of a tube or transistor oscillator circuit, the quartz sheet will constrain the oscillation frequency of the circuit within a very narrow range which is characteristic of the way the sheet was cut from the crystal, and on the dimensions and shape of the sheet.

For this very accurate oscillator frequency control, the "cut" of the sheet is made so that the temperature coefficient of the characteristic frequency is a minimum or zero over as wide a temperature range as possible.

It is possible, however, to cut the sheet from the quartz crystal so that the temperature coefficient of the frequency is a maximum and use has been made of this type of "cut" in a commercial "Linear Quartz Thermometer", developed and marketed by Hewlett-Packard, that is sensitive to a temperature change of 1/10,000°C between -40°C and +230°C[1].

Because the infrared radiation at 12.5μ is heat radiation, it is proposed to modify this commercial "electronic" thermometer to serve as detector for the radiation. This would be done by removing the central portions of the deposited gold electrode from both sides of the circular, quarter-inch-diameter quartz wafer, and focussing the heat radiation on this clear spot on the sensor.

The clear quartz sensor will preferentially absorb heat radiation of the wavelength of its own absorption, and will thus act as a specific detector of such radiation.

If such a quartz detector is irradiated with infrared radiation, say, from a platinum filament heated to 1300°C in air, it will absorb at the wavelengths specific to quartz and will rapidly reach heat equilibrium with its surroundings. The frequency of the associated oscillator will show a change linearly proportional to the temperature change of the crystal.

If, now, a quartz sheet is inserted between the infrared source and the detector, it will absorb some of the specific "quartz" radiation and less will fall on the detector. The resulting change in temperature of the detector, and in the oscillator frequency will be proportioned to the thickness (amount) of the quartz sheet inserted in the beam.

With such a device, we have in principle a non-dispersive infrared analyser specific for alpha-quartz, but, first, we have to study two aspects of its practical feasibility:-

(i) to determine which of the absorption peaks of alpha-quartz is most free from interference from absorption peaks of related minerals, such as silicates, and of minerals associated with quartz in rocks.

(ii) to calculate the expected sensitivity and
limit of detection of such a device,

MINERAL INTERFERENCES

The minerals which would be expected to interfere are:-

Olivines,

Pyroxenes,

Amphiboles,

Micas,

Feldspars,

Clays.

The infrared absorption spectrum of alpha-quartz has been studied and interpreted by B. D. Saksena 1940[3] and E. R. Lippincott, 1958[4], and our record from 200 - 1200 cm^{-1} appears as Figure 2.

The peaks shown have the frequencies and assignments shown in Table 2.

TABLE 2

Assignments, Wavelengths and Frequencies of Alpha-Quartz Spectrum

Assignments	Wavelengths (μ)	Frequencies (cm^{-1})
Distortion	37.7	265
Si-O Bend	25.2	397
Si-O Bend	21.3	470
Si-O Bend	19.5	513
Si-Si Stretch	14.3	698
Si-Si Stretch	12.8	780
Si-Si Stretch	12.5	800
Si-O Stretch	9.1	1097

The most suitable absorption peak and that used in preliminary experiments, is the Si-Si stretch at 12.5μ (800 cm^{-1}). Table 3 lists the wavelengths of the absorption peaks nearest this wavelength and most likely to interfere, belonging to the previously mentioned minerals.

As is evident, of the potentially interfering minerals previously listed, only the micas, feldspars and clays need be considered.

It was, however, considered advisable to confirm these literature indications, by experiment, and we therefore obtained samples of a typical Elliot Lake ore ("Nordic"), a mica, a feldspar and a pyrite. The spectra of these four materials are shown in Figures 3 to 6. *7, 3, 4 & 5 respectively* All these materials, including the alpha-quartz (Fig. 2) were recorded in transmission, at a concentration of 0.5 per cent in a caesium bromide pellet. Because all the spectra have been recorded with the same amount of each mineral, they share the maximum (and unachievable) interference of one mineral with another.

Although the "Nordic" ore is known from mineralogical examination to contain mica, feldspar and pyrite, it is clear from comparison of its spectrum with those of the individual minerals, that its main constituent is quartz. A study of Figure 8 which shows the position of the peaks of all the constituent minerals makes this even clearer.

Further examination of this composite record, indicates that of all the alpha-quartz peaks, the chosen one at 12.5μ, is the most free from interference -- only minor peaks of 100 per cent mica and feldspar and a weak broad absorption from 100 per cent pyrite being involved.

Because of the large amount of interference on the quartz peaks other than that at 12.5μ, it is essential to prevent them having any effect on the quartz detector, and this has to be achieved by selective filters, which will pass only a narrow wavelength range on either side of 12.5μ.

In the preliminary work, it was found that the air-filter made of polyvinylidene chloride ("Saran") had a transmission "window" in the desired range, *(see Fig. 6)* and is therefore a suitable choice as a component of the selective filter. By combining four layers of "Saran" sheet (as used in the household), an optical filter was available which had negligible transmission

TABLE 3

Infrared Absorption of Quartz and of Related Minerals

Mineral	Wavelength in microns						
	8	9	10	11	12	13	14
α-Quartz	8.6	9.2	10.95		12.5, 12.8		14.4
Amphiboles		9.0-9.8	10.1-10.8		12.8[1]	13.1	14.6-15
Feldspars	8.7-8.8	9.1-9.9	10.0-10.9		12.2, 12.7[2] 13.0	13.1-13.8	14.6
Micas		9.4-9.7	10.0, 10.3	11.0	12.1, 12.5[3], 12.8	13.4	14.8
Olivine			10.0, 10.5	11.2, 11.9		13.1	
Pyroxene		9.4-9.8	10.4, 10.9	11.5			
Clays	8.9-9.0	9.6-9.9	10.7	11.0	12.1, 12.5, 12.6, 12.8	13.3	14.5

(1) Hornblende only; (2) albite and oligoclase; (3) muscovite only

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over a large amount of the range wanted, and a window of 70% transmission at 12.5μ. Some radiation is passed beyond 13.5μ, and an additional filter of "Irtran-2" (zinc sulphide) which is transparent up to 14μ, but absorbs strongly at longer wavelengths, is therefore suggested.

The resulting composite filter need have little thickness and would conveniently consist of a sheet of "Irtran-2" covered on one side with one sheet of "Saran", and on the other with two sheets of "Saran" -- the air-filter used for collecting the dust sample provides the fourth "Saran" sheet.

Examination of the composite spectrum of Figure 8, shows that the "Saran" filter will remove interference from the Si-O stretch absorption peaks of mica and feldspar at 1000-1100 cm^{-1} (9.1 - 10μ), and with the addition of the "Irtran-2" filter will remove interference from 780-200 cm^{-1} (12.8 - 50μ).

There remain three peaks, which might interfere, a minor mica peak at 829 cm^{-1} (12 μ), a minor feldspar peak at 777 cm^{-1} (12.8μ), and a broad pyrite peak at 800 cm^{-1} (12.5μ). The "pyrite" peak is undoubtedly due to quartz in the pyrite, as records of other pyrites known to be free from quartz impurity, do not display this absorption peak. Interference from the minerals associated with the "Nordic" ore is thus limited to mica and feldspar. It is to be noted however, that the peaks compared, derived from 100 per cent of each mineral, and the amounts normally present in this ore are much less, being of the order of 5-20 per cent. The resulting interference would in consequence be much less, and in proof of this view, in the spectrum of "Nordic" ore, the 12μ mica peak appears as a hardly observable inflection on the short-wavelength side of the 12.5μ quartz peak, and the effect of the feldspar peak is not observed.

OPTICAL DESIGN OF "SILICA-METER"

The instrument can be designed either as a single-beam or as a double-beam analyser. In the first case, the power supply for the infrared source must have very good short-term and long-term stability and constancy, whereas in the second, these requirements do not arise and a much simpler and cheaper power supply can be used.

The double-beam arrangement is preferred, in spite of the small additional complexity, not only for the reason presented in the preceding paragraph, but because it enables the absorption of the "Saran" and "Irtran-2" filters to be balanced out. The frequency difference between the sample and the reference beams would then be a measure of the absorption due to alpha-quartz (silica) in the sample.

Assuming the platinum strip (10 mm long, 1 mm wide) infrared source is a perfect blackbody, it can be calculated that at a temperature of 1200°C, it will emit 3.355×10^6 ergs/cm^2/sec. If a concave mirror of 5-cm dia at 6-cm distance is used to focus this radiation on the detector, the latter will receive 1.455×10^5 ergs/sec. For 1°C rise in temperature, the detector must absorb 1.326×10^6 ergs, and therefore the detector will require 9.1 sec to rise 1°C. Such a theoretical response time is adequate, and indeed a 10-sec response time is quoted by Hewlett-Packard for their "Linear Quartz Thermometer".

PRACTICAL TESTING

It is proposed to construct a simple prototype in order to find out the limit of detection and the precision of analysis for apha-quartz in mine-dust.

This will consist of a 10 x 1-mm platinum strip run at 1200°C in air. The infrared radiation from it will be focussed by

two front-surface aluminized concave mirrors on to the two sensors of the "Linear Quartz Thermometer", modified as previously described. In front of each sensor there will be a composite filter of "Saran" and "Irtran-2", and a sample holder to take, in the one case, the sample air-filter and, in the other case, a blank air-filter.

REFERENCES

(1) "Linear Quartz Thermometer", Donald L. Hammond and Albert Benjaminson, "Instrument and Control Systems" 38, 115, (1965).

(2) "Infrared Absorption Spectra of Minerals and other Inorganic Compounds", John M. Hunt, Mary P. Wisherd and Lawrence C. Bonham, Anal. Chem. 12, 1478, (1950).

(3) "Analysis of the Raman and Infrared Spectra of -quartz", B. D. Saksena, Proc. Ind. Acad. Sci., 12A, 93, (1940).

(4) "Infrared Studies in Polymorphs of Silicon Dioxide and Germanium Dioxide", E. R. Lippincott, A. van Valkenburg, C.S. Weir and E.S. Bunting, J. Res. N.B.S. 61, (1958).

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CAPTIONS FOR FIGURES:
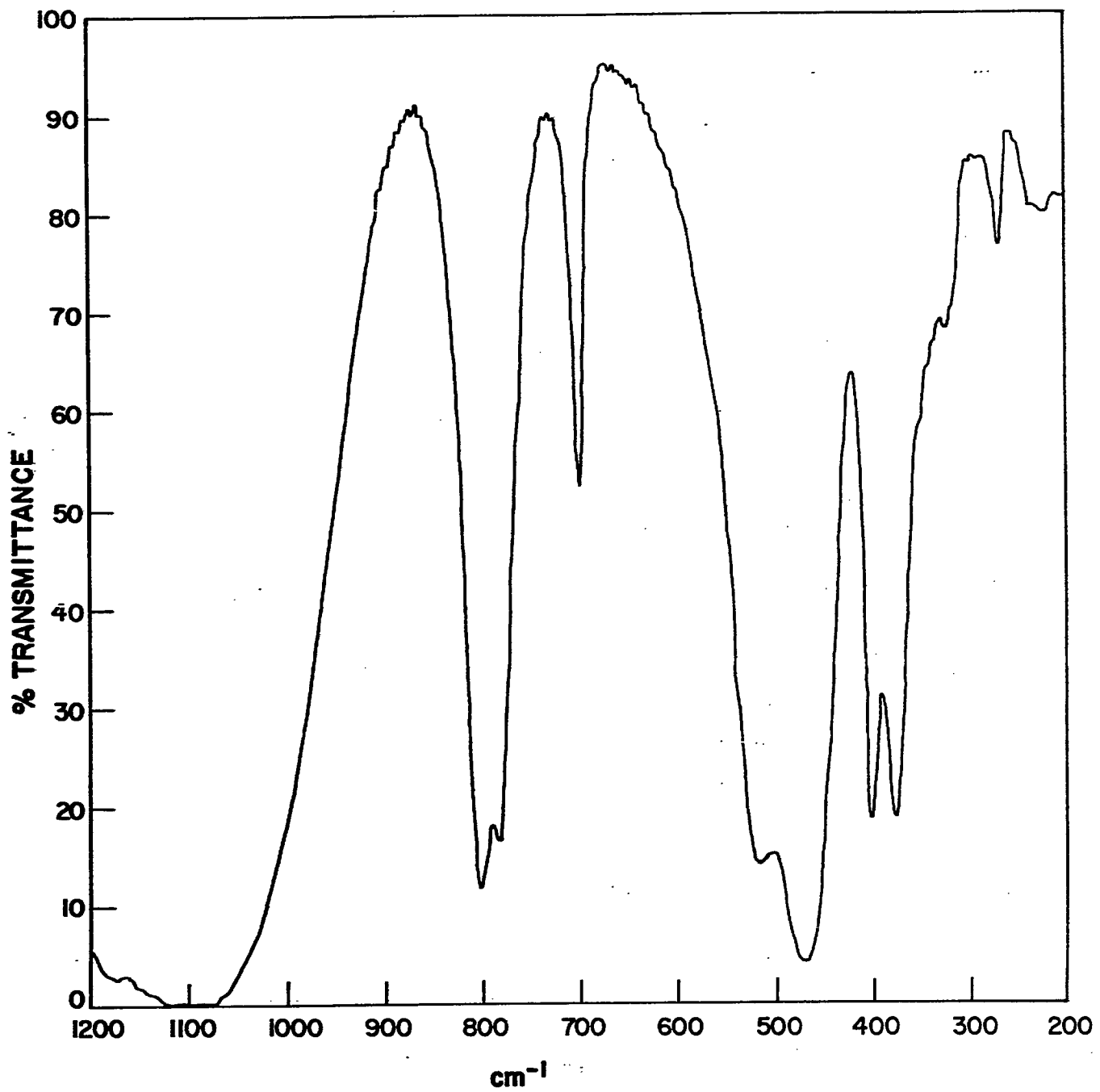
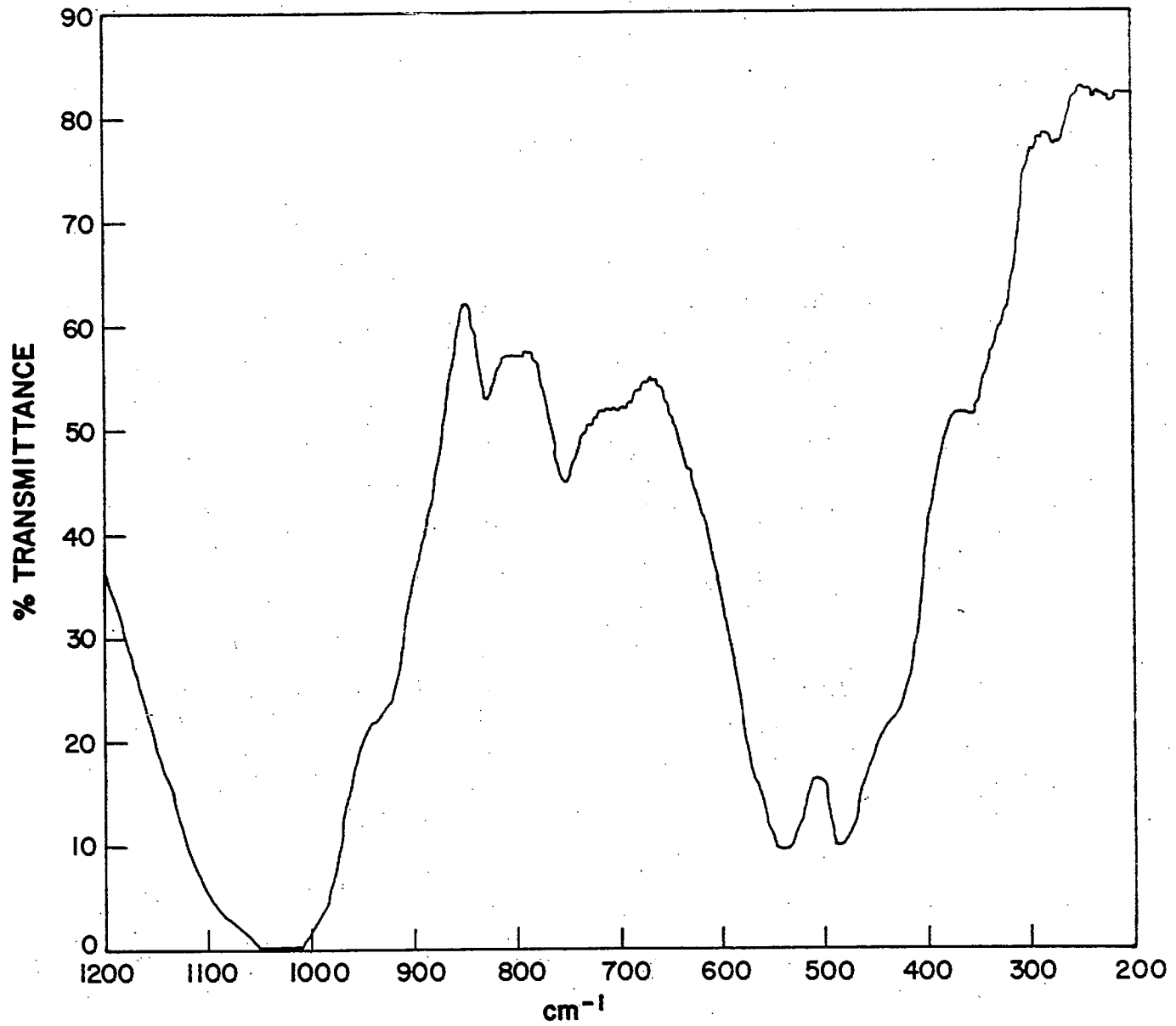Figure 1 - Absorption of Alpha-Quartz at 12.5μ (800 cm^{-1}).
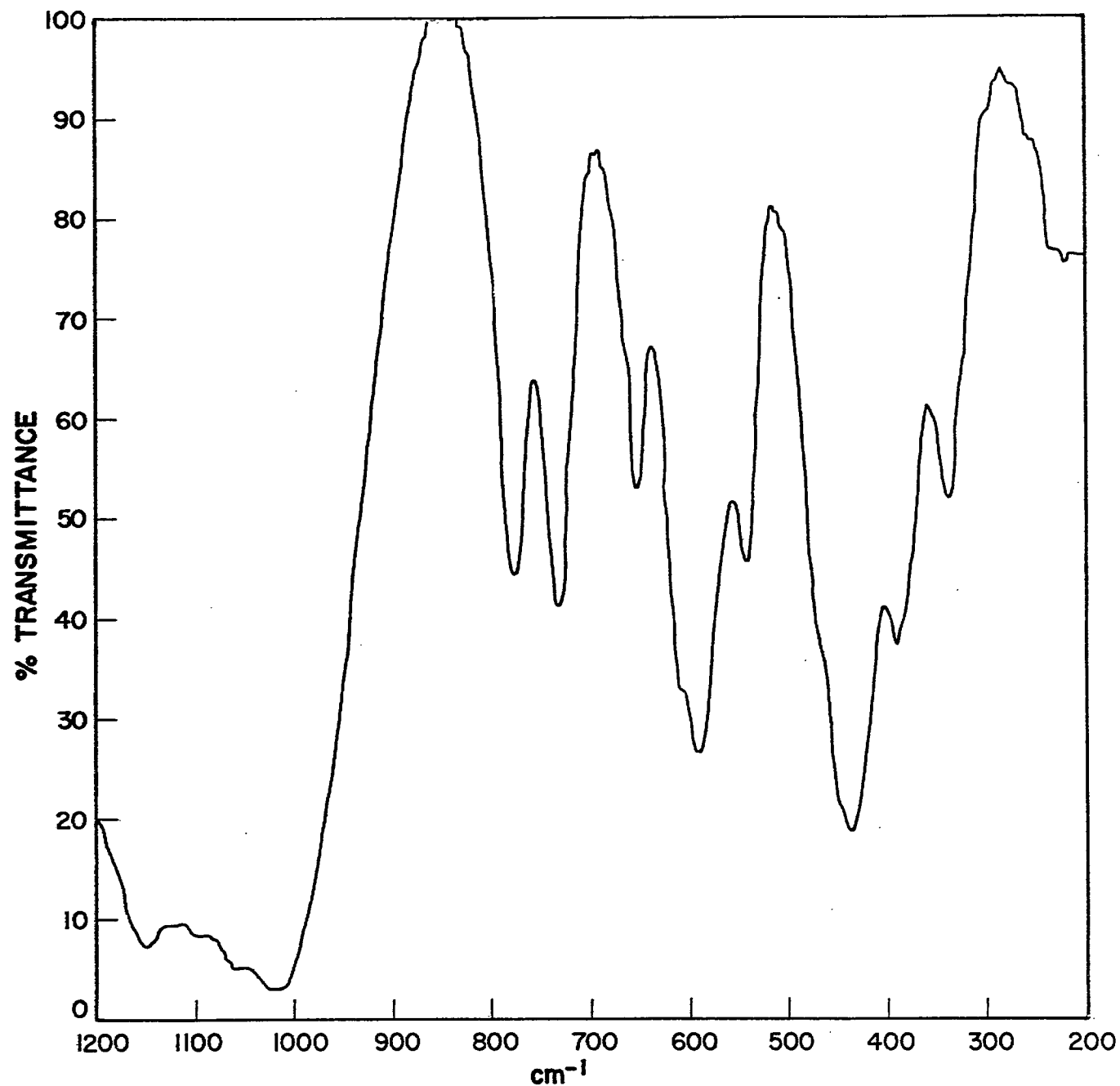
Figure 2 - Alpha-Quartz.
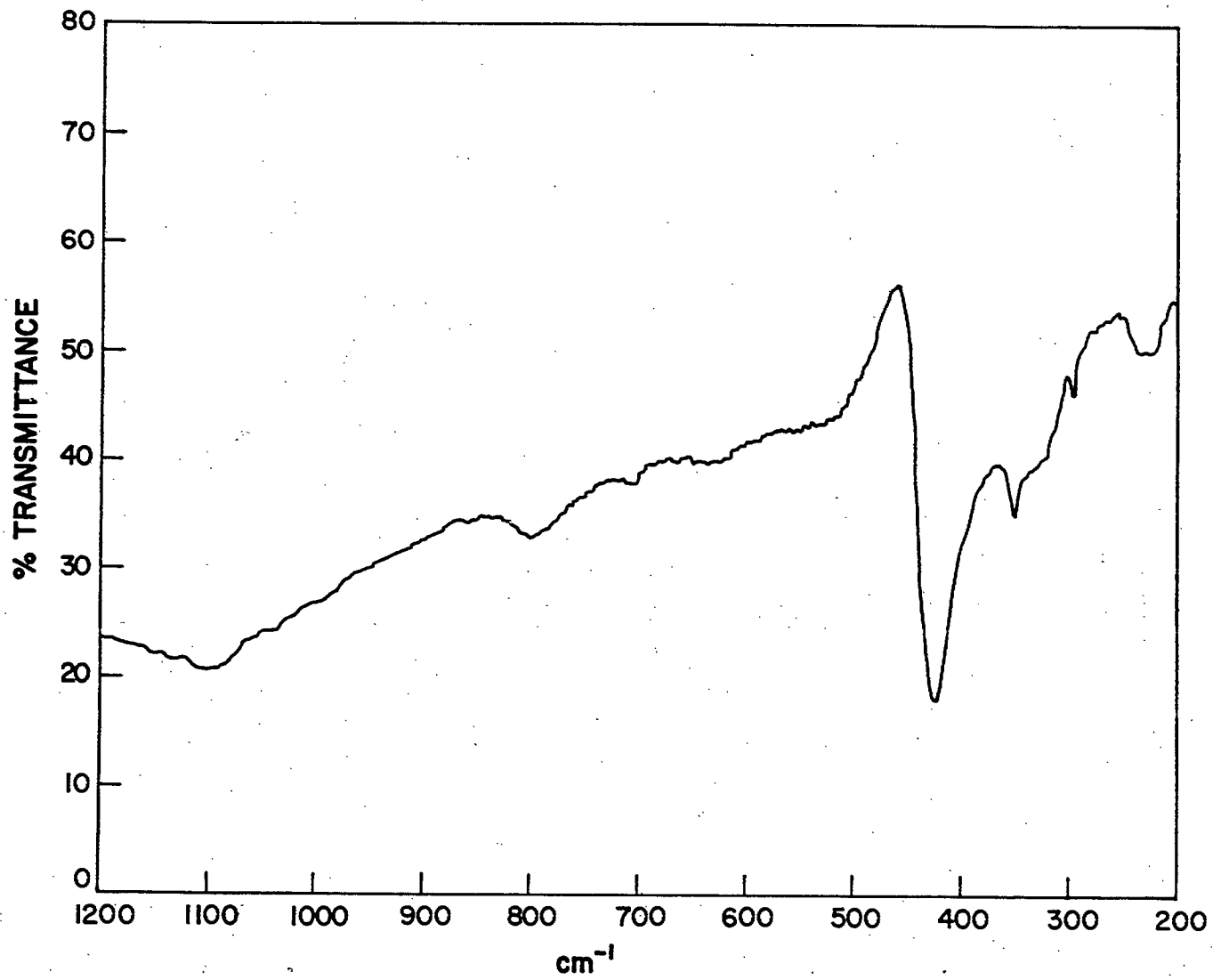
Figure 3 - Mica.

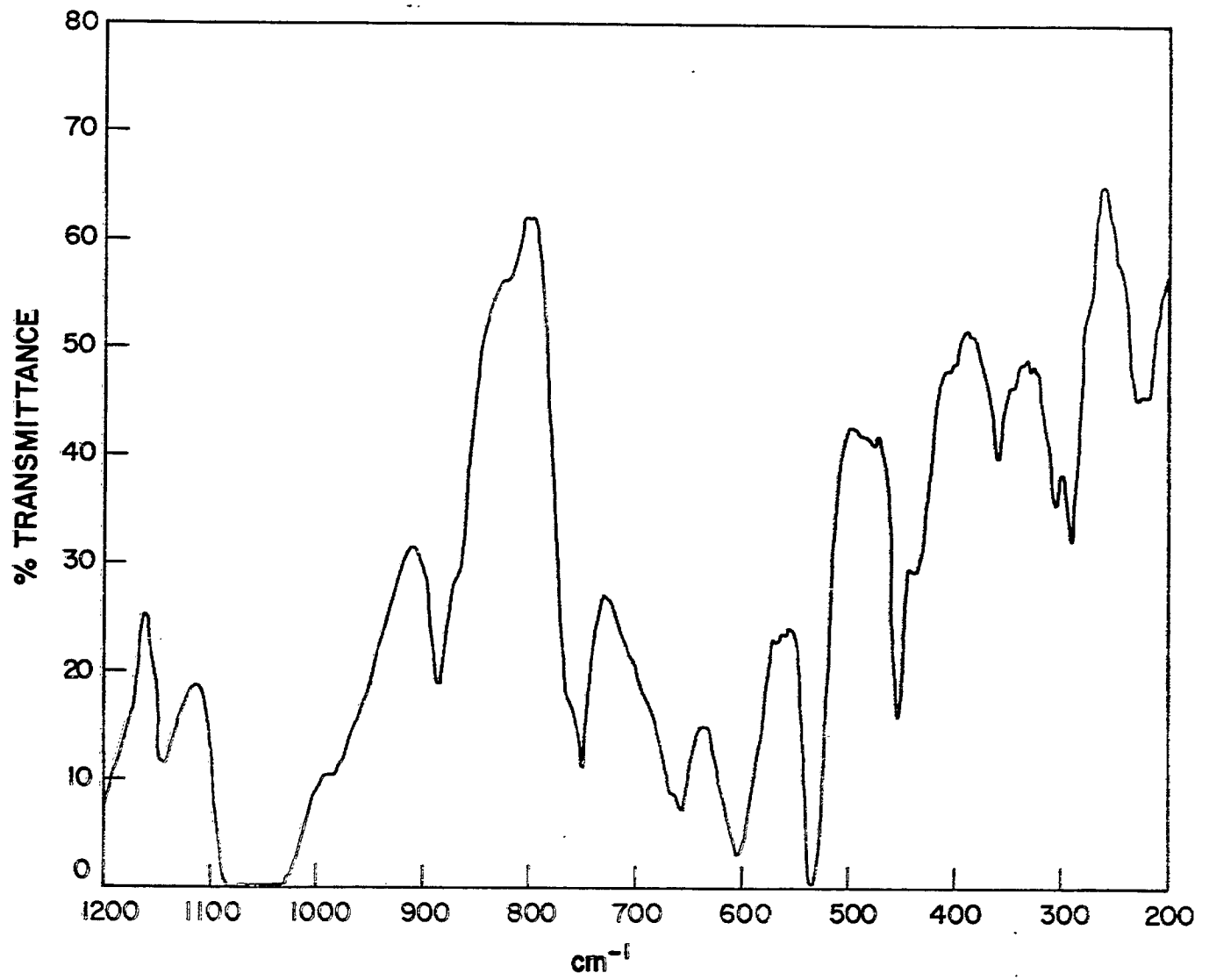Figure 4 - Feldspar.

Figure 5 - Pyrite.

Figure 6 - Polyvinylidene Chloride.

Figure 7 - Nordic Ore (Elliot Lake).

Figure 8 - Composite Spectrum.

Figure 9 - Absorption by Alpha-Quartz at 12.5-Micron Wavelength.
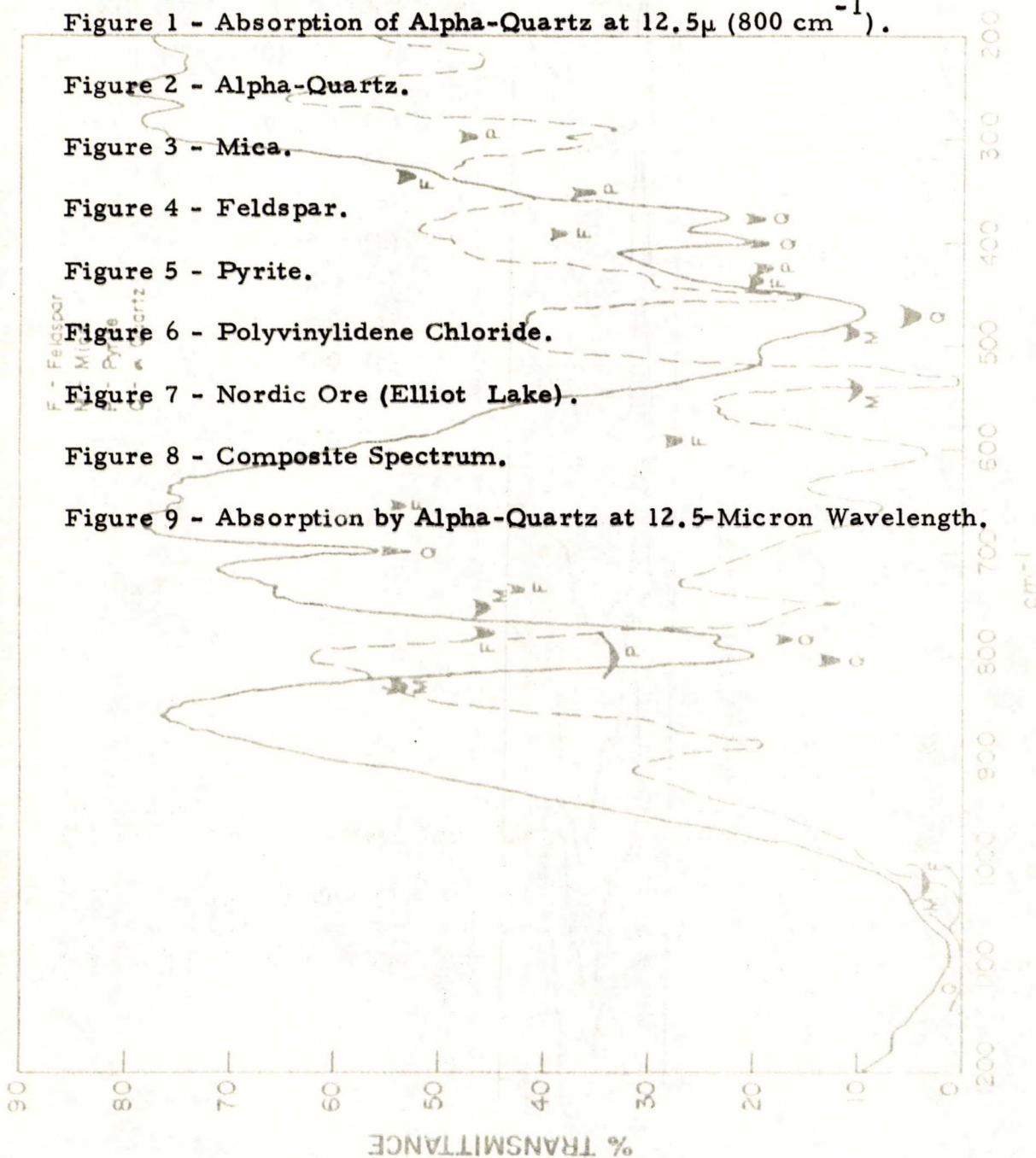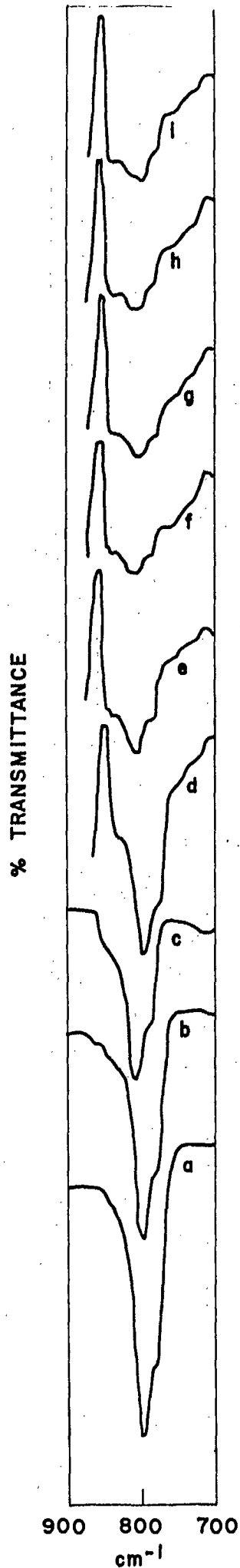
FIGURE 1

ABSORPTION OF ALPHA-QUARTZ

AT 12·5 μ (800 cm⁻¹)

(a) 1·1 mg
(b) 0·79
(c) 0·58
(d) 0·42
(e) 0·23
(f) 0·18
(g) 0·12
(h) 0·11
(I) 0·10

FIGURE 2   ALPHA - QUARTZ

FIGURE 3 MICA

FIGURE 4 FELDSPAR

FIGURE 5 PYRITE

FIGURE 6 POLYVINYLIDENE CHLORIDE

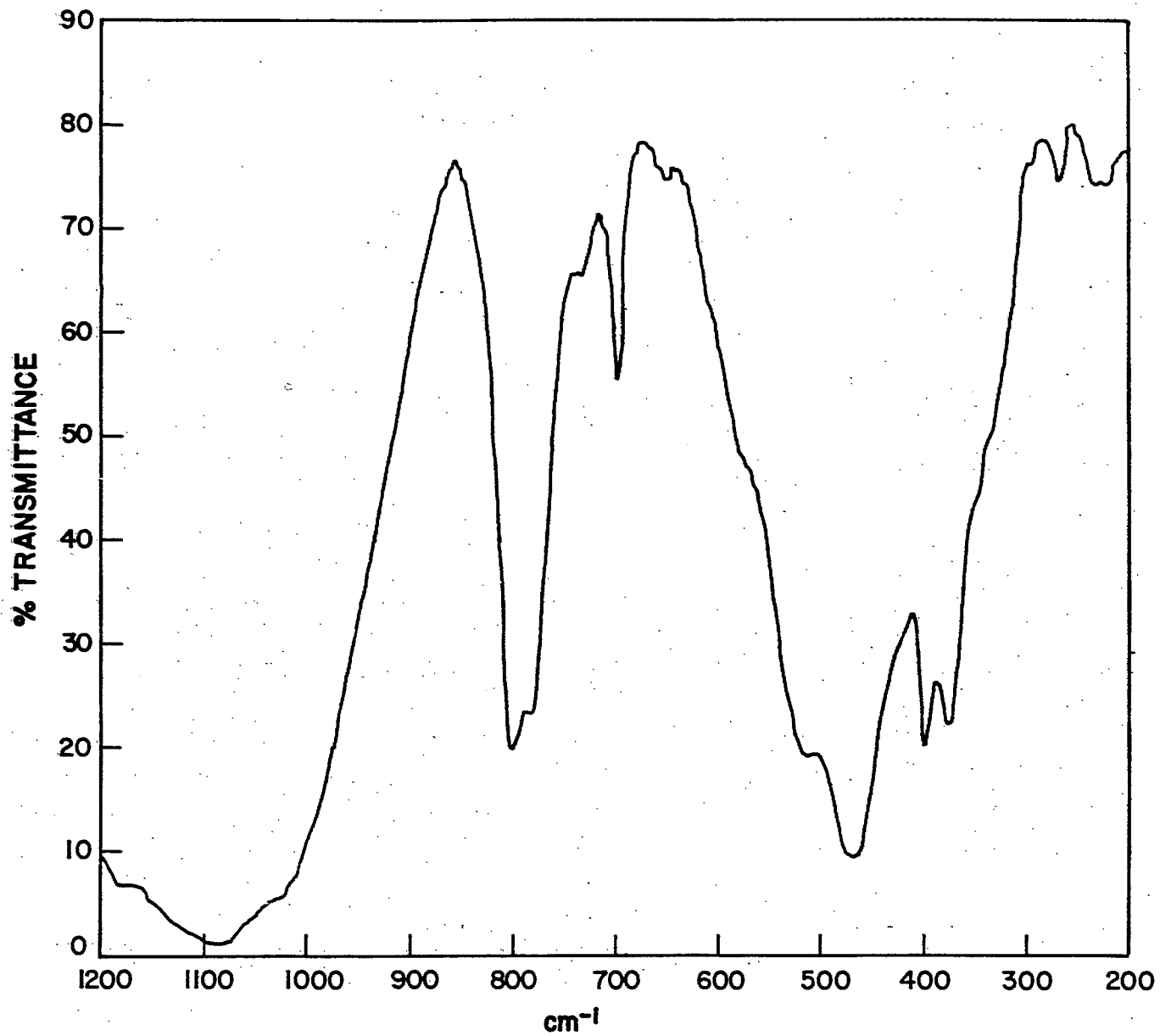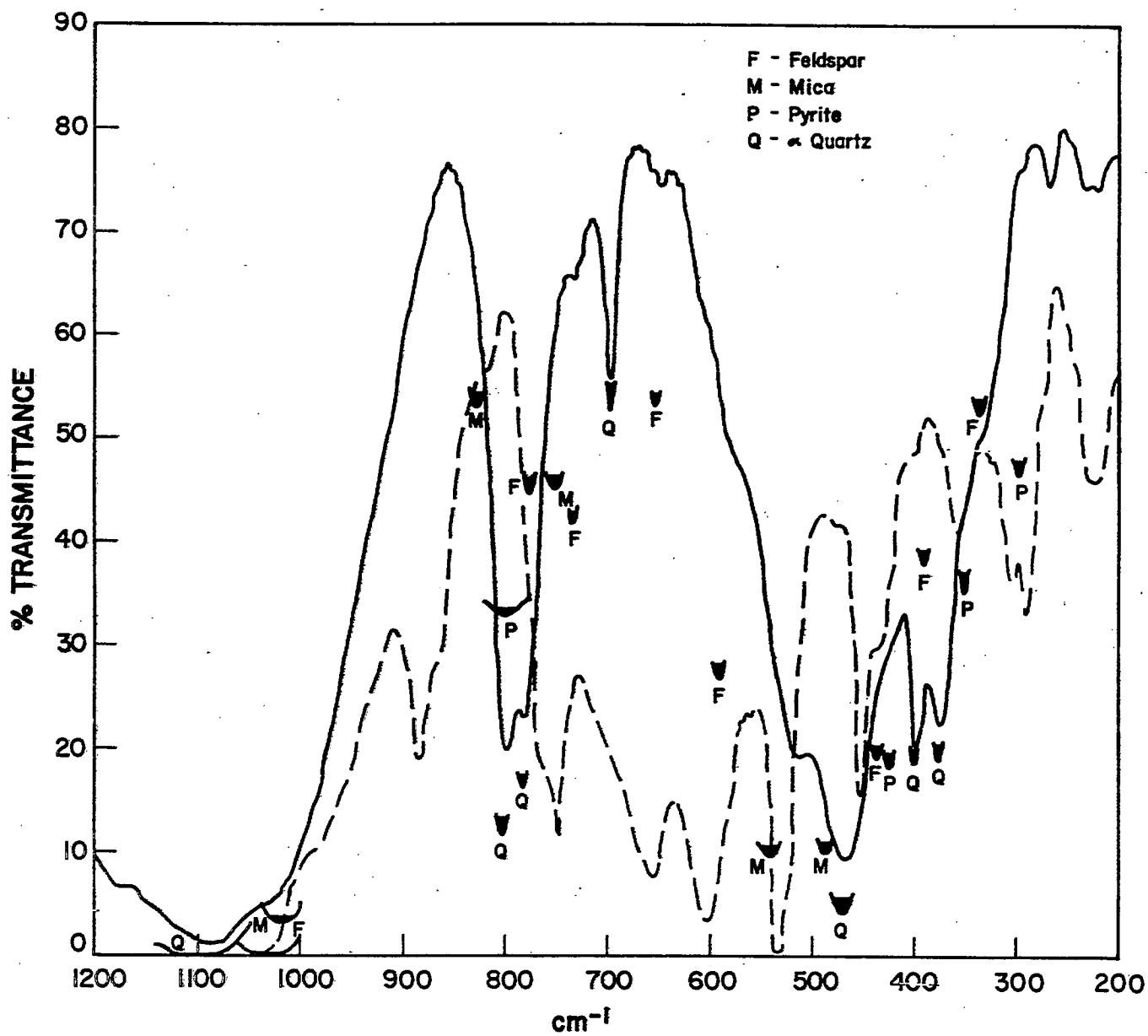FIGURE 7 NORDIC ORE (ELLIOT LAKE)
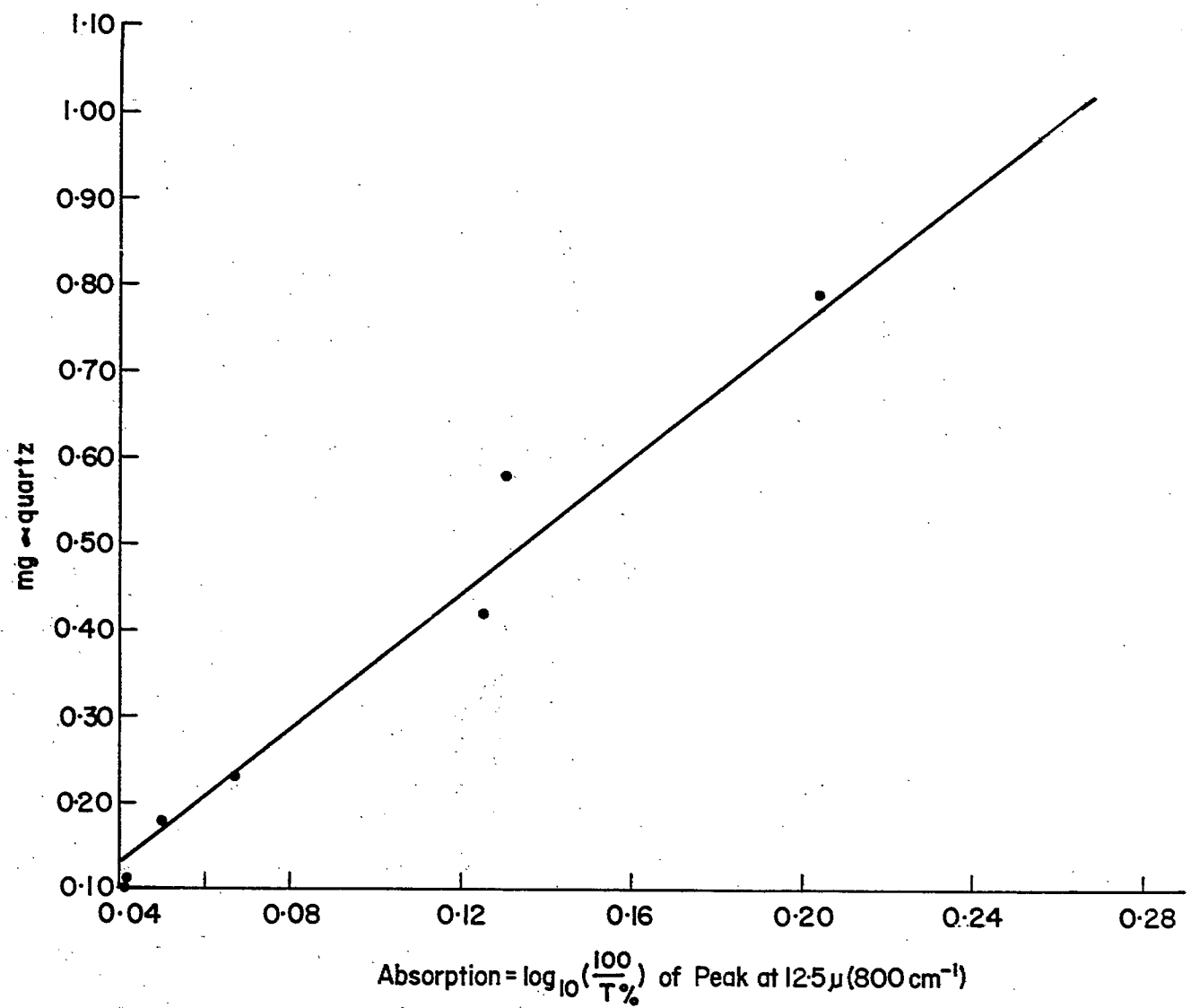
FIGURE 8   COMPOSITE SPECTRUM

FIG. 9   ABSORPTION BY ALPHA - QUARTZ AT 12·5 MICRON WAVELENGTH