

NEAR-IR AND MID-IR PROCESS ANALYSIS — A CRITICAL COMPARISON

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ABSTRACT

Over the past several years, both near infrared (NIR) and mid infrared (MIR) spectroscopy have steadily gained acceptance as powerful methods for at-line and on-line analysis. These methods share the advantages of high speed, robust calibration, and low service requirements compared to more established process analytical techniques such as gas chromatography. However, despite their many similarities, NIR and MIR are often viewed as distinct technologies, competing for the same market segments. This paper reviews the fundamentals of infrared analysis from the spectroscopic viewpoint, stressing both the common and disparate features of NIR and MIR and highlighting the fact that — rather than being two distinct technologies — NIR and MIR represent the endpoints of a continuum of analytical possibilities. Particular emphasis is placed on the spectral characteristics of typical organic materials and on the effects of these on the choice of spectral region and sample interfacing method for use in a given analysis.

INTRODUCTION

Near infrared and mid infrared spectroscopy are closely related technologies. Both analyze functional group vibrations of organic molecules by monitoring their absorption of radiation as a function of frequency in the infrared spectrum. However, despite their common fundamental basis, the instrumentation used in the two fields has traditionally been quite different, even to the point of using different spectral scales (nanometers in the near-IR and wavenumbers in the mid-IR). The two fields are thus usually viewed as distinct measurement techniques often competing for the same applications. While there is some truth in this view, to a larger extent it is an artifact of the separate historical development of each field. We are now seeing a convergence of near and mid IR, with the infrared spectrum increasingly being viewed as a continuum. Common instrumentation is increasingly being applied across the spectrum with various portions of the IR spectrum being used for particular

measurements.

A comprehensive comparison of the use of different spectral regions for process analysis would necessarily cover several topics, including the nature of the analyzers available, the means available for optical transmission, and the applicability of various chemometric data analysis routines. I will, however, limit my treatment to the nature of the interaction between the sample and the measurement system, discussing both the available sample interfacing methods and the spectroscopic properties of typical organic samples as viewed by these methods. This should assist in the process of choosing the appropriate spectral region and measurement technique for use in a given application, a process which is often obscured by the ubiquitous presence of full spectrum chemometrics. By first optimizing an analysis from the spectroscopic point of view, it is often possible to substantially reduce the magnitude of the chemometric calibration task required.

HISTORICAL DEVELOPMENT

To understand why near IR and mid IR have traditionally been viewed as distinct technologies, it is useful to review the histories of these two fields. This will also shed some light on the evolution of the different types of instruments that have been employed.

Mid Infrared Analysis:

The history of infrared spectroscopy began with the pioneering work of W. W. Coblentz in 1900 (ref. 1). However, its first practical application did not occur until World War 2. The advances made during the war led to two different paths of subsequent development. The first was the development of practical dispersive IR spectrometers for general purpose laboratory analysis. The second was the ongoing development of non-dispersive infrared (NDIR) instruments for dedicated industrial applications. IR spectroscopy quickly gained acceptance as one of the key analytical methods widely used in analytical laboratories as a result of its ability to directly display the intensities of absorption bands corresponding to fundamental functional group vibrations.

During the 60's and 70's the expanding capabilities of mid-IR spectroscopy were driven by the increasing demands of organic chemistry research and industrial laboratory analysis, with emphasis on increasingly higher resolution. A major advance took place in 1970 with the introduction of the first commercial FTIR spectrometers. Although the early FTIR instruments were considerably more expensive and delicate than dispersive instruments, their much higher resolution, sensitivity, and speed amounted to a major breakthrough in laboratory infrared capability. Eventually, with the development of reliable moderately priced instruments in the early 1980's, FTIR replaced dispersive IR in virtually all segments of the laboratory market.

The attractiveness of FTIR for process applications was obvious from an early date. However, progress in this direction was hampered by the relatively small size of the process market and by the fact that major advances in environmental tolerance and stability were required to meet the needs of the process environment. In view of the limited and unproven market, the established suppliers of laboratory instalments simply did not have an incentive to invest in an effort to solve the difficult problems barring

entry. This step was eventually taken by a couple of smaller firms who's lack of a major position in the laboratory market provided them with the freedom to pioneer new challenging applications areas.

In parallel with the development of first dispersive spectrometers and later FTIR spectrometers for the sizable laboratory market, mid infrared technology did find application in the smaller process market. But until the 1980's, process mid infrared was limited almost entirely to the use of infrared filters to monitor a few specific IR bands — hence the use of the common abbreviation NDIR for nondispersive infrared. These two independent lines of development finally came together with the emergence of rugged environmentally tolerant FTIR spectrometers, continued advances in sample interfacing technology, and the development of efficient means to transmit IR radiation between the spectrometer and the measurement site (ref. 2). The result has been the successful application of process FTIR to a wide variety of industrial tasks.

Near Infrared Analysis:

Commercial near infrared spectroscopy is a later development than mid infrared spectroscopy, (ref. 3). It was born of a need to solve practical quality control problems rather than the desire to perform high resolution molecular structure analysis in the laboratory. In a sense, it can be viewed as a new applications area for the general types of instrumentation employed in mid infrared NDIR process analyzers. However, in contrast to the mid infrared NDIR field, near infrared spectroscopy has continued to evolve vigorously, first moving to higher resolution through the use of dispersive technology and then incorporating powerful chemometric software routines.

The use of filter technology for the early NIR instruments was dictated by the nature of the samples being analyzed. Agricultural products such as grain are highly scattering in the near infrared and hence must be studied in either diffuse reflection or diffuse transmission. The resultant need for a large collecting area and maximum optical signal level at the sample necessitates the use of a spectroscopic technique having the highest possible throughput. In this regard, filter instruments are generally superior to dispersives.

As near IR instrumentation began to be applied to nonscattering systems such as clear liquids, the emphasis shifted to the need for higher resolution rather than maximum throughput — thus creating the opportunity for the use of dispersive technology. Both approaches are continuing to be employed to meet the needs of diverse applications.

The growth of NIR analysis has benefitted greatly from the availability of high quality fused silica optical fibers. Large fiber bundles are being used to enhance the utility of the instruments employed in applications requiring high throughput, while economical single fibers allow multiplexing of multiple sampling devices and transmission of signals to and from remote sampling locations. A second factor stimulating the growth of NIR is the fact that, from its inception, it has been largely a QC and process monitoring tool. The manufacturers of NIR instruments have thus been able to concentrate their development and marketing efforts on opening up new dedicated applications.

As the demands of new and diverse applications have become progressively greater, considerable emphasis has been placed on the use of sophisticated chemometric software to develop calibrations for

highly complex chemical systems (ref. 4). This, in turn, has raised the stakes by greatly increasing the level of stability required from the instruments themselves. Even a slight change in instrument frequency scale can necessitate a complete recalibration, a painstaking procedure often requiring scores of samples. This situation has created an opportunity for the wide scale application of FTIR spectroscopy to near IR analysis — providing further enhancement of both resolution and frequency stability and breaking down the barriers which previously existed between the instrumentation used in different spectral regions.

An Emerging Synthesis:

The emergence of rugged and stable FTIR spectrometers has brought about a major change in the way we can view dedicated infrared analysis. It is now possible to achieve a high level of performance across the whole IR spectrum, from 800 nm ($12,000\text{ cm}^{-1}$) to 25,000 nm (400 cm^{-1}), with a single type of instrument. To optimize performance for a particular spectral range of interest, we simply have to select the appropriate beamsplitter, radiation source, and IR detector. Of course it should be pointed out: that, despite its very attractive features, FTIR is not likely to displace earlier types of instruments for all applications. This is particularly true of applications requiring very high throughput, in which case filter based analyzers should remain a significant factor.

INFRARED SAMPLE INTERFACING TECHNIQUES

This section will briefly review some of the considerations involved in selecting a sample interfacing method for use in a given process application. More detailed discussions of specific methods can be found in a variety of references (ref: 2, 5, 6).

Transmission:

Transmission analysis is by far the most widely used sample interfacing technique in infrared process analysis. In the case of gases, it is virtually the only applicable technique since the relatively low absorbances of gases necessitate quite long pathlengths. The considerations are more complex for liquids. The fundamental absorbances corresponding to the functional groups of organic chemicals fall in the mid infrared "fingerprint" region of the spectrum. These absorbances are generally very strong. The use of a transmission cell for such a system would require a window spacing of typically 25 μm or less. This requirement gives rise to a number of problems including poor flow characteristics, marked interference fringes due to the high refractive indices of most appropriate window materials, and the nonlinear response which occurs if the sample gap is wedged enough to overcome the interference effects (ref. 7). As a result, transmission cells are seldom used in this spectral region.

As one moves to the first overtone region, the optimum pathlength increases by more than an order of magnitude to typically 0.5 mm. At this thickness, it becomes practical to wedge the gap enough to overcome interference effects. However, two problems remain: the difficulty of fabricating appropriate wedged spacers for the still relatively small gaps and the need to minimize dead volume. At higher frequencies yet — where the observed bands are typically due to second and third overtones and combination tones — optimum sample gaps are usually 5 mm or greater. At this point, interference

fringes no longer pose a problem and dead volume is generally quite low relative to cell volume. The sample interfacing task has become rather easy, albeit at the expense of considerably more difficult spectral analysis.

The application of transmission analysis to solids requires an appropriate combination of short pathlength and weak absorption. As a result, on-line applications are generally limited to web processes and to the use of overtone and combination tone bands. Even here, problems can occur. The most serious is the occurrence of interference fringes. These can be troublesome whenever the fringe spacing is greater than, or of the same magnitude as, the resolution of the instrument.

Attenuated Total Reflectance:

Attenuated total reflectance (ATR) makes the analysis of fundamental bands practical by providing the equivalent of a very thin transmission cell — typically 1 μ m to 25 μ m depending on ATR element material and number of reflections employed. However, ATR has its own set of concerns. In particular, a potential for performance variation results from the fact that the effective pathlength depends on the angle of incidence of the IR radiation at the interface between the ATR element and the analyte. Any mechanical change which affects the distribution of optical ray angles will result in a change in measured absorbance. Within the past few years, process compatible ATR cell and probes have been developed which minimize both the range of angles used and the potential for any change in this distribution (ref. 2).

A second potential limitation of ATR results from the fact that it is inherently a surface effect. Any condition which involves a nonuniform distribution of chemical composition in the analyte — such as adhesion of material to the ATR element — can lead to faulty measurements. However, experience has shown that this effect is less often a problem than one might expect. Of greater concern is the fact that the materials which have suitable IR transmittance and sufficiently high refractive index to be used as ATR elements in the fingerprint region are often attacked by strongly reactive chemicals. Particularly troublesome are strong acids and bases and oxidizing agents. It is usually necessary to evaluate applications on a case by case basis to determine their feasibility.

Reflectance:

Diffuse reflectance has been widely used in near IR analysis since the development of the first near IR agricultural product analyzers in the late 1960's. In addition to a great variety of off-line tasks, NIR diffuse reflectance has found widespread use in a number of on-line applications, most notably the measurement of moisture content in substances such as food products and paper (ref. 8).

The key requirements of diffuse reflectance are a large solid angle of collection and, to a lesser extent, a relatively large illuminated area. This latter requirement is dictated by the need to average out sample inhomogeneities. These two requirements together necessitate a high system throughput, a quality more typical of filter instruments than of dispersive or FTIR instruments.

Specular reflectance is a much less common technique in IR analysis. Although it is not presently used for process analysis, it does have some unique features which may make it applicable in some situations.

It is more likely to find use in quality control and product identification. An illustration of the potential utility of specular reflectance will be given below.

SPECTRAL CHARACTERISTICS OF ORGANIC MATERIALS

The three properties of materials which have the greatest influence on their spectroscopic analysis are absorption, specular reflection, and scattering. Diffuse reflection can be thought of as a secondary phenomenon resulting from a complex combination of the other three on a microscopic scale. The sections below will provide examples of the relationships between physical properties and infrared spectral properties of typical organic materials and will discuss those characteristics which influence the choice of spectral range and measurement technique to be used in an analysis.

Clear Liquids:

Clear liquids are generally the easiest types of samples for process analysis. In this case, we are dealing with pure absorptions corresponding to the vibrations of the various bonds of individual molecules. Of particular interest are the vibrations of the functional groups which determine the chemical reaction characteristics of a given substance. The fundamental frequencies of virtually all of these fall in the traditional mid infrared region of the spectrum ($400 - 4000 \text{ cm}^{-1}$). The corresponding absorptions are usually very strong. This is illustrated by Figure 1, spectra of a base gasoline and of the same gasoline with the addition of 6% MTBE run in a 0.5 mm thick model LFV-410 transmission cell (ref. 9). The fundamental bands in the fingerprint region ($400 - 1700 \text{ cm}^{-1}$) are too strong to be used for a reliable analysis. The absorbance values could be reduced by further reducing the thickness of the cell. However, a generally better approach is the use of attenuated total reflectance (ATR). Figure 1 exhibits some weaker bands in addition to the fundamental absorptions below 1700 cm^{-1} . These are overtones and combination tones of the fundamentals. In many applications, these bands will exhibit sufficient information to be useful for quantitation.

Figure 2 was obtained with the same samples as Figure 1 except by using a model TNL-120 ATR cell rather than transmission (ref. 9). In this case, the bands of interest are well within the desirable absorbance range for analysis.

Figure 3 is a plot of the integrated absorbance of the 1085 cm^{-1} band of MTBE as a function of concentration based on spectra obtained with a two reflection DPR-210 ATR probe (ref. 9). The excellent linear fit illustrates one of the strengths of mid infrared analysis. As long as the chemical system is not too complex, simple and transparent routines can often be used to provide very good quantitative results. Real-world gasoline, of course, is not that simple.

Figure 4 includes three near infrared spectra obtained with an FPT-720 transmission probe having a 4 mm gap (ref. 9). The spectra correspond to (A) pure gasoline, (B) gasoline with a 6% admixture of MTBE, and (C) pure MTBE. The bands are all overtones or combination tones of lower frequency fundamentals. Although the near IR spectra of gasoline and MTBE are quite similar, there is sufficient information present to allow quantitative analysis.

Gasoline is a particularly interesting type of sample for two reasons. First, the commercial product is a mixture of substantial number of different substances, ranging from pure alkanes of various chain lengths to aromatics like benzene, toluene, and various ethers. Second, the information required from an analysis can include both a generalized quantity such as octane and the specific concentrations of various additives. In view of this twofold complexity, and of the economic significance, it is no wonder that a tremendous amount of effort has been devoted to developing calibration techniques for infrared gasoline analysis.

Commercial gasoline analyzers are currently being marketed using both of the above sampling techniques and four different regions of the IR spectrum. These are: ATR in the fingerprint region, short path transmission in the first overtone region, medium path transmission in the traditional NIR region, and long path (eg: 10 cm) transmission in the short wave NIR region (800 to 1200 nm). An even greater number of chemometric calibration approaches have been developed for use with the various sampling systems. The spectrometers themselves fall into at least three categories: mechanically scanned dispersive, diode array dispersive, and FTIR. All in all, there seem to be almost as many different approaches to gasoline analysis as there are petroleum companies.

The current status of IR gasoline analysis illustrates two of the main points of this paper. First, the historical distinction between near and mid infrared is no longer relevant. Second, in view of the multidimensional complexities encountered, it is often quite difficult to determine the optimum approach to a given task.

Turbid Liquids

The analysis of liquids can become more difficult in the presence of factors other than simple absorption. For example, the presence of either bubbles or particulate matter will lead to scattering. In the limiting case of very small scattering centers, the effect is proportional to X^4 (where X is the wavelength). As a result, scattering is much more of a problem at high frequencies (NIR) than at low frequencies.

Figure 5 includes near IR transmission spectra of silicone oil containing three different admixtures of titanium dioxide. The sampling device in this case was an FPT-720 transmission probe with a 10 mm gap. For the pathlength used, a concentration of 0.125% is sufficient to reduce the transmission in this spectral region by more than a factor of 20, greatly reducing our ability to perform an analysis.

Figure 6 includes spectra of pure silicone oil and of silicone oil containing 0.5% titanium dioxide obtained in the mid IR with a two reflection DPR-210 ATR probe (ref. 9). The complete overlap of the two traces — except for the region of CO₂ interference — illustrates the insensitivity of ATR to scattering.

Solids:

The analysis of solids provides a very good illustration of the interplay between absorption, reflection, and scattering in determining the nature of an analysis. In this case, scattering is often a requirement for an analysis rather than a problem. It is fundamental to diffuse reflectance, the most common

sample interfacing method used for dedicated applications.

Figure 7 includes reflectance spectra of aspirin in three different forms: A — pure aspirin powder, B — KBr powder with an admixture of 1% aspirin, and C — an aspirin tablet with the coating scraped off. Both diffuse and specular components were collected. The spectra are ratioed against a spectrum of pure KBr powder.

In the fingerprint region of Figure 7A, absorption dominates over scattering. The weak spectrum obtained is the combined result of both diffuse and specular reflectance and is thus of very little use. At high frequencies, scattering dominates over the weak overtone absorbances resulting in usable diffuse reflectance spectra.

Diluting aspirin in 99% KBr powder (Figure 7B) reverses the relationship between scattering and absorption at low frequencies and thus results in well behaved diffuse reflectance spectra. At higher frequencies, the band strengths are appropriately weaker than in Figure 7A.

The smooth surface of the scraped aspirin tablet (Figure 7C) provides a pure specular reflectance spectrum in the fingerprint region. The features observed are the result of the large excursions in refractive index which occur in regions of high absorption. This spectrum can be converted to the corresponding absorbance spectrum by means of the Kramers-Kronig transform (ref. 10). At high frequencies, the spectral properties of the tablet are similar to those of the pure aspirin powder.

CONCLUSIONS

This paper has surveyed the characteristics of representative chemical systems with a view toward shedding some light on the process of choosing appropriate spectral regions and sampling methods for use in particular IR process analysis tasks. A dominant theme has been the concept of treating the infrared spectrum as a continuum rather than being split between mutually exclusive near IR and mid IR regions. In fact, with current spectroscopic instrumentation, most samples can be analyzed in any of three or four distinct regions of the spectrum by appropriate choice of sample interfacing technique, infrared detector, IR radiation source, and other optical components.

The most fundamental decision to be made in planning an IR process analysis installation is whether to base the measurement on fundamental vibrational modes or on overtones and combination tones. Sometimes the decision is easy. The presence of a slurry or other scattering medium may dictate the use of ATR and hence fundamental vibrations. On the other hand, the need for an instrument to communicate with one or more remote measurement sites may dictate the use of fiber optics which, in turn, restricts the analysis to the high frequency overtone regions. More often, both approaches will be possible. It will then be necessary to take into consideration a wide range of factors such as material compatibility, optical transmission versus sample transport, spectral characteristics of the chemical system, and the applicability of various chemometric approaches. In many cases, the information available will not be sufficient to support a rational decision and the choice will simply come down to a matter of personal preference. The real problem is the overwhelming range of powerful hardware and software tools that have become available within the past few years. Various combinations of these

can be brought to bare on any given task, with each offering the prospect of yet another successful implementation of process infrared analysis.

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FIGURE 1: Transmission spectra of: A — pure gasoline, and B — gasoline with a 6% admixture of MTBE. (Pathlength = 0.5mm.)

FIGURE 2: Attenuated total reflectance (ATR) spectra of the same samples as used for Figure 1. (9 reflection TNL-120, ZnSe element.)

FIGURE 3: Integrated absorbance of the 1085 cm^{-1} band of MTBE as a function of concentration. (2 reflection DPR-210 ATR probe, ZnSe element.)

FIGURE 4: NIR transmission spectra of: A — pure gasoline, B — gasoline with a 6% admixture of MTBE, and C — pure MTBE. Traces B and C are offset for clarity. (Pathlength = 4 mm.)

FIGURE 5: NIR transmission spectra of: A — pure silicone oil, and silicone oil containing B — 0.015%, and C - 0.125% TiO_2 .

FIGURE 6: Superimposed mid infrared ATR spectra of pure silicone oil and silicone oil containing 0.5% TiO_2 .

FIGURE 7: Combined diffuse and specular reflectance spectra of: A — pure aspirin powder, B — 1% aspirin mixed into KBr powder, and C — a smooth aspirin tablet. Spectra B and C are offset vertically for clarity.

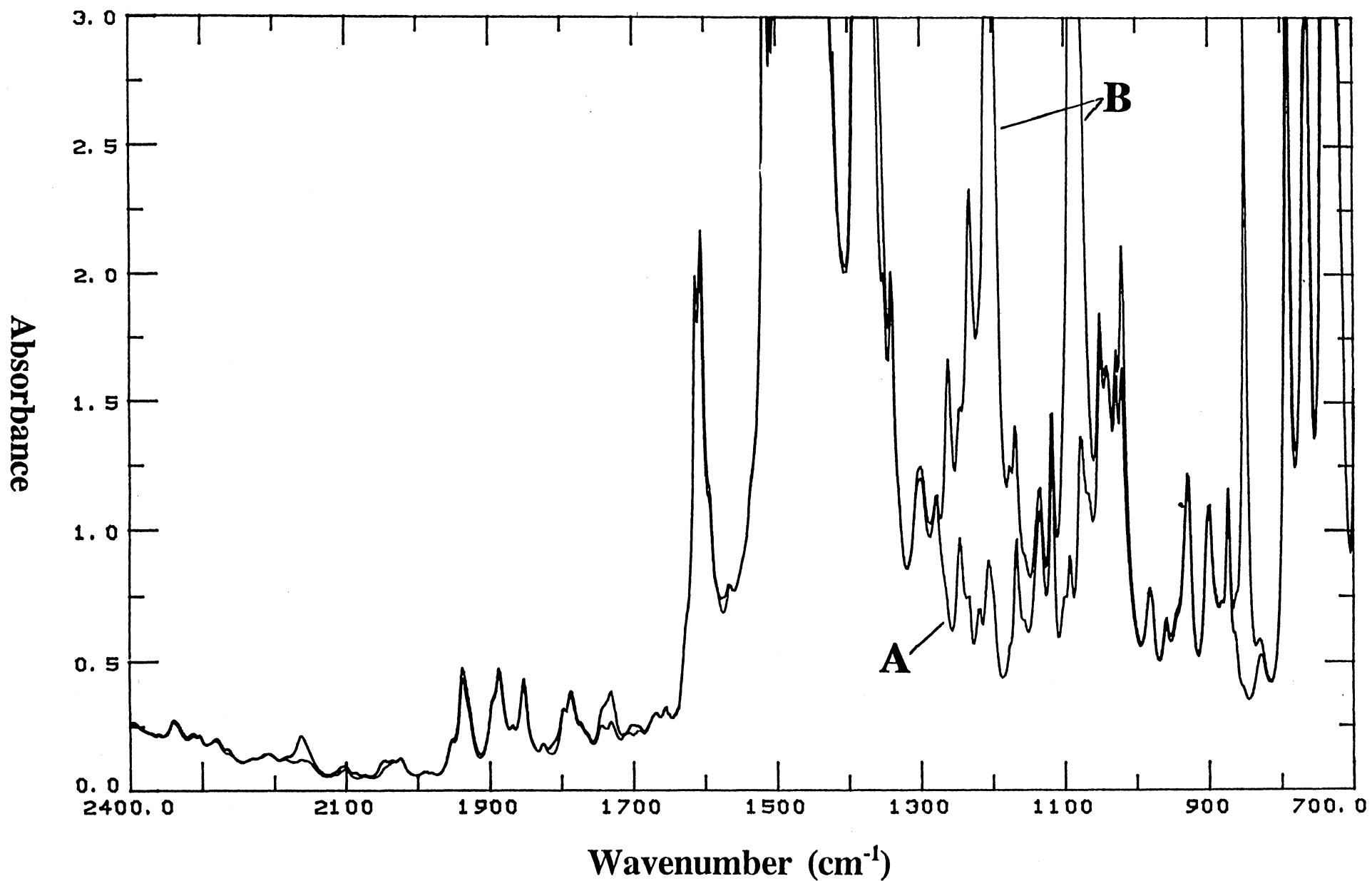


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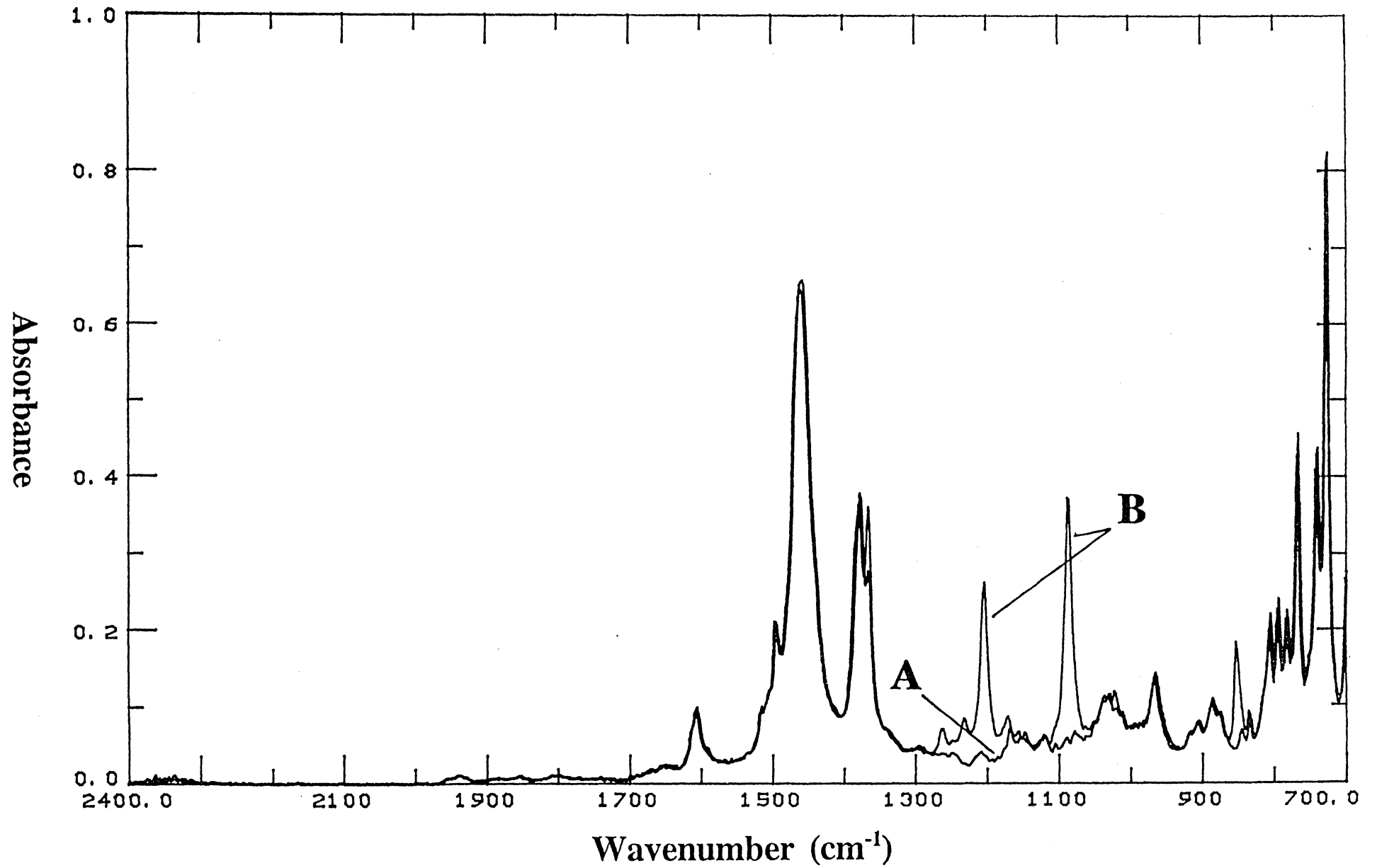


FIGURE 2: Attenuated total reflectance (ATR) spectra of the same samples as used for Figure 1. (9 reflection TNL-120, ZnSe element.)

MTBE Absorbance by Dipper ATR Probe

Analect FT-IR/ Axiom DPR-210

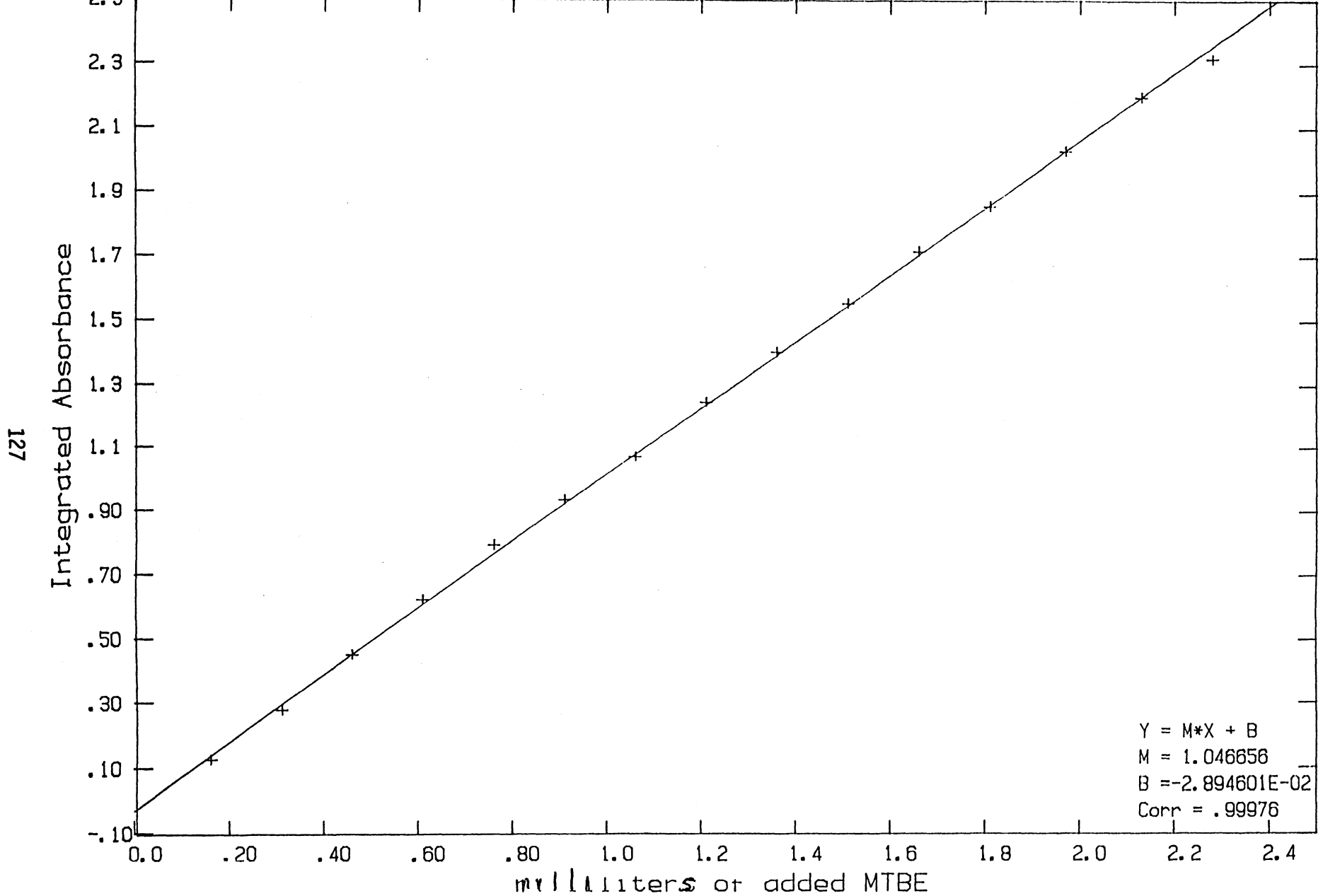


FIGURE 3: Integrated absorbance of the 1085 cm⁻¹ band of MTBE as a function of concentration. (2 reflection DPR-210 ATR probe, ZnSe element.)

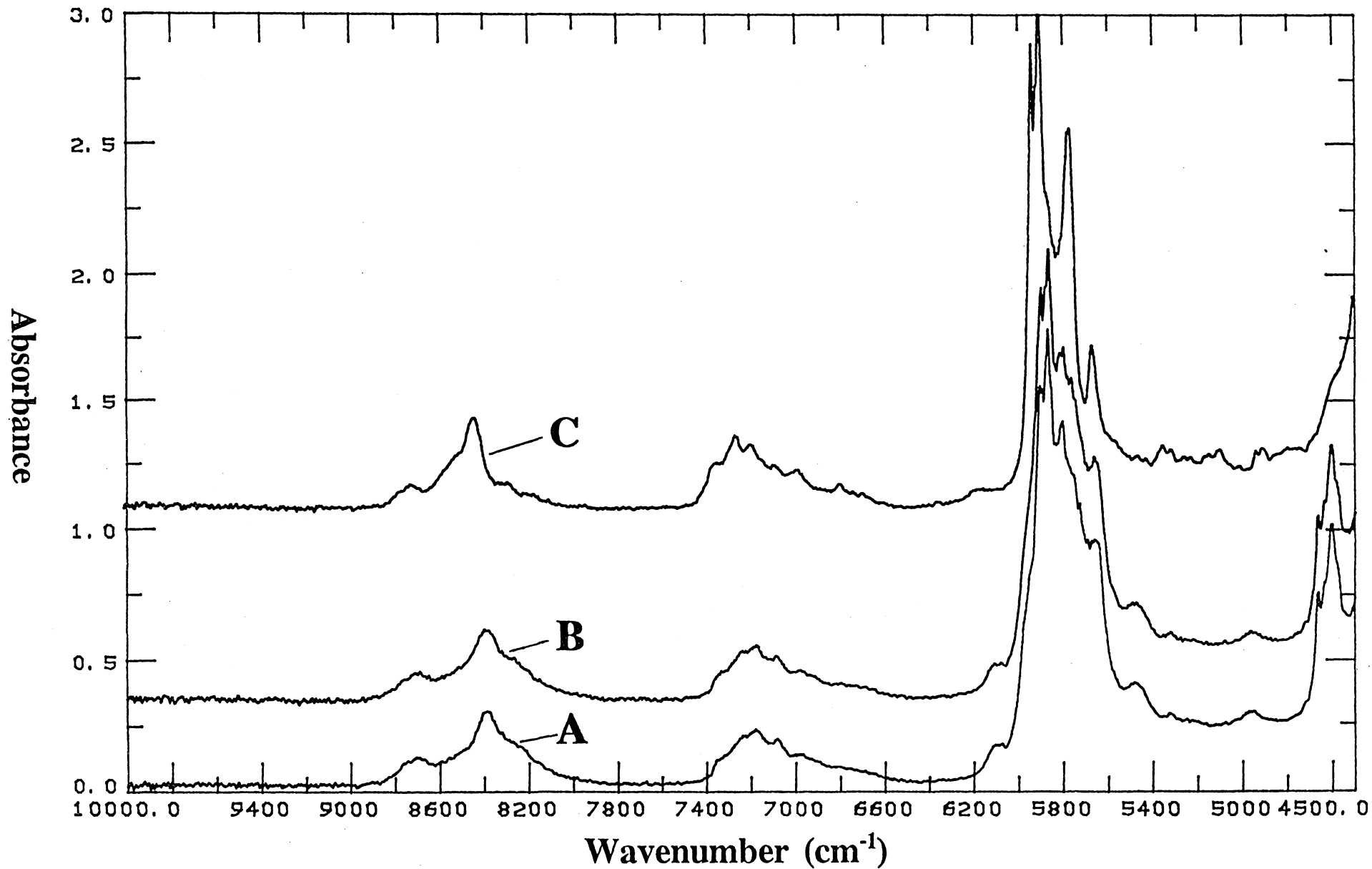


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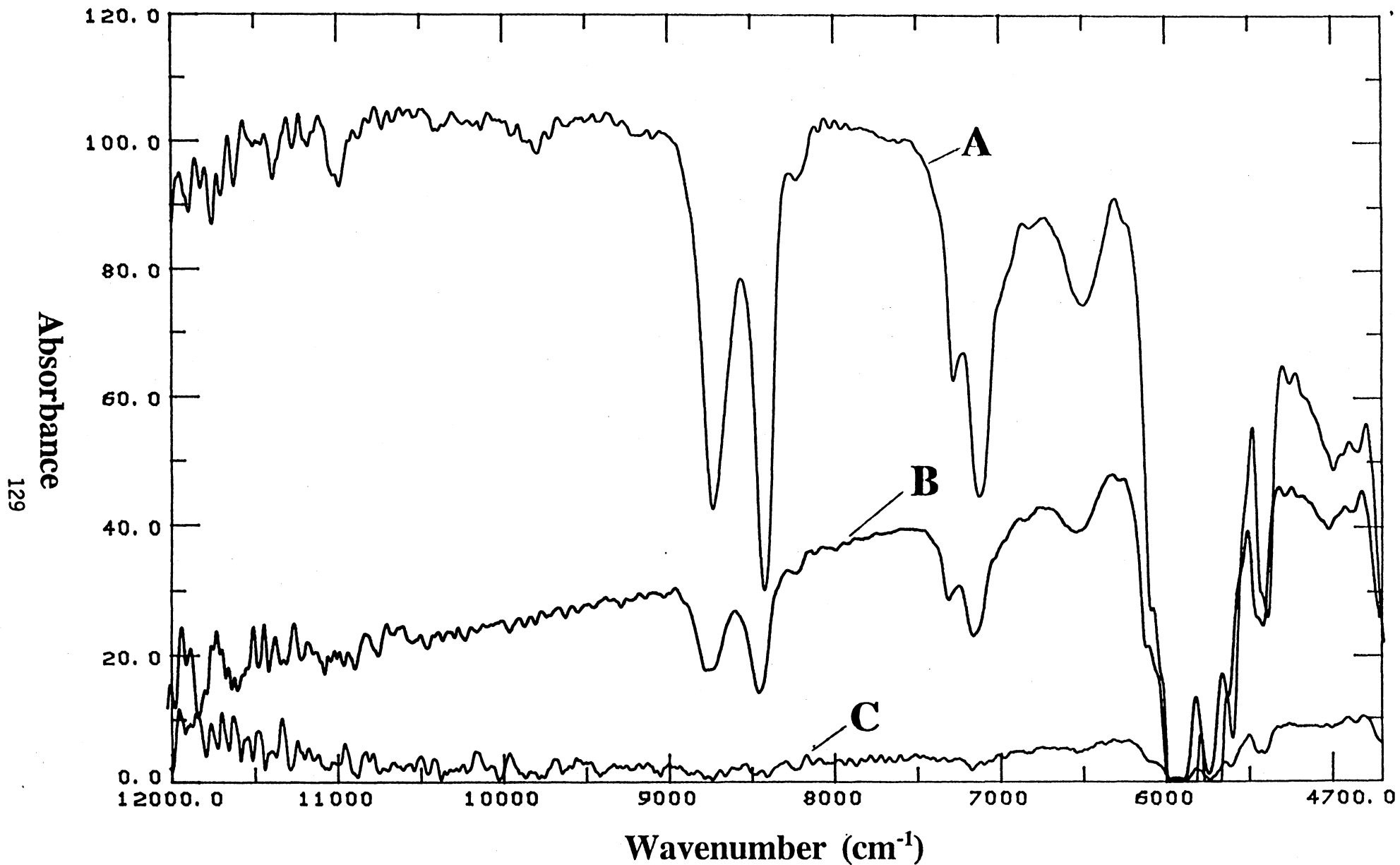


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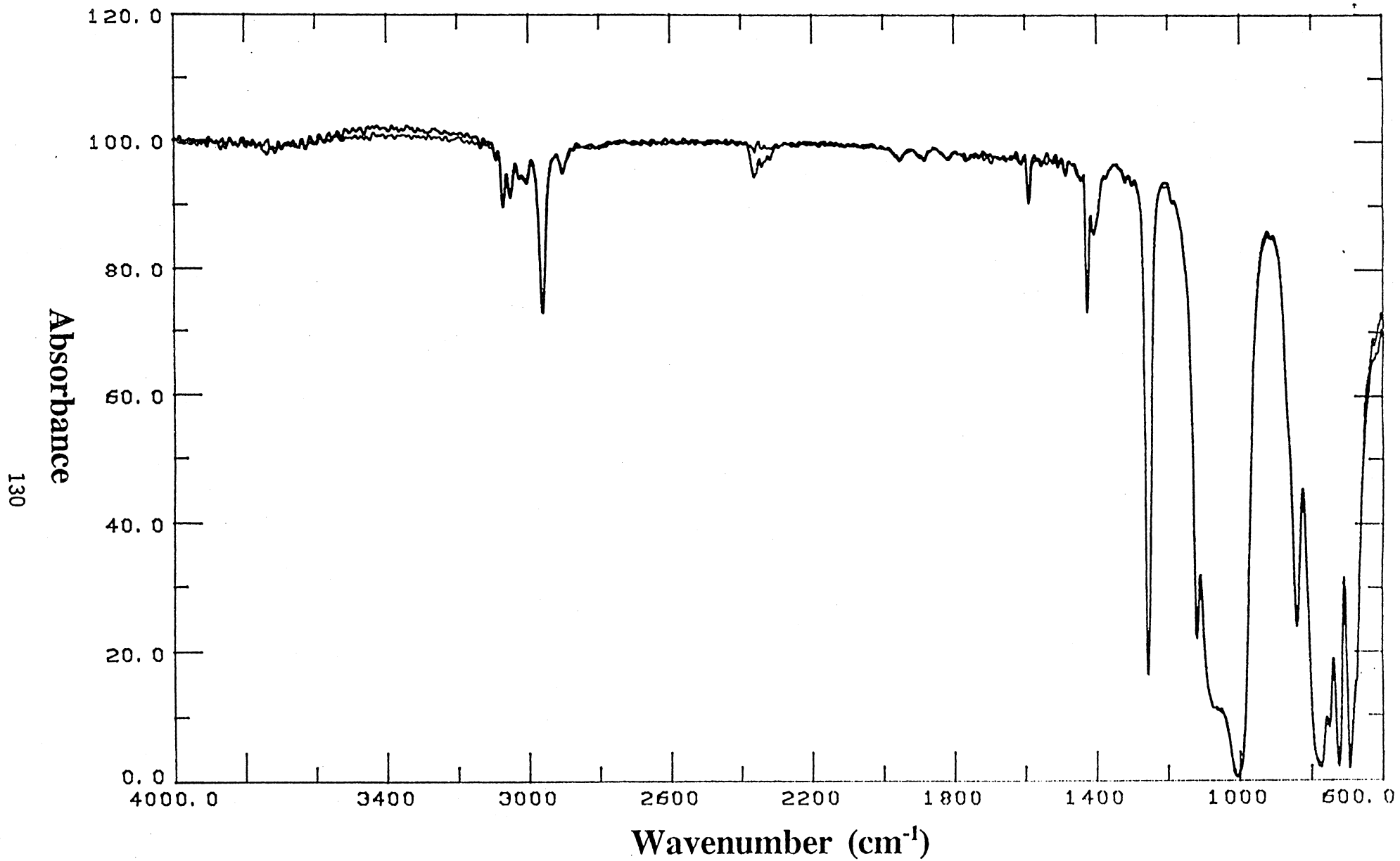


FIGURE 6: Superimposed mid infrared ATR spectra of p-re silicone oil and silicone oil containing 0.5% TiO₂.

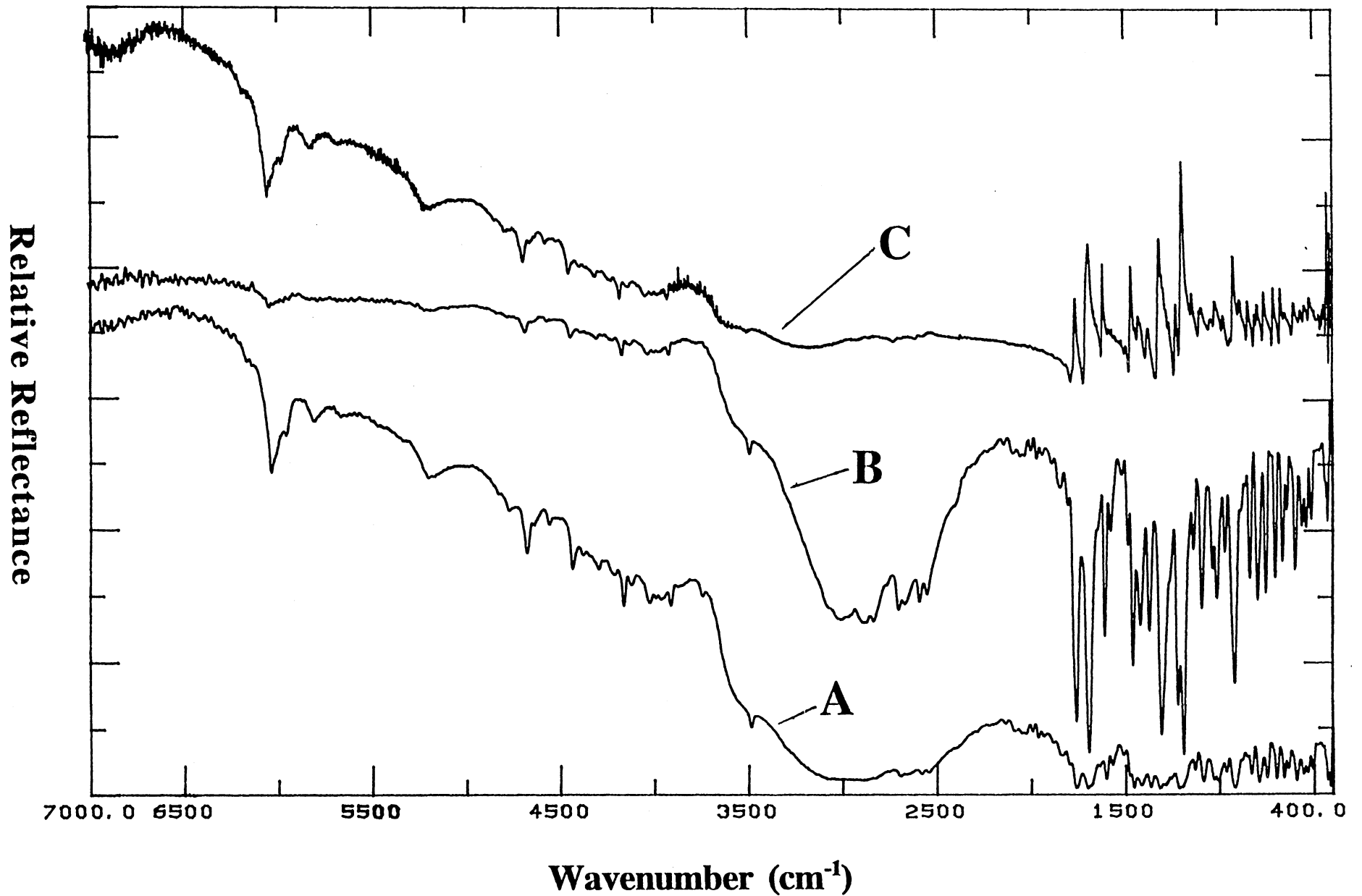


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