SUGAR INDUSTRY APPLICATIONS OF FOURIER TRANSFORM INFRARED SPECTROSCOPY. IDENTIFICATION OF FIBER SAMPLES

INTRODUCTION

Infrared (IR) spectroscopy can be a very valuable analytical technique in a variety of problems encountered in the food industry[1]. The mid-range infrared region (200 to 4000 cm^{-1}) can be used to assist in the identification of a wide variety of organic and inorganic substances. [The near infrared (NIR) region 4000-7000 cm^{-1} is also applied in the food industry but is usually useful for the quantitative analysis of mixtures of known constituents and will not be discussed here.] Although it is not widely used in the sugar industry, mid-range IR spectroscopy has, for some time, been used in our laboratory for numerous applications. Previous papers have discussed the application of an older dispersive IR spectrophotometer to the identification of rubber particles[2] and the identification of white sugar contaminants[3]. This paper will discuss the advantages of modern Fourier transform infrared (FTIR) spectrophotometers and discuss several applications related to identification of fibers.

RESULTS AND DISCUSSION

A. Advantages of FTIR Spectrophotometers

The original IR spectrophotometers, depended on an infrared beam which passed through a sample and was then dispersed into an infrared spectrum by means of a prism or diffraction grating. Light in a small region of the spectrum passed through a slit and absorbance at that particular frequency was recorded. With such an instrument, referred to as a dispersive spectrophotometer, a scan of the complete IR spectrum is achieved by rotation of the diffraction grating and requires as long as 10-15 minutes depending on the instrument.

Fourier transform infrared (FTIR) instruments, which have come into increasing use in the last ten years, are mechanically simpler. Rather than a moveable grating and slit, a Michaelson interferometer generates an interferogram containing all spectral

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[1] Kochbar, S. P. and J. B. Rossell, Spectroscopy 4 (4), 34 (1989).

[2] Henscheid, T. H. and H. R. Fisher, paper presented at Seventeenth General Meeting, A.S.S.B.T., 1972.

[3] Rearick, D. E., paper presented at the Twenty-Fourth General Meeting, A.S.S.B.T., 1987 and published in Zuckerindustrie, 114, 405 (1989).

information about the sample. The interferogram must be mathematically converted to a conventional frequency versus absorbance spectrum using a Fourier transform. Unlike dispersive spectrophotometers, an FTIR instrument analyzes all wavelengths simultaneously. A slit to admit only the light region of interest is not used and thus the full IR beam can be utilized. A more thorough description of FTIR spectrophotometry is beyond the scope of this paper but the technique has several advantages over dispersive spectrophotometry.

(1) Infrared beam throughput, from source to detector, is higher.

(2) Signal to noise ratio is higher.

(3) Since recording the complete spectrum requires only a few seconds, multiple scans can be accumulated and electronic noise averaged out.

The combined advantages of FTIR spectrophotometry produce a technique which can be used on much more difficult samples than dispersive IR. Dispersive IR techniques generally give good spectra only with materials that can be finely powdered or spread in a very thin layer. FTIR techniques can be used on thicker more opaque materials (such as fibers) and on extremely small samples.

B. Sugar Industry Applications of FTIR Spectrophotometry

Potential sugar industry applications of IR spectroscopy have been mentioned in earlier papers[2,3]. Briefly they include:

(1) Identification of process equipment scale. Organic salts such as oxalates and even polyatomic inorganic anions such as sulfate or carbonate give distinctive IR spectra.

(2) Identification of foreign materials in product. IR spectroscopy can assist in the identification of fiber, rubber particles, paint chips, and contaminants accidentally introduced by the customer.

(3) Identification of other materials of interest such as process chemicals, insulation, bagging materials, and lubricants.

Since FTIR is especially useful for difficult samples such as fibers, two separate application areas will be discussed: fibers associated with the sugar end and identification of factory insulating materials.

1. Sugar End Materials

Various pieces of equipment in the sugar end, for example sugar conveyor belts, contain fibrous material which can conceivably become a sugar contaminant. Organic fibrous samples,

due to their flexibility, cannot be treated by the most common IR analysis technique, grinding with potassium bromide. In our laboratory some samples had been characterized further by the pyrolysis technique[3] but this requires a fairly large sample and does not give direct information about the parent fiber. Such fibrous materials are generally too thick and opaque to obtain good spectra with a dispersive IR instrument. For example, in 1987, an unknown fibrous material recovered from a white sugar sample was scanned in our Perkin-Elmer 700 dispersive IR instrument producing the poor spectra shown in Figure 1. Really only a single peak at about 1710-1720 cm^{-1} can be distinguished. A small sample of this fibrous material was still on hand after purchased of our Perkin-Elmer 1600 FTIR instrument in 1989 and an IR spectrum was recorded using a few untreated fibers directly in the beam. The spectrum in Figure 2 shows a carbonyl (C=O) peak at 1718 cm^{-1} in addition to much fine structure. In fact, the spectrum is essentially identical to that of a known sample of polyester (Figure 3). With IR spectra of the quality shown in Figures 2 and 3 a suspected fiber source, such as a frayed conveyor belt, may easily either be shown to contain the same type of fiber or totally eliminated as the cause of a problem.

In another sugar end application of FTIR a small fiber sample isolated from sugar was found to contain the same type of fiber as a particular piece of sugar handling equipment (Figure 4). In this case, both samples are polyester. For these samples a beam condenser was used to focus the IR beam on a 1000 micron (1 mm) aperture or mask. Using this technique only enough sample is required to partially cover the 1 mm aperture, usually just a few individual fibers.

A final example of application to fiber analysis in the sugar end was the analysis of a fibrous sample recovered from a sugar end dust collector. The main question to be answered was whether or not the fibrous material was polyester from a frayed belt. The sample in question gave the IR spectrum shown at the top of Figure 4. The intense peaks at 3350 cm^{-1} (O-H bonds) and 1030 cm^{-1} (C-O bonds) are characteristic of carbohydrates and the spectrum is virtually identical to that of cotton fiber, as shown in the bottom half of Figure 5.

2. Identification of Insulating Materials

During factory maintenance and construction projects it frequently is necessary to disturb insulating materials that were installed before the health effects of asbestos were known. IR spectroscopy is not a trace analysis method for small amounts of airborne asbestos but does perform well in the identification of bulk insulating materials[4]. In fact, IR spectroscopy can be used not only to identify asbestos but to distinguish one type of asbestos from another. Proper precautions can then be taken during removal or disturbance of the insulating material.

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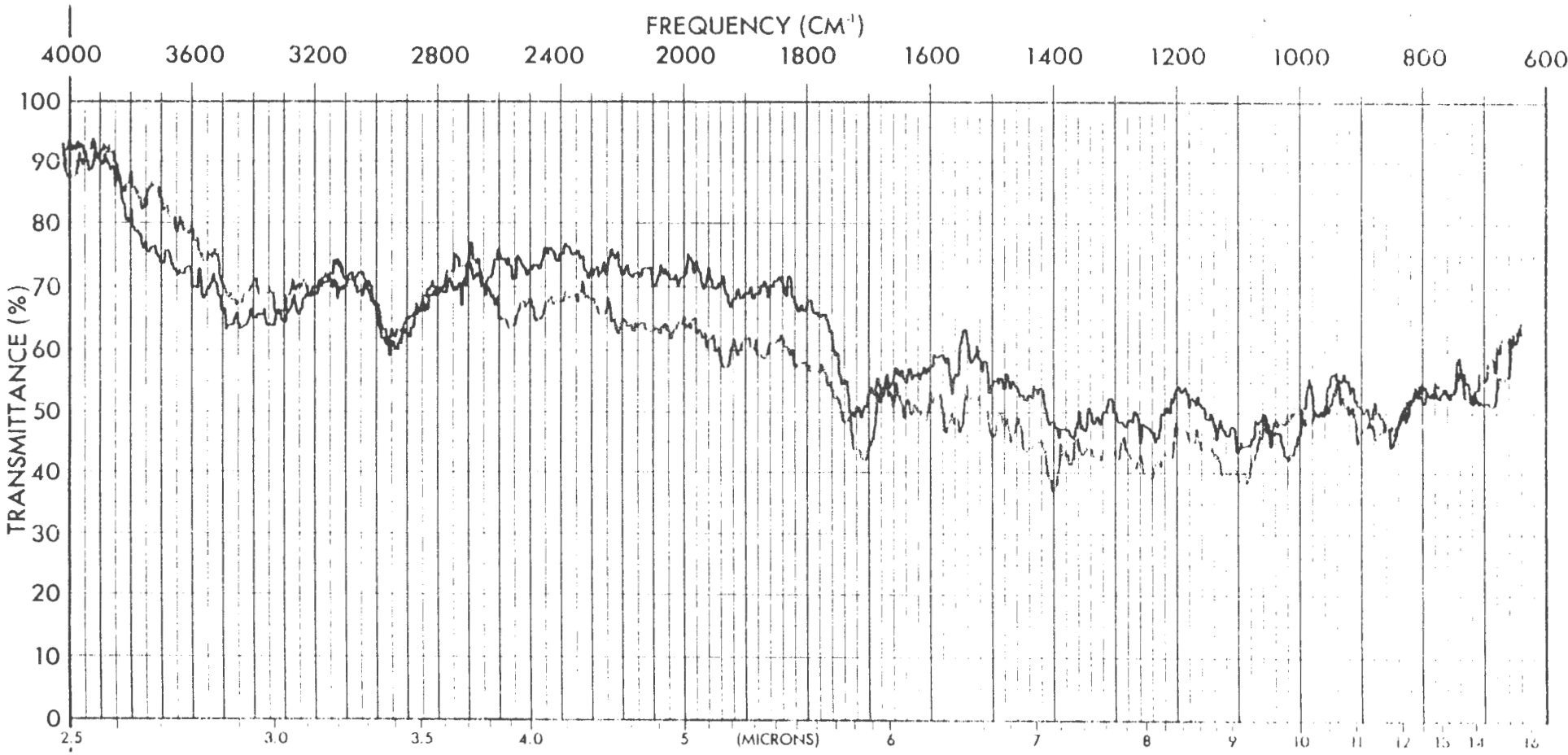
[4] Luoma, G. A., L. K. Yee, and R. Rowland, Anal. Chem. 54, 2140 (1982)

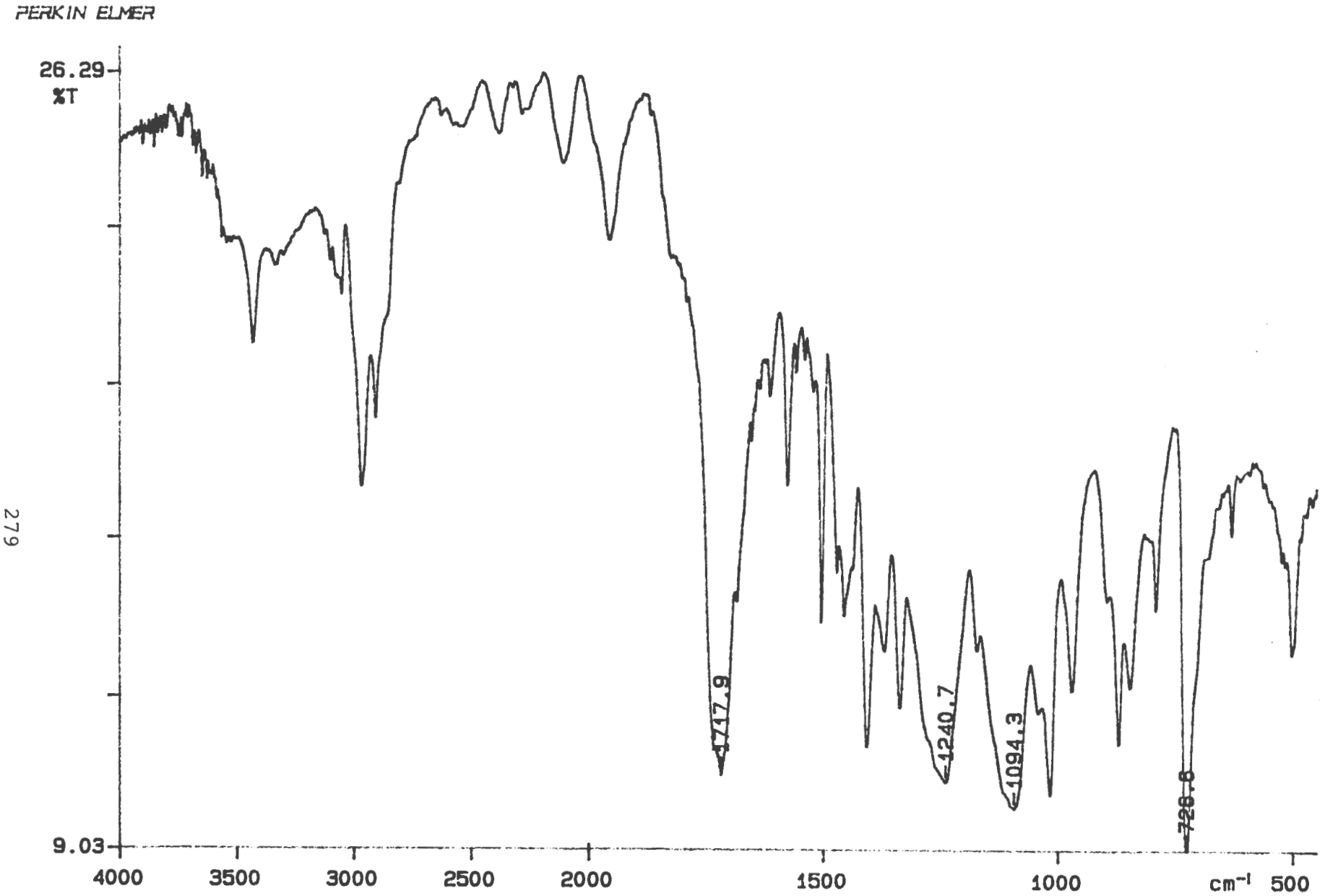
FIGURE 1

FIBER SAMPLE FROM SUGAR

FEBRUARY 24, 1987

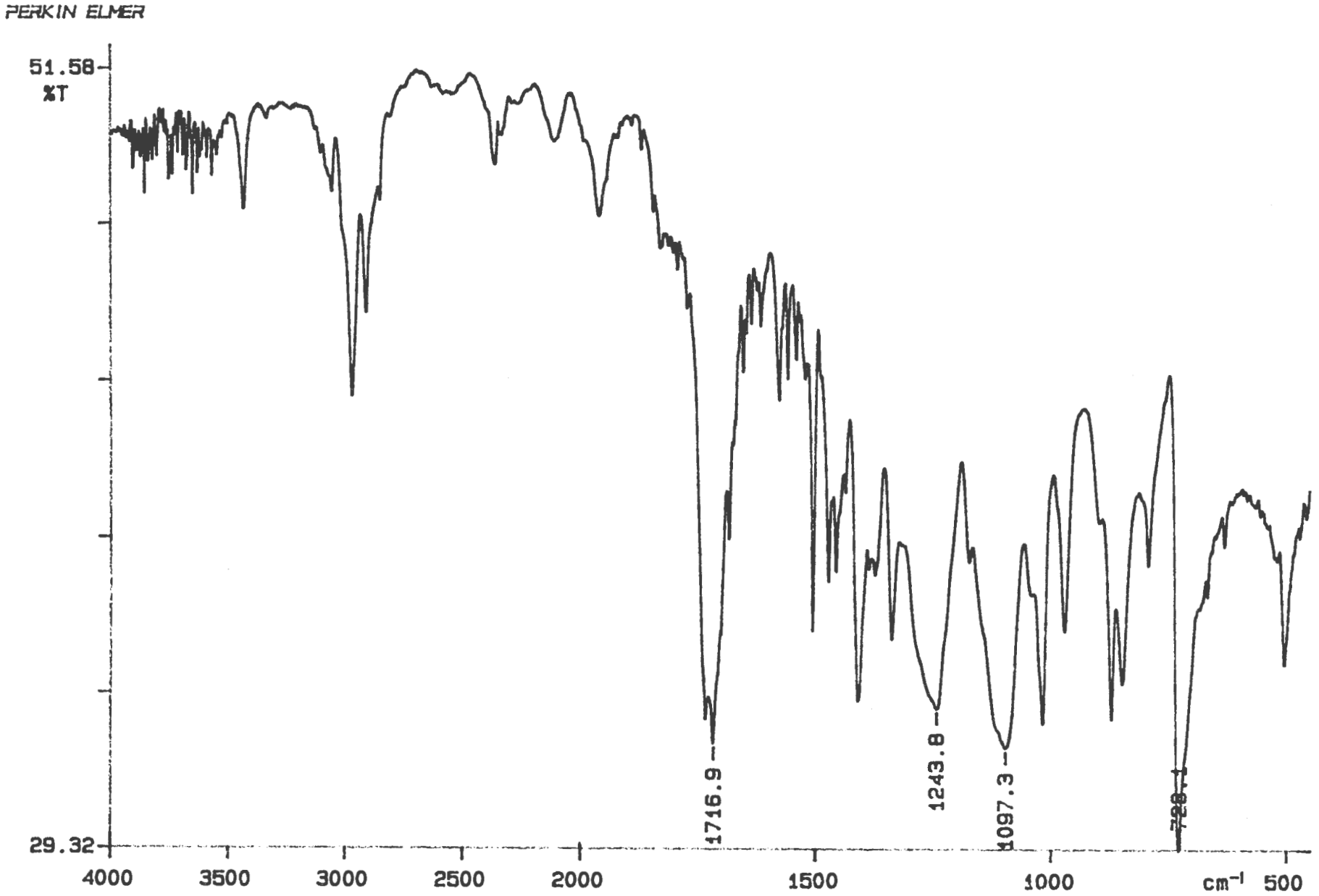
(Perkin-Elmer 700)
(Dispersive IR)





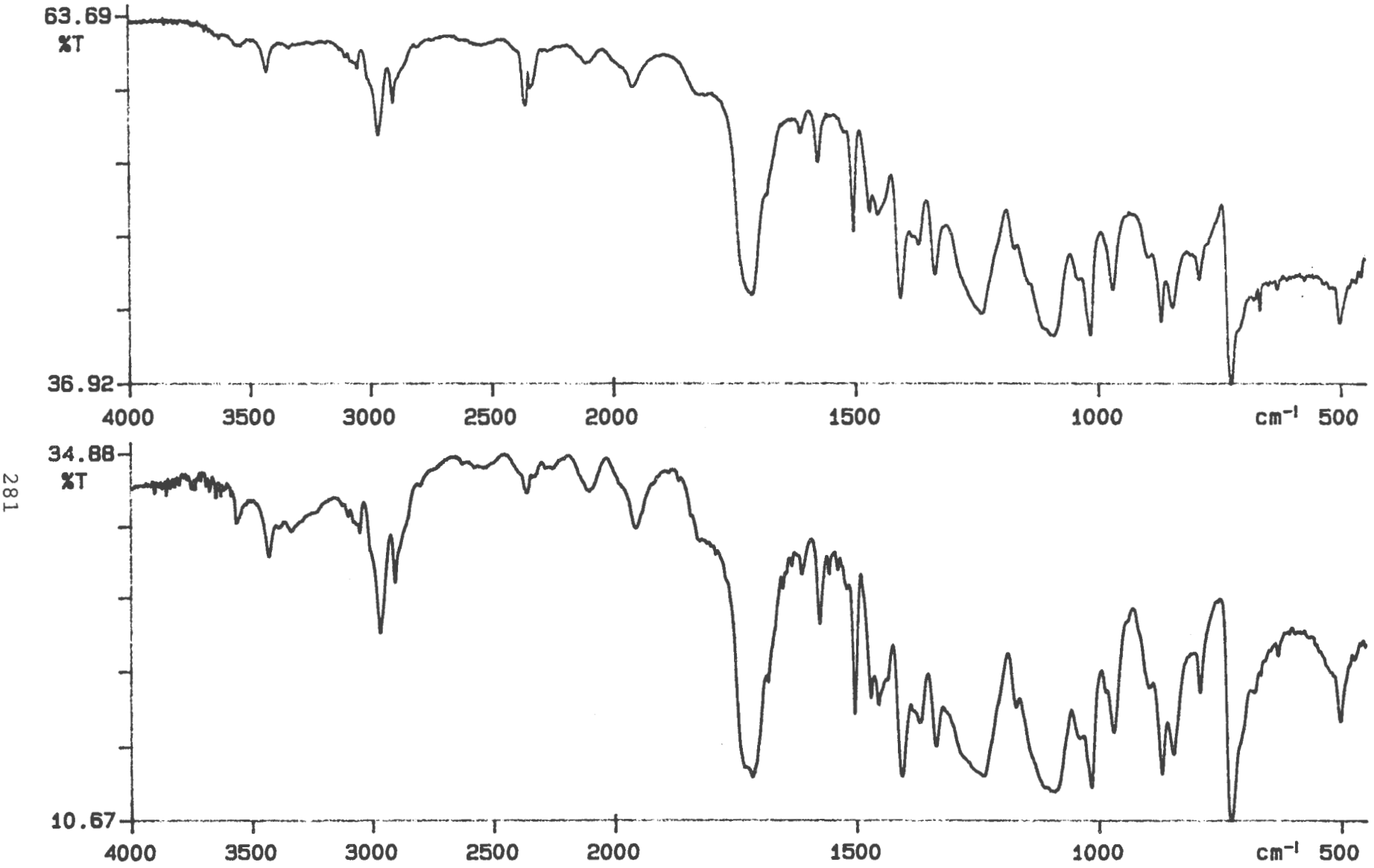
89/11/13 15:33
16 scans, 4.0cm-1

Fig.2 Fiber from white sugar

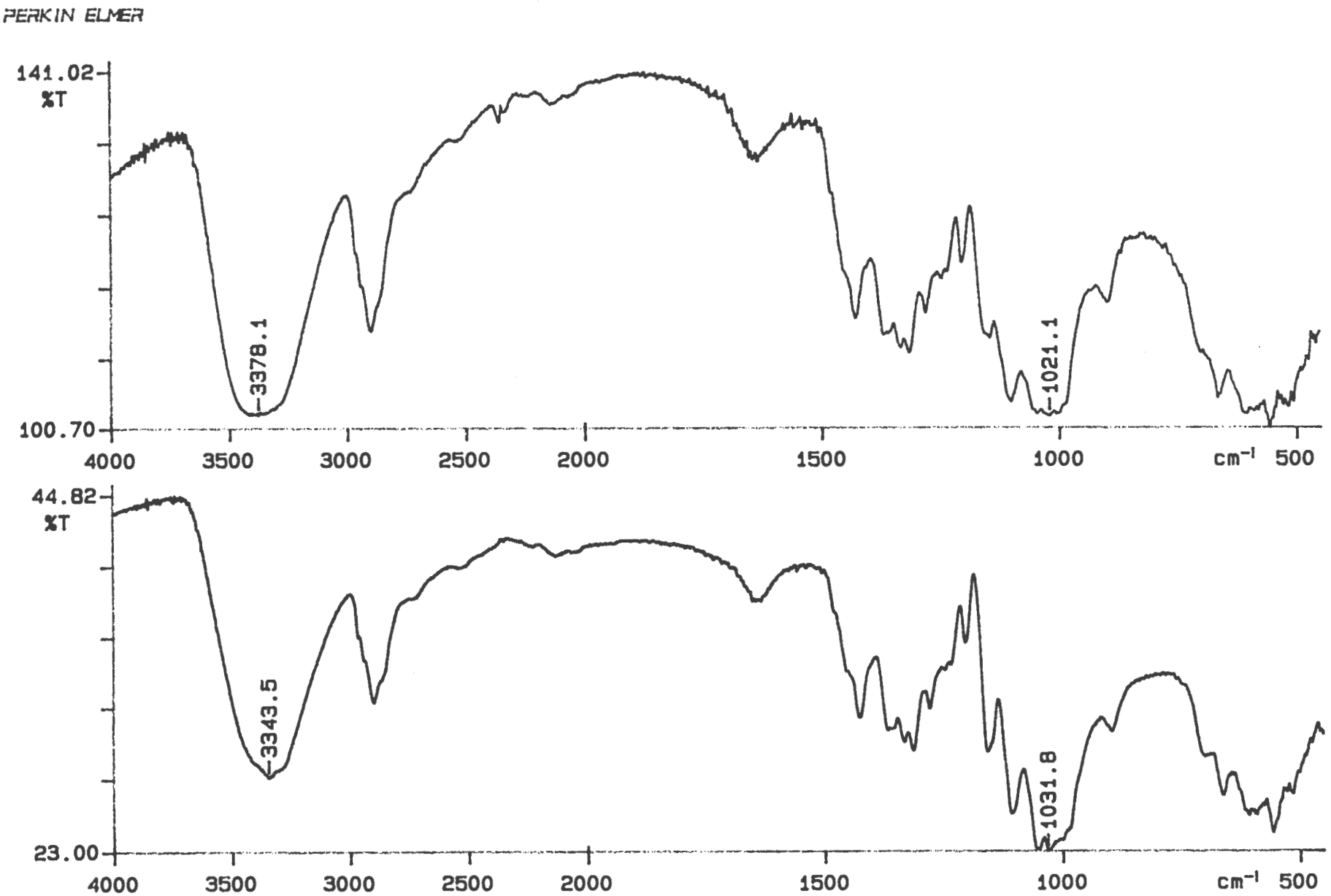


89/11/13 13:36
32 scans, 4.0cm-1

Fig.3 Polyester thread



89/06/08 09: 40
16 scans, 4.0cm-1
Fig.4 Top: Fiber from sugar Bottom: Fiber, equipment



90/12/12 10:06
mc90fb02: 16 scans, 4.0cm-1
Fig.5 Top: Dust collector samp Bottom: Cotton

Insulating materials usually contain non-fibrous binders such as calcium sulfate and in our laboratory the usual practice is to treat an insulation sample with approximately 15% hydrochloric acid to dissolve any binders. This generally leaves only the fibrous insulation components undissolved. After a simple washing with water and drying, the fibrous material is usually examined under a microscope to determine if the sample is homogeneous or if more than one type of fiber is present. A small fiber sample is then selected and subjected to FTIR examination.

An insulation sample from a factory steam line was treated as described and examined microscopically. A number of fairly coarse fibers were observed and examined further by FTIR spectroscopy. The spectrum shown in Figure 6 is typical of glass, showing only a broad, poorly defined peak centered around 1000 cm^{-1} (silicate absorbance). The fibers examined were evidently fiberglass but this particular insulation illustrates one precaution that must be taken when examining very small samples: the need to insure that the portion analyzed is representative of the bulk sample. In this case it was obvious from examination under the microscope that a second type of fiber was also present. A small sample of these long, fine fibers was analyzed by FTIR and the spectrum shown at the top of Figure 7 was obtained. The strong silicate absorbance at 900-1000 cm^{-1} is found in most minerals but the peaks at 594 cm^{-1} and especially the two sharp absorbances at 3686 and 3647 cm^{-1} are characteristic of chrysotile asbestos (bottom of Figure 7). Chysotile, the fibrous form of serpentine (a magnesium silicate), is the most common asbestos and accounts for about 90% of the asbestos in use[5]. Thus microscopy should be used in combination with FTIR to verify that small samples represent all of the fibrous material present.

Of the numerous insulation samples examined in our laboratory one of the more interesting ones gave the infrared spectrum shown at the top of Figure 8. Again the strong peak at around 1000 cm^{-1}, characteristic of silicates, is present but notice the absence of the strong 3686 and 3647 cm^{-1} peaks present in chrysotile spectra. The peaks at 472, 636, 703, and 772 cm^{-1} are characteristic of amosite asbestos, as shown in the bottom of Figure 8. Amosite is one of the amphibole asbestoses. Amphibole asbestoses were never used as commonly as chrysotile but at high levels have been directly implicated in the occurrence of mesothelioma, a rare type of cancer, among asbestos miners and millers. Although in the United States all asbestos varieties are considered equally hazardous, many countries, particularly in Europe, regulate use of amphibole asbestos more stringently than chrysotile asbestos[5]. Obviously any insulation sample containing fibers with an infrared spectrum so nearly identical to amosite (Figure 8) has to be taken quite seriously. The other most common members of the amphibole group, crocidolite (blue asbestos) and anthophyllite can be

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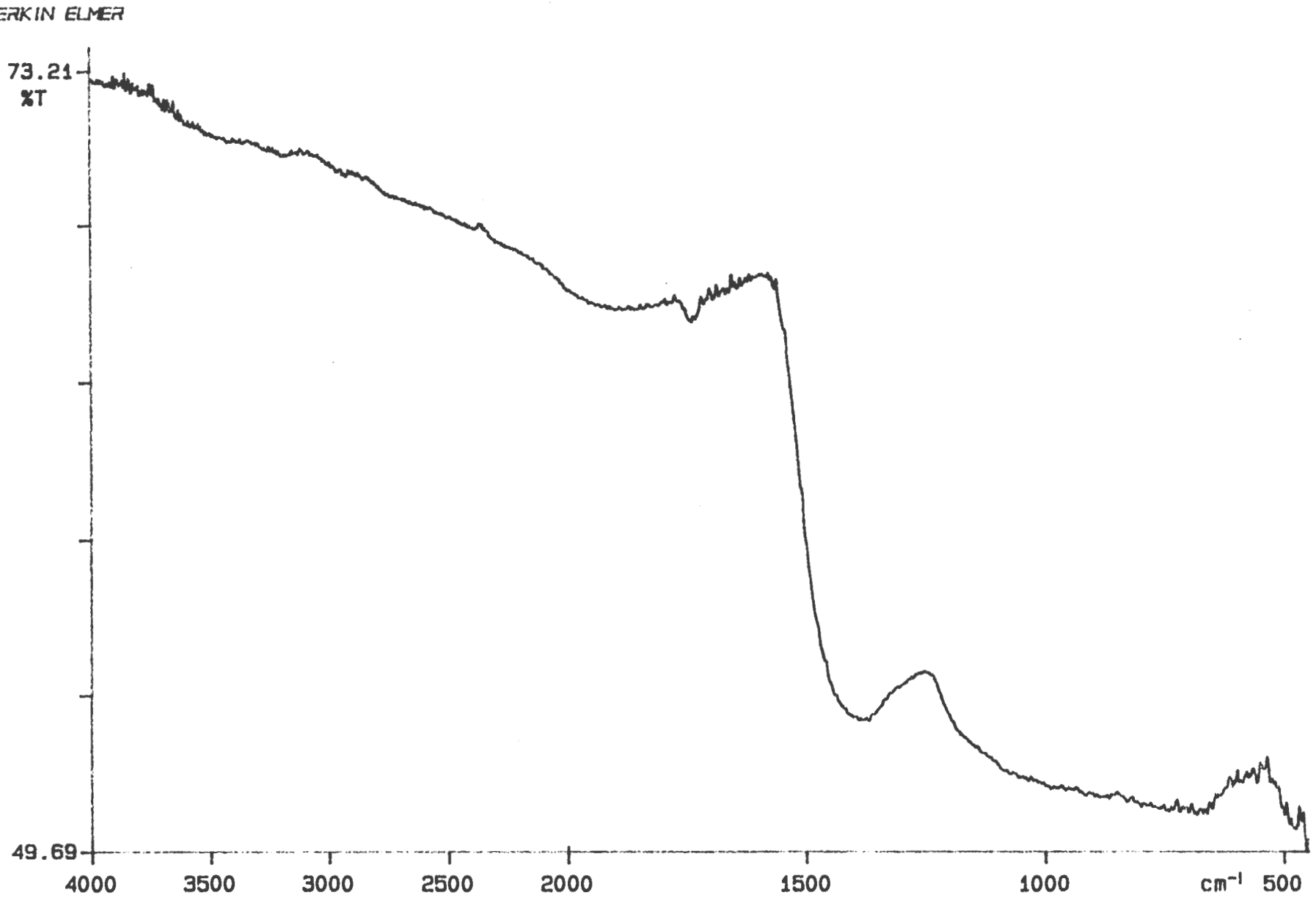
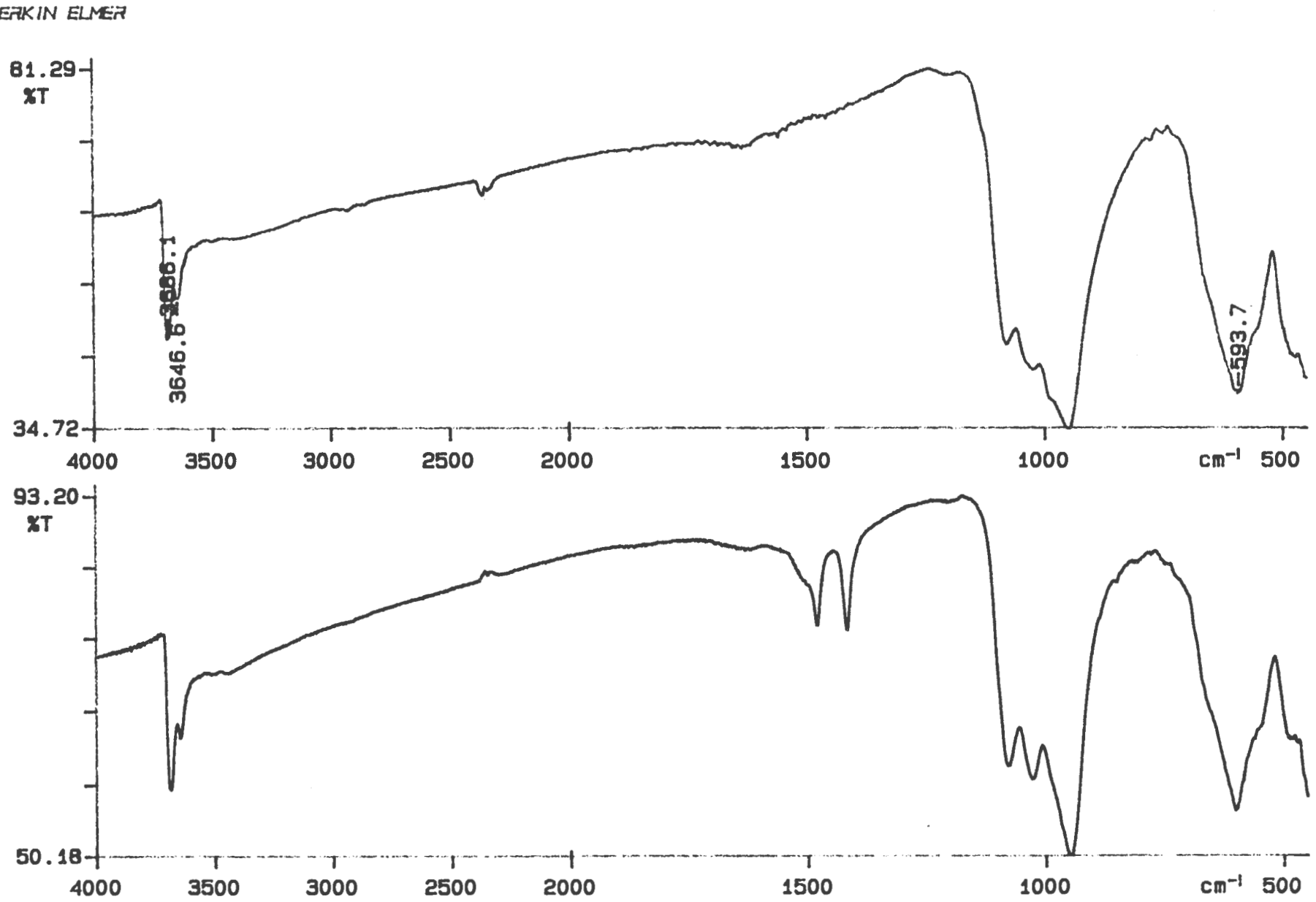
[5] Mossman, B. T., J. Bignon, M. Corn, A Seaton, J.B.L. Gee, Science, 247 294 (1990)



90/03/09 15:08
tfins114: 16 scans, 4.0cm-1
Fig.6 Steam line insulation, coarse fibers



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tfins113: 16 scans, 4.0cm-1
Fig.7 Top: steam line, fine fibers bottom: chrysotile

90/03/21 10:59
tf90in01: 16 scans, 4.0cm-1
Fig.8 Top: uknown insulation Bottom: amosite

distinguished from other asbestos varieties by FTIR spectroscopy although they have not been encountered in our laboratory, except as standard samples.

Other than fiberglass and asbestos varieties the only other fibrous insulating material encountered in our work is cellulose (cotton) which has an infrared spectrum (see Figure 5) unmistakable from either fiberglass or asbestos.

In summary, FTIR spectroscopy can give very useful information and assist in identification of fiber samples directly even when the amount of sample is very limited.

EXPERIMENTAL SECTION

All infrared spectra were, unless otherwise noted, recorded on a Perkin-Elmer 1650 FTIR spectrophotometer equipped with a DTGS (deuterated triglycine sulfate) detector, at 4 cm^{-1} resolution. Fiber samples were analyzed using a Perkin-Elmer 1700 microfocus attachment, which focuses to a beam diameter of about 1.5 mm. Samples were attached to a 1000 micron circular aperture beam mask for analysis.

Standard reference asbestos samples were obtained from Duke Scientific Corporation, Palo Alto, California. Because asbestos standards were obtained in a powder form, standard spectra were recorded using potassium bromide pellets.