FIBER PROBES FOR NEAR AND MID INFRARED SPECTROSCOPY

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ABSTRACT

Recent developments of specialty silica and non–silica optical fibers in synergy with innovative designs of fiber catheters, bundles and probes have promoted the growth of various fiber applications. There are three main areas of fiber usage: telecommunications, fiber sensing and assisted remote spectroscopy and laser power delivery. This paper briefly reviews only the exciting area of fiber applications to remote specroscopy.

SPECIALTY OPTICAL FIBERS

In contrast with telecom fibers, where the commercial technology of standard silica fibers has essentially reached the level of intrinsic optical losses at several wavelengths and the cost of these fibers is less than 10 cents per meter, specialty optical fibers for various other applications are still in the dramatic, early stages of development of their manufacturing technologies and engineering design. Silica and non–silica fibers for laser power delivery in medical and commercial applications have been reviewed in other conferences, but the main types and their properties are mentioned here for comparison with specialty fibers for remote spectroscopy.

The family of fibers for laser power delivery consists of large–core pure silica fibers, rare earth doped "laser" fibers and several types of non–silica IR–fibers; namely, chalcogenide fibers, fluoride and chalcogenide glass fibers, polycrystalline silver and thallium halide fibers, single crystall sapphire fibers and the hollow metal and dielectric waveguides. The specific features of these specialty fibers are determined by their application demands. They must possess not only minimal optical losses at laser wavelengths, but also a high threshold for laser induced damage, high flexibility and special metallic or polymer coatings which are resistant to high temperature. Further the fibers should not be hydroscopic nor toxic, especially for medical laser applications. Silica fibers, when fabricated with pure silica cores and thin fluorine doped cladding, possess these requirements. For high transmission in the near IR [NIR] region, 1 to 2.7 μm, the silica core glass must be purified to a super dry level, less than 1 or 0.1 ppm of OH content, in order to provide low optical losses and high thresholds to laser induced damage by holmium:YAG lasers at 2.1 μm and chromium–thulium–erbium lasers at 2.69 μm. Using super dry silica preforms, Corning and CeramOptec have produced fibers approaching the intrinsic limit with losses of 6 dB/m at 2.69 μm. In contrast with the super dryness required for NIR–silica, the requirements for silica in UV transmission, especially of intensive pulses of excimer lasers at 308 and 248 nm are satisfied by using high OH–content (800–1000ppm) silica and suppressing the process of laser induced color center formation. The latter are responsible for the drop in fiber transmission under intensive UV–laser pulse-periodic power delivery.

In improving specific parameters for laser power delivery, the fibers also become better candidates to satisfy specific demands in remote sensing applications. Thus polycrystalline IR fibers present an interesting applications development history ranging from IR imaging [mainly for military purposes: IR–lidars, IR–horizon seekers, IR–early alarm systems] to CO_2–laser power delivery in laser medicine. Among these silver halide MIR–fibers [Mid IR] have become the most promising fibers for remote IR–spectroscopy. To reach low optical losses at 10.6 μm of 0.1 to 0.5 dB/m and the capacity to transmit laser power outputs as high as $30kW/cm^2$ [corresponding to $40–50kW/cm^2$ input power], the extrusion technology was developed to reduce extrinsic absorption. This has lead to a suppression of the extrinsic absorption peaks in the MIR–fibers over the range of 4 to 16 μm, and thus enhancing and simplifying their use in spectroscopy applications.

These developments have lead to a fast growing family of fiber sensors covering more and varying application areas: fiber optic gyros for navigation systems; remote measurements of temperature, of electric and magnetic fields; acoustic, pressure and position sensing; distributed and multiplexed fiber sensing in chemical process control and in medical diagnostics, etc. In the paper we will concentrate, however, only on some specialty fibers for remote spectroscopy.

SPECIALTY FIBERS FOR REMOTE SPECTROSCOPY

As described earlier, silica based fibers improved in transmission for UV– or NIR–laser power delivery provide simultaneously a unique opportunity to cover a wide spectral range providing for the control of chemical processes or for the monitoring of environmental pollutants through the use of remote spectrometers, positioned from a few meters to 1 km away from the sensing site. The broad range of suppressed extrinsic absorption in the MIR–fibers, likewise permits remote sited spectrometers to control or monitor processes/chemicals absorbing in the 4–16 μm region.

There are at least 3 different types of fiber design for spectroscopy uses.

I. Transmission or reflection fiber probes employ transmission or reflection spectra at the distal end of the fiber, which consists of single– or multi–fibers cable with or without collimating optics at the end. Specific requirements for the silica fibers in such probes are not very different from those required for laser power delivery: high transmission in the UV– or NIR– region and cladding of minimum thickness for high flexibility and dense packing in bundles. Suppressed color center formation and the use of high temperature resistant coatings enhance the durability of the fiber probes for applications under conditions of intensive irradiation or high temperatures in hazardous environments.

The geometry of the bundle ends can be optimized for efficient optical coupling with various light sources, monochromator and spectrometer slits, arrays of photoconductors and optical cells at the distal ends [Figure 1]. For example, a typical kind of Y–shaped reflection probe, used for rapid identification of solid samples without preparation, is very simple in design; one bundle of fibers brings the light from the FT–IR spectrophotometer to the distal end, where the fibers are randomly mixed with fibers from another bundle which bring the reflected light to the detector. Such probes allow straightforward use by untrained personnel for in–line or non–invasive control of liquid or solid samples [even in powder form] without time–consuming sample preparation. A Y–shaped or bifurcated silica fiber bundle is one of the most popular accessories for NIR–spectroscopy [such as Bruker IFS/NIR FT–IR spectrometers]. Another design is the ring–type catheter for photodynamic diagnostics of tumors [PDD]. It consists of a central fiber for the delivery of laser light to excite the tissue fluorescence and the surrounding fibers in the ring to collect this fluorescent signal and deliver it to the spectrometer. Such a devise might also be used to deliver the intensive laser light for the destruction of the tumor cells [PDT PhotoDynamic Therapy].

A new family of simpler, more dedicated devices do not use expensive spectrometers and are called process–photometers. Due to the practical need to control only several components for most industrial processes, such process–photometers consist of a light source, interference filters and optical cells connected to the photometer by optical fibers. The choice of filters is determined by the specific wavelengths which characterize the controlled components. Multiplexed fiber photometers for real time in–line or non–invasive control are available now – Perkin–Elmer Models FAGOS 100 or PIONEER 1024. These provide a smart way for achieving high quality products in the petroleum, pharmaceutical and other fabrication areas as well as for environmental monitoring.

II. Evanescent fiber probes and sensors are based on the physical effect of partial penetration of the electromagnetic field at the lateral surface of a bare fiber core into the surrounding media, as light propagates through the fiber core. A corresponding spectrum of the surrounding media absorption appears in the fiber spectrum. For evanescent sensors IR–fibers are preferable for the reasons summarized in the table below. The family of commercially available IR–fibers consists of : glass fibers – fluoride–based for 2–4 μm, and chalcogenide–based for 2–12 μm regions; and polycrystalline MIR–fibers for 4–16 μm. More exotic chalcohalide glass fibers and single crystal sapphire fibers are still at the R&D stage.

Mid IR region [2.5–20μm]	Near IR region [1–2.5μm]
Fundamental bands with high absorbances	Overtone, combination bands with low absorbances [0.01–0.001]
Sharp, isolated peaks with easy quantization	Strong peak overlap with complex quantization, chemometrics necessary
High resolution gives more information, spectral libraries are available	Low resolution needs high S/N & reproducibility, many spectra are "unknown"
High sensitivity, hence trace analysis possible	Low sensitivity, unable to do trace analysis

A comparison of polycrystalline MIR–fibers, extruded from crystals of solid solutions of AgCl:AgBr, reveals their advantages over the other IR–fibers. An MIR–fiber spiral probe is shown in Figure 2 along with a sample spectrum.

In contrast with typical spectra of fluoride and chalcogenide glass fibers with their multiple absorption bands from impurities, MIR–fibers possess wide and smooth transmittance spectra [Figure 3], that coincide with the so–called "fingerprint" spectra for most molecular vibrations. Other advantages include that MIR–fibers are non–toxic in comparison with chalcogenide fibers; non–hydroscopic in contrast with fluoride fibers; very flexible in contrast with the fragility of both the IR–glass fibers; and their melting temperature, ~700K, is substantially higher than the IR–glass transition points, ~500K.

Silver halide fibers were developed within the last 10 years in Israel [Tel–Aviv University], Russia [General Physics Institute] and Japan [Matsushita, Sumitomo, Asahi Glass Co.]. Now bare core and core/clad MIR–fibers are commercially available from the group of CeramOptec Companies in Germany, USA, Russia and Malaysia.

The synergy of novel MIR–fibers with IR–spectroscopy in the "fingerprint" region opens unique opportunities for in–line control of chemical processes, for in vivo medical diagnostics and in situ environmental pollutant monitoring. Trials of the first MIR–fiber prototype accessories with FT–IRs and tunable laser diode spectrometers reveals very promising results. Sample spectra, obtained with an evanescent MIR–fiber probe connected to a Bruker IFS–113v FT–IR spectrometer, are shown in Figure 4. These spectra were measured with a bare core 700μm diameter fiber – inserted into beer [A]; inserted into petroleum [B]; or in contact with malignant or healthy human lung tissue [C] over 1–2cm. Identification and calibration of various spectra would permit use in food quality control – e.g. alcohol, protein, or sugar content – or in petrochemical, chemical or polymer curing process monitoring for the real time feed back control needed for the automatization of high quality manufactured products.

MIR–fiber spectroscopy creates the opportunity for new kinds of medical diagnostics for in vivo early discovery of cancerous tissue without the need to inject potentially hazardous photosensitizers as in PDD; for non–invasive monitoring of glucose in the blood of diabetics; and for many other diseases which are characterized by changes in the molecular composition of the human body.

For environmental monitoring, the sensitivity of evanescent MIR–probes can be enhanced substantially if their lateral surface was coated with polymers or porous cladding that accumulate small traces of distinct chemicals from the immersed medium; air, water, etc. Recently Professor Kellner's group at Vienna University enhanced the detectability of chlorinated hydrocarbons in water to the level of 1 ppm with MIR–fiber probes coated with a thin layer of polyethylene. In Dublin City University, Drs. Vince Ruddy and Kevin Lardner detected 2.5% by volume of methane in air samples exposed to fluoride fibers clad with polytetrafluoroethylene, using an absorption peak at 3.36 μm.

III. Fiber probes with optrodes, i.e. special porous distal tips or fluorescent layers at the output fiber ends, represent another approach where classical fibers are combined with a target whose spectrum is sensitive to its environment. Such fiber sensors are described in numerous recent publications and conference proceedings and their description will thus not be dealt with in this short review.

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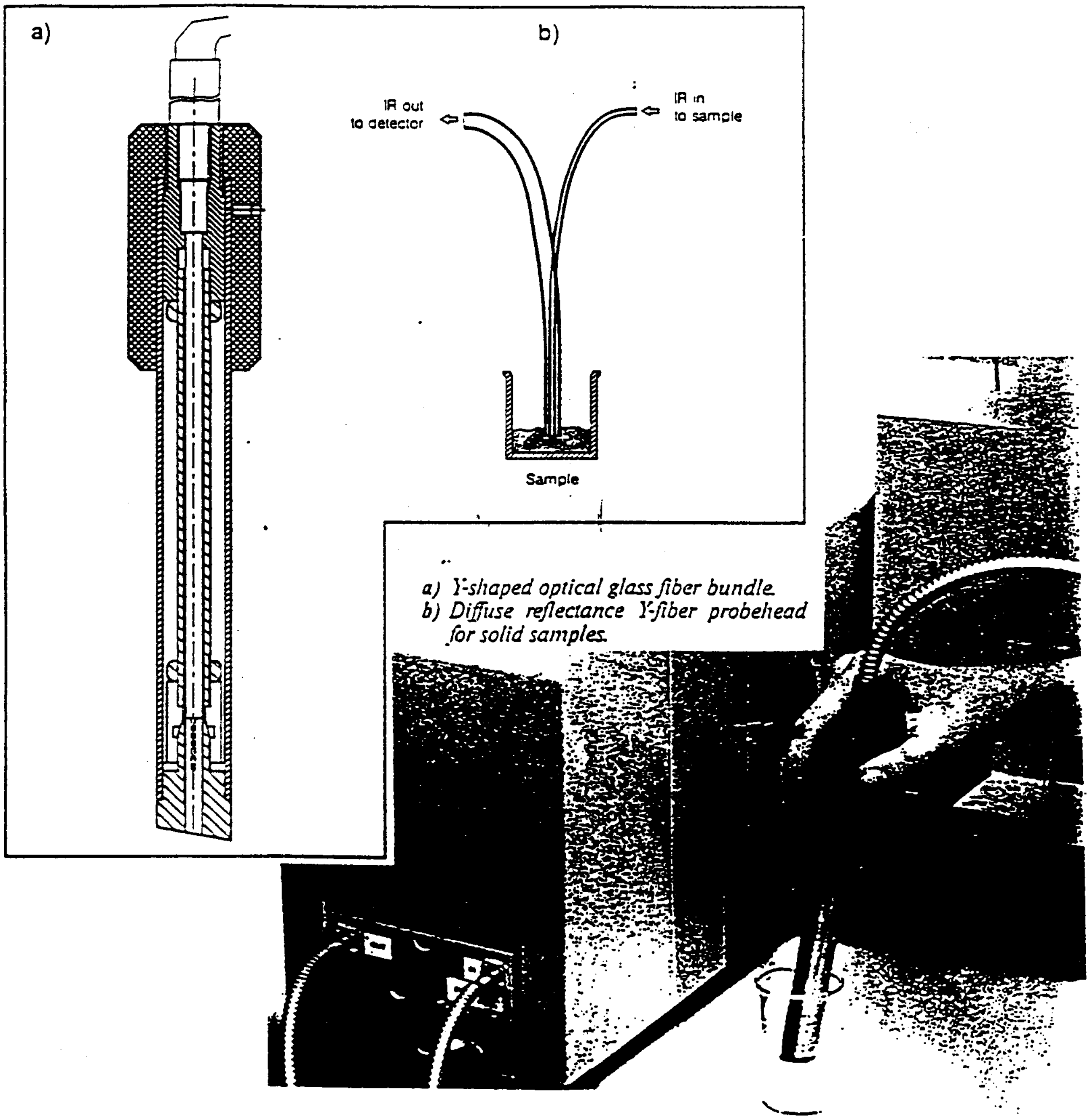

Fig.1 Y-shaped silica fiber bundle probe for diffuse reflectance remote spectroscopy in Near IR, connected with "Bruker" FT-IR spectrophotometer

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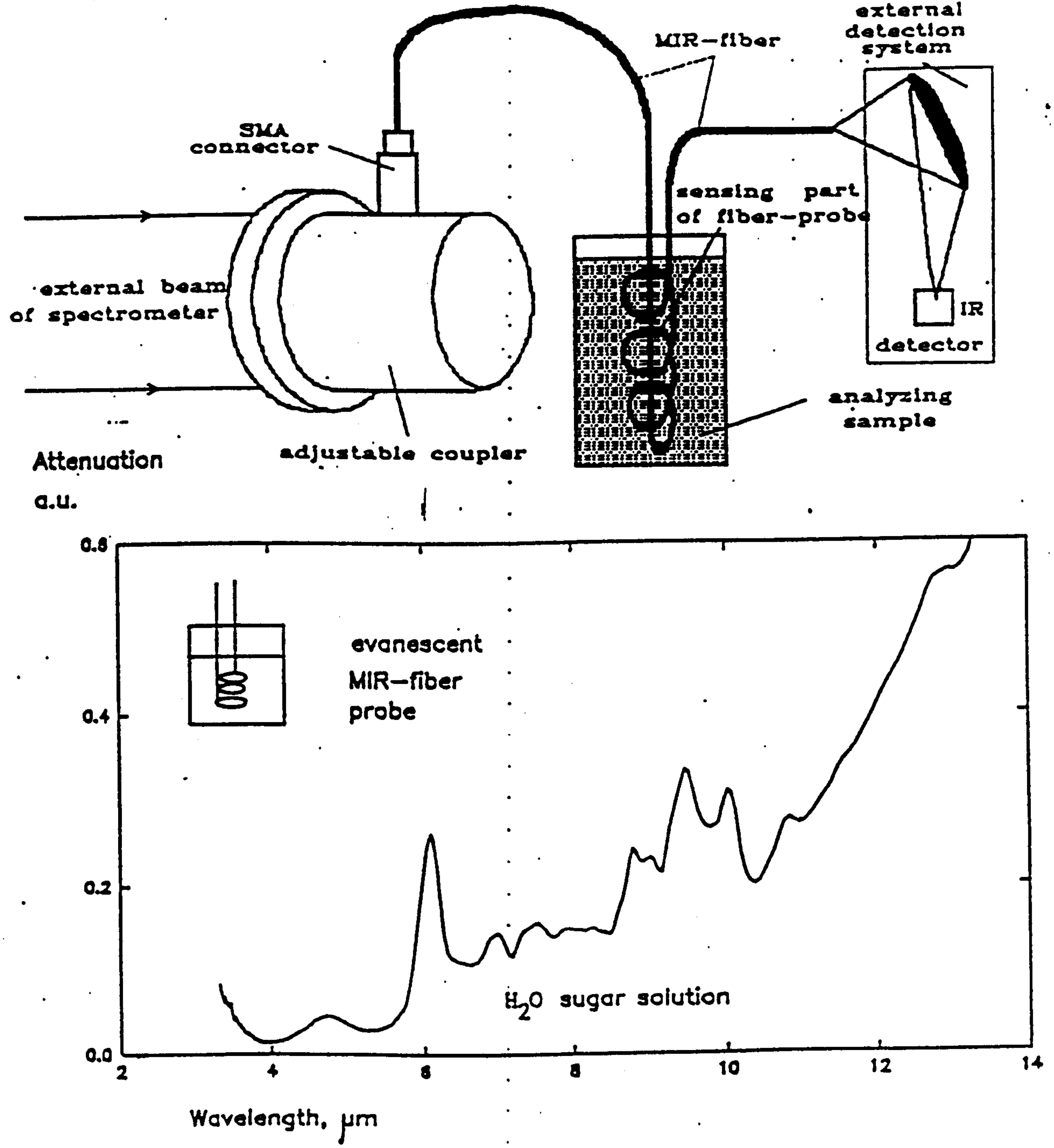

Fig.2 Spiral evanescent probe, based on bare core MIR-fiber

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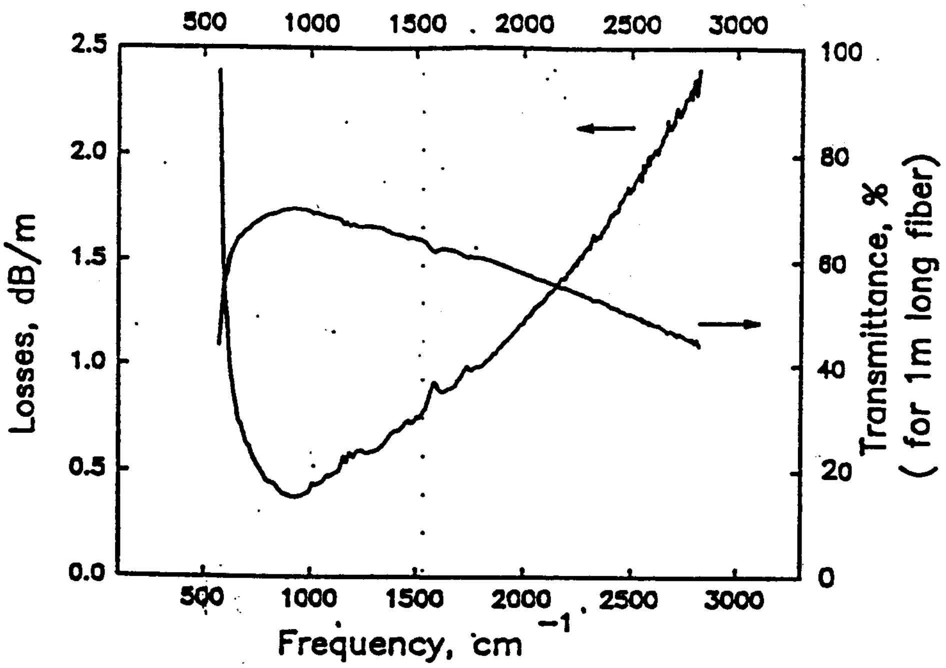
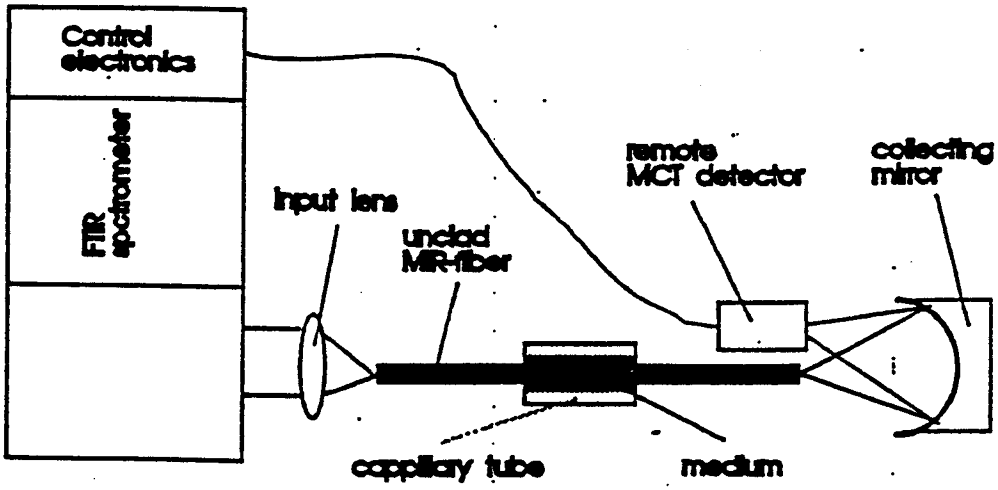


A : Spectra loss and transmittance of unclad MIR-fiber.



B . Experimental setup.

Fig.3 Bare core MIR-fiber for evanescent IR spectroscopy with FT-IR spectrophotometer

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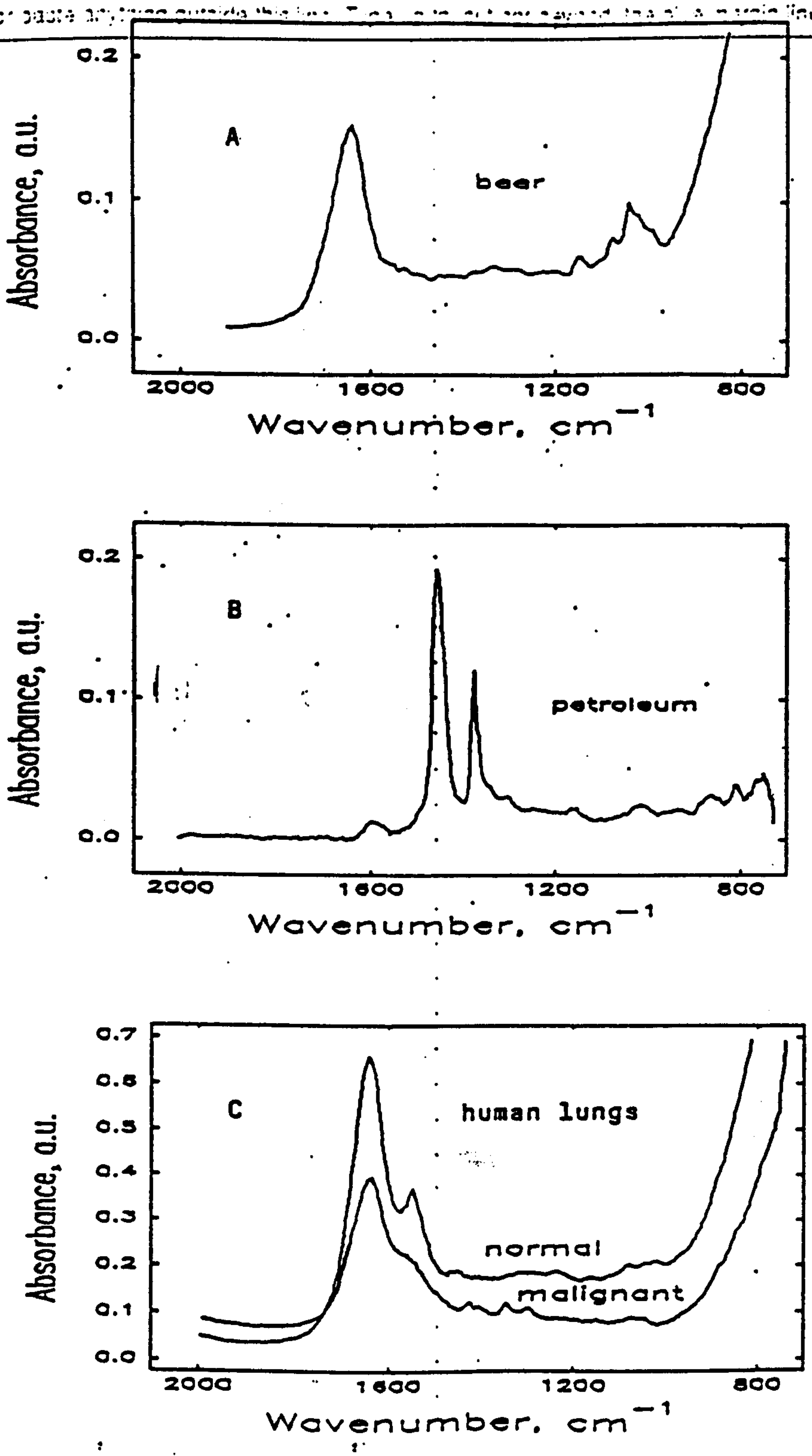

Fig.4 Evanescent spectra with MIR-fiber probes