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Mid-IR fibre optics spectroscopy in the 3300–600 cm^{-1} range

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ABSTRACT

The latest development in IR fibre optics enables to expand spectral range of process spectroscopy from 3300 to 600 cm^{-1}. Mid-IR wavelength range from 5000 to 1700–1000 cm^{-1}may be covered by chalcogenide IR glass (CIR) fibres while polycrystalline infrared (PIR) fibres made of silver halides solid solutions transmit radiation of the whole most informative "finger-print" part of the spectrum from 3300 to 600 cm^{-1}. PIR fibre based immersion ATR probes had been manufactured and successfully tested with FTIR spectrometers in the field of remote spectroscopy of chemical reaction and fuel analysis. The sensitivity of different ATR elements, performance and permanence of the probes are considered in temperature range 20–150 °C.

1. Introduction

Oxygen-free polycrystalline infrared (PIR) fibres manufactured from silver halides solid solutions $AgCl_{1-x}Br_x$ [1–5] are the main material for middle-IR fibre optics. These innovative fibres enable to expand spectral range of process-, in situ- and in vivo-spectroscopy from 3300 to 600 cm^{-1} (3 μm up to 17 μm).

Up to now fibre systems are already produced for broad variety of process-control application using transmission, reflection, fluorescence and Raman spectroscopy but their spectral range is limited to transmission of silica fibres from 50,000 to 4200 cm^{-1}. Nowadays the longer mid-IR wavelength range from 5000 to 1700–1000 cm^{-1} may be covered by chalkogenide IR-glasses while polycrystalline IR-fibres made of silver chloride–bromide solid solutions can cover the whole "finger-print" range of the spectrum from 3300 to 600 cm^{-1}, i.e. its the most informative part on absorption bands of specific molecular vibrations. As a result mid-IR fibre probe spectroscopy is successfully used as an effective measuring tool for molecular analysis of liquids and solids [2,5,6].

The present discussion of PIR fibre probes is intended to compare the sensitivity and general performance of PIR fibre probes with different ATR elements: cones made of ZnSe, diamond and Ge and PIR unclad fibre loops of different shape.

2. Experimental

ATR fibre probe had been designed as suitable for the application in the laboratory environment. ATR fibre probe appearance and construction are presented in Fig. 1. Three ATR-probes have been manufactured for this investigation using ZnSe, Ge and diamond cones of 3 mm diameter (Fig. 1b) as ATR elements with minimal two-bounce internal reflection.

PIR fibre with core-clad diameter 900/1000 μm was used for probe fabrication. The probes had bifurcated design and fibre length was 1.5 m from connectors to probe tip. Titanium, Hastelloy C276, and PTFE were used as construction materials for the probe tip. Durable PEEK polymer (poly-ether-ether-ketone) and flexible metal jackets were used for fibre protection. SMA-905 optical fibre connectors enable the coupling with most of spectrometers. Probe tip with outer diameter 12 mm and immersible length of 250 mm had been manufactured to be compatible with LabMAX reactor fabricated by the 'Mettler Toledo' company. The probe tip had no recesses that would allow hang upon of materials and was sealed hermetically to withstand the pressure ≤ 100 psi.

The ATR element of the immersion probe directly contacts with investigated substances so it should be made of chemically resistant and mechanically durable material. Some materials such as ZnSe, Ge, Si and diamond can be used for this purpose in wavenumber range 3300–600 cm^{-1}. Some drawbacks of these materials limit their application. ZnSe element is the most preferable due to its optical properties for the measurements connected with biological solutions and tissues as well as food and

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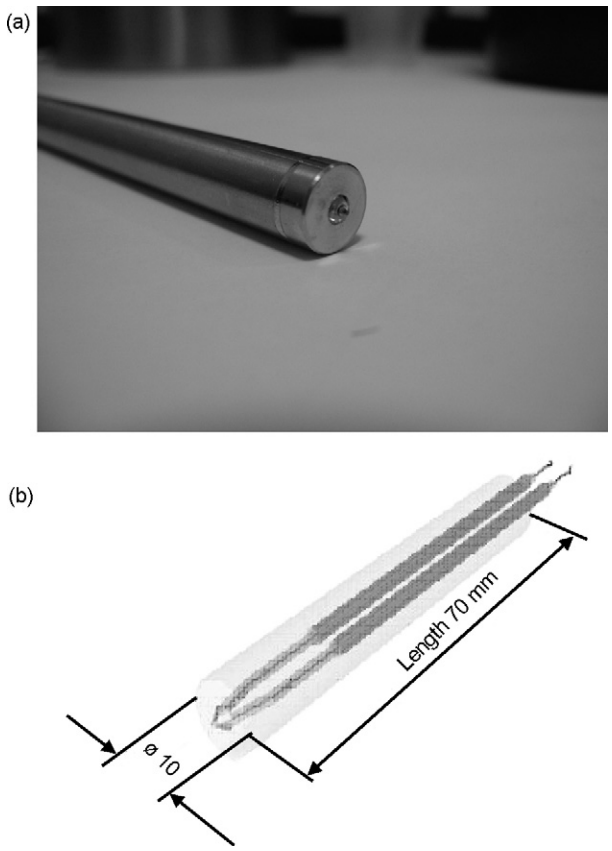

Fig. 1. Appearance (a) and design (b) of fibre probe tip with ATR cone element.

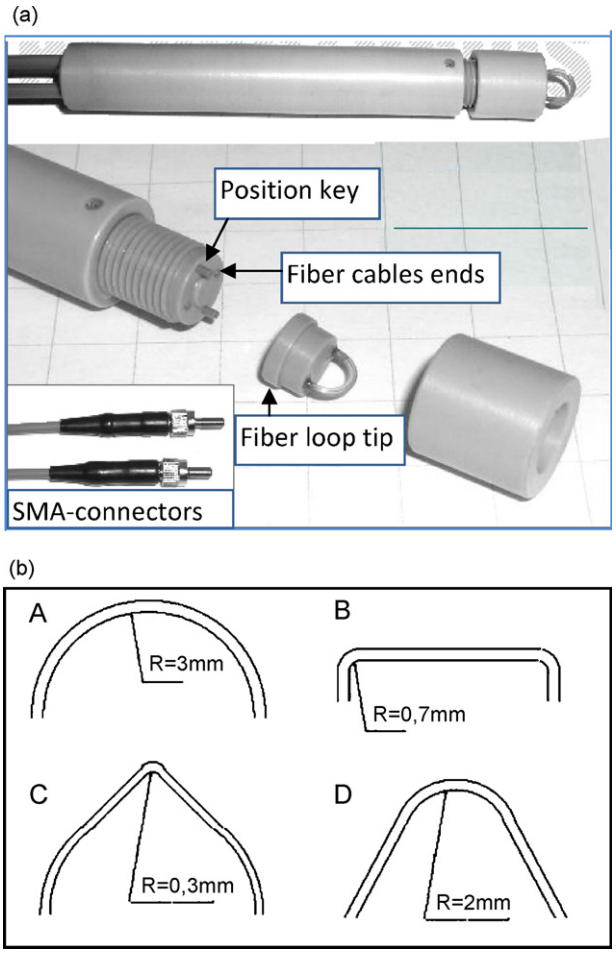

Fig. 2. Appearance and design of fibre probe tip with detachable loop ATR element (a). Disposable fibre loops of different shape (b): standard U-shaped (A), "rectangle" (B), "triangle" (C) and V-shaped (D).

drugs inspection "in vitro". However, this material is toxic so it cannot be used in medicine or cosmetology for "in vivo" spectroscopy. Ge and Si are non-toxic and chemically stable but high refractive index of these materials provides low sensitivity of ATR elements. The same circumstance enables the high signal transmission through the element due to small divergence of radiation beam in this material so its use is well founded in most cases. The diamond is the most preferable for ATR element fabrication but a wide absorption gap at 2000 cm^{-1} limits its application, for example, for the analysis of some catalyses and petrochemical products.

AgClBr polycrystalline fibre itself is appropriate material to make ATR element [4,5,7]. The piece of unclad fibre serving as sensitive element is inexpensive, can be easily replaced up to the disposable and offers the possibility to reach higher sensitivity by means of fibre bending.

ATR probe with a detachable fibre loop tip has been designed and manufactured. ATR fibre probe appearance and construction are presented in Fig. 2. PIR fibre with core-clad diameter 900/1000 μm was used for probe fabrication. Unclad PIR fibre of 1000 μm diameter was used to fabricate disposable tips with fibre loops of different shape. No coupling elements were used between core-clad fibre and fibre loop tip. Fibre ends face-to-face distance was about 100–200 μm. The probe had bifurcated design and fibre length was 1.5 m from connectors to probe tip. Probe handpiece of 14 mm diameter and 80 mm length was made of PEEK polymer. PTFE ring was used to seal fibre loop tip hermetically to the probe handpiece. PEEK polymer tubes were used for fibre protection. SMA-905 optical fibre connectors were used for fibre termination.

Estimated characteristics for all the probes were signal-to-noise ratio, acetone peak height and acetone-to-noise ratio using FTIR-spectrometer ReactIR-1000. All the spectra have been taken as a result of 128 scans with resolution 4 cm^{-1}.

Signal-to-noise ratio SNR was defined as 1/RMS noise calculated from 5 × 100% lines in the region from 1042 to 1142 cm^{-1} for each probe. Acetone peak height (APH) was defined as the peak height at 1092 cm^{-1} relative to the baseline at 1018 cm^{-1}. Acetone-to-noise value (ANR) was defined as the APH × SNR.

We consider ANR as an observable value for probe performance characterization. SNR characterizes the background signal level. The sensitivity can be assessed roughly as absorption peaks height. It is well known that higher sensitivity of ATR elements is achieved due to multi-bounce design as well as due to the minimization of radiation incidence angle [8]. However, this practice used for fibre probes leads to probe transmission decrease due to two different reasons—the first one is increasing of radiation divergence after multiple bouncing inside ATR element. This results to imperfect radiation collecting into output fibre. However, additional focusing optics complicates the probe tip construction. In addition, minimization of radiation incidence angle is not always possible in the practice of fibre optics for the same reason of construction complication. As for ATR elements made of unclad polycrystalline fibre our experience shows that any arrangement for sensitivity increasing such as fibre bending, flattening, etc. leads to the increase of scattering in the fibre element and resulting transmission drop of the probe. Therefore, in both cases the separation of weak absorption peaks may be impossible in the noisy spectra of high sensitive probes.

ANR = SNR × APH shows the average value of peaks to noise ratio and characterizes the possibility to separate meaningful peaks from noise.

Thus in this work the performance of each probe was evaluated as ANR value. Another substance displaying distinct absorption peaks in 2000–600 cm^{-1} spectral range may be used instead of acetone.

3. Results and discussion

The study of fibre probes with ATR cone elements showed that their background spectra remained unchanged during 12 months storage. However, the background signal decreased about 10% in wavenumber range 1250–600 cm^{-1} and up to 20% in the range 3300–1250 cm^{-1} during the intensive work. It was connected with polycrystalline fibre structure deterioration due to multiple bending cycles even with bending radius above minimal permissible value [9]. Fibre deformation took place near the connectors where fibre was fixed. In this place some small length can be bent with radius less than the minimum. No damage was revealed when bent probe position was stable without bending cycles.

Stability of background signal was observed in temperature range 20–100 °C and some decrease of probe transmission up to 5% had been revealed at 140 °C in spectral range 3300–1250 cm^{-1} with recovery when the temperature decreased. This was connected with polycrystalline fibre structure change during temperature cycling [10].

The study of fibre probes with unclad fibre loop ATR elements revealed the above-mentioned deterioration connected with fibre cable bending and temperature cycling. Additionally the aging of fibre loop was observed as an unavoidable phenomenon for unclad fibre. Therefore, the disposable loop design of this probe demonstrated its value in practice.

The sensitivity of ATR-probes using two-bounce cone optical element made of different materials is presented in Table 1 and Fig. 3.

The results are in good agreement with refractive index values of these materials: the acetone peak height is much lower for the probe with Ge cone so its ANR value 500 is only half as much as ANR = 1084 in the case of ZnSe cone probe though SNR of Ge probe is higher than that of ZnSe probe because of smaller divergence of radiation beam in Ge. Diamond probe demonstrated ANR = 972 close to that of ZnSe cone probe so diamond probe can be used in a line with ZnSe probe in dependence on application conditions. Diamond probes can be recommended for use in harsh environments or for medicine applications.

The sensitivity of detachable loop probe depends on fibre loop shape as shown in Fig. 4. Background signals of the probe presented in Fig. 4a agrees completely with the idea of radiation scattering at fibre bending. The unclad fibre loop bending with very small radius (see Fig. 2B and C) results in significant decrease of probe transmission. Of course, in this case the probe has higher sensitivity (Fig. 4b) because of large amount of beams onset with reflection angles close to critical. However, only small amount of these beams propagate through the clad fibre cable to the spectrometer detector. Thus probe transmission and SNR, respec-

Table 1
Parameters of fibre probes with ATR cone elements made of different materials

Parameter	Cone material		
	ZnSe	Ge	Diamond
SNR	5125	11,773	4523
APH	0.211	0.0425	0.215
ANR	1084	500	972

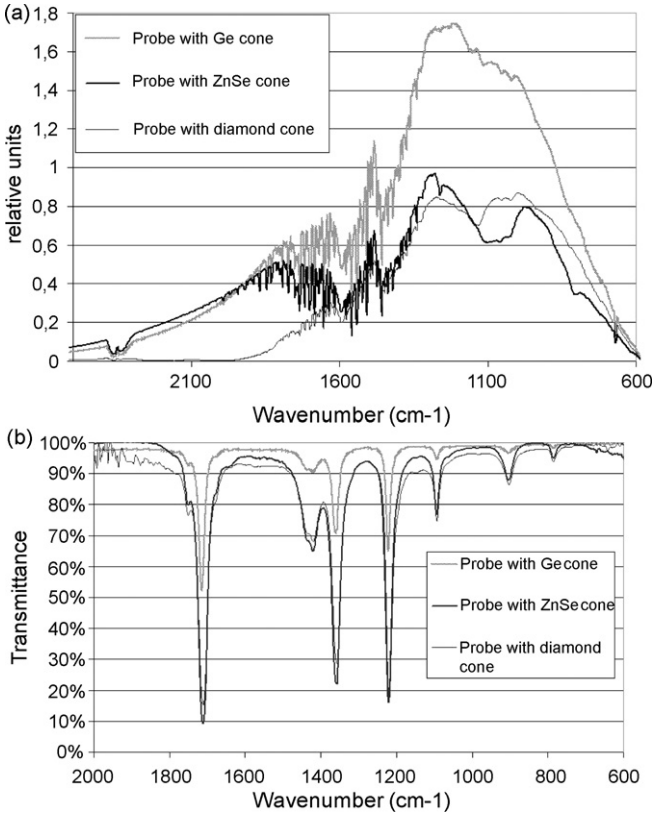

Fig. 3. Background (a) and acetone transmission (b) spectra obtained using ATR-probes with two-bounce cone optical element made of different materials.

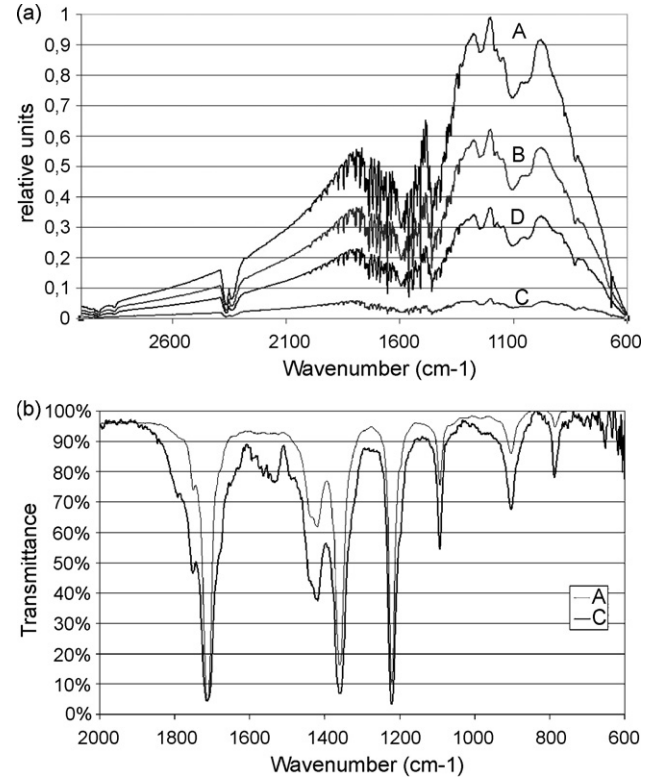

Fig. 4. Background (a) and acetone transmission (b) spectra obtained using ATR fibre loop probes with different shaped loop tips.

Table 2
Parameters of detachable loop probe using fibre loops of different shape (see Fig. 2b)

Parameter	Loop shape			
	A	B	C	D
SNR	5143	2673	274	1428
APH	0.22	0.24	0.41	0.35
ANR	1131	641	112	500

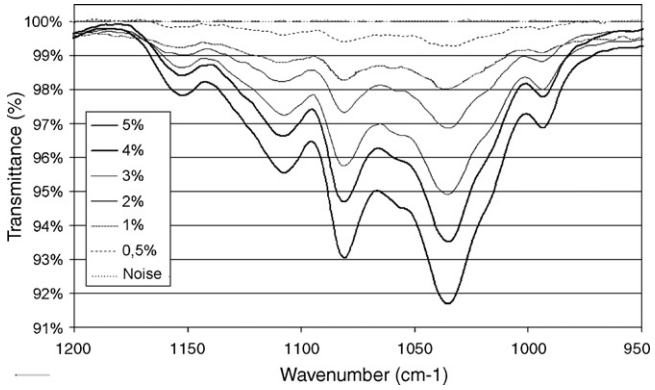

Fig. 5. Transmission spectra of glucose at different concentrations in water.

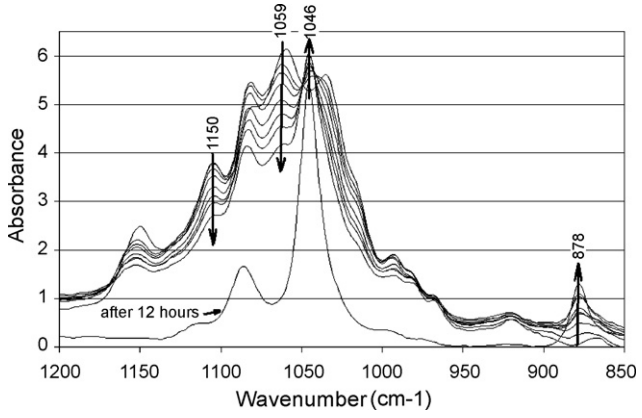

Fig. 6. Absorption spectra of chemical reaction mixture of alcohol fermentation as function of time (measurements carried out every 60 min): absorption bands of ethyl alcohol (increasing) and sugar (decreasing).

tively, is small in this case and ANR is smaller as against other cases listed in Table 2 and Fig. 4.

According presented results a U-shaped loop is more effective for analysis than more complicate shapes. We can add that any change of fibre shape such as tight bending, flattening or tapering leads to its mechanical properties deterioration and inconvenience of the handling. It was revealed in the course of this work as well as in other research [2].

Spectra of glucose had been measured using a ZnSe cone probe (Fig. 5). It was possible to detect concentrations up to 0.5% in water solution using the experimental setup mentioned above. Further development of the probe performance coupled with a new

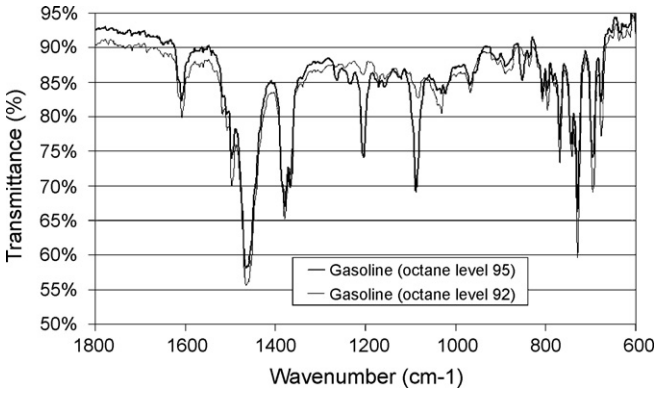

Fig. 7. Transmission spectra of different kinds of fuel.

generation of FTIR spectrometers allows to use "touch" probes for glucose detection in blood by non-invasive means [5].

Monitoring of alcohol fermentation reaction had been carried out using ATR fibre probe with ZnSe cone element. The formation of ethanol and consumption of sugar during this process can be traced according absorption peaks of ethanol at 878 and 1046 cm^{-1} and sugar at 1059 and 1155 cm^{-1} as shown in Fig. 6.

Fuel spectra presented in Fig. 7 had been measured using diamond ATR-probe. The distinct difference is seen between benzene mixtures with different octane levels.

So the monitoring of a lot of reactions in food, pharmaceutical and petrochemical production can be carried out using ATR fibre probes because this "in situ" technique enables to measure all changes of liquid composition without sampling.

4. Conclusion

Unique properties of polycrystalline fibres enabled to develop durable fibre ATR probes working in mid-IR spectral range.

Flexible fibre process-analysis systems provide high selectivity and sensitivity molecular analysis of liquid and solids on-line and in situ in 3300–600 cm^{-1} spectral range.

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