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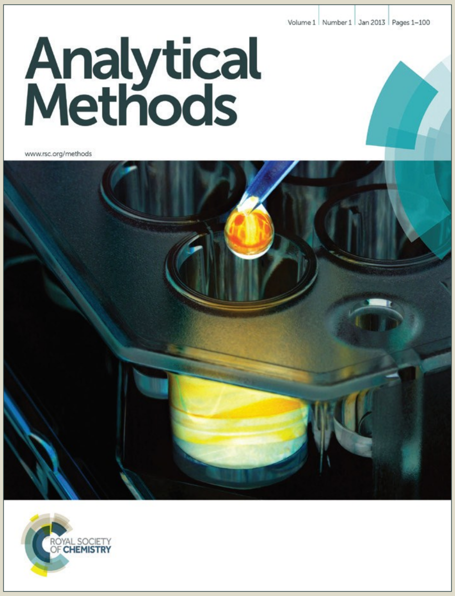

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QUANTIFICATION OF COPOLYMER COMPOSITION (METHYL ACRYLATE AND ITACONIC ACID) IN POLYACRYLONITRILE CARBON-FIBER PRECURSORS BY FTIR-SPECTROSCOPY

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Abstract – Conditions for simple and sensitive FTIR quantitative determination of acrylonitrile, methyl acrylate, and itaconic acid in their copolymer films used as precursor products in carbon-fiber manufacturing are proposed. The measurement mode is IR-spectrophotometry (transmission) with internal spectrum normalization using the peak of acrylonitrile at 2242 cm^{-1} as the main component and the determination of itaconic acid and methyl acrylate by their overlapping carbonyl peaks at 1740–1700 cm^{-1}. The calculations of comonomer concentrations were made using an external-standards method. The LOQs of itaconic acid and methyl acrylate are 0.5 and 2% w/w, respectively. The RSD of measurements is no higher than 7% rel. for methyl acrylate, 8% rel. for itaconic acid, and 1% rel. for acrylonitrile, which was shown by an example of analysis of PAN fiber samples with known concentrations of the components. The procedure was tested with several thermally unprocessed PAN precursor samples.

Keywords: PAN fiber, FTIR-spectroscopy; quantification; methyl acrylate; itaconic acid

Introduction

The polymerization products of acrylic acid and its nitrile (acrylonitrile, **AN**) — polyacrylate and polyacrylonitrile (**PAN**), respectively — are major state-of-the-art industrially manufactured polymers.[1] They are widely used in various branches of technology. In addition to long-existent areas of their application, for example, textile industry, nowadays they are required in the production of synthetic fibers[2-4] and high-strength carbon[5-8] or composite materials.[9-12] They are also used in manufacturing biocompatible nanoparticles for the targeted delivery of drugs.[13-15] These polymers also are found application in novel-type biofuel cells[16] and as ion-exchange membrane materials.[17] As a whole, acrylic polymers are first-ranked among all natural and arificial fibers produced in industrial scale due to their resistance to environmental factors as well as to chemical and biological agents.

Polyacrylate and PAN homopolymers are chemically durable, but rather nonfunctional, show low elasticity, and are not very suitable for colouring and fiber formation process, etc.[18] As a result, they are produced only when chemical resistance and material durability are the key parameters of the product. However, the majority of PAN-family technological mixtures include specially selected comonomers of polyacrylate or PAN of different nature (methyl acrylate (**MA**), methyl methacrylate, methacrylic and itaconic acids (**IA**), acrylamide, butyl acrylate, vinyl acetate, etc.)[19] that alter the physical properties of the polymer body or the functional composition of its surface, improve the diffusion of dyes into the polymer fiber and solubility in technological solutions, etc.[19-24] This, in turn, has a major impact on the morphology of the fibers, resins, and nanoparticles in their manufacture.

Especially important is the selection of ionogenic and nonionogenic comonomers for the production of carbon fibers with desired properties from PAN fibers (precursors).[20, 24-27] Most often, IA and MA are used toward this aim, and their ratio plays an important part in the final material features.[1, 28-30] In particular, itaconic acid facilitates the oxidation of the fiber, its exothermicity, and formation of thermally induced structures[21] and governs the precursor carbon yield.[28] Methyl acrylate acts as a plasticizing comonomer for facilitating the molding process of the PAN fiber from the spinning solution. A deviation from the technological composition of the mixture (even in some fractions of percent) leads to a drastic shift in parameters of the formation of the precursor fiber and the conditions of its processing into the carbon fiber, which entails the risk of spoilage in production, raises the production costs, etc.

Therefore, to control the process and products of polymerization, reliable methods of identification and quantitative analysis of the composition of the process solutions and fibers are needed at all the production stages (spinning and stabilization).[31] The quality control of the composition of the PAN-based copolymers requires approaches that, on one hand, are sensitive and selective, and, on the other hand, provide a fairly simple, cheap, and rapid analysis. Very desirable is that the procedure provides the determination of all the main components by a single technique.

FTIR-spectroscopy is the primary method of identification (qualitative analysis) of polymers, as well as of the determination of the main component, AN, and almost any functional comonomers and the elucidation of the structural changes during the process.[32-34] However, quantitative analysis of such polymers is often implemented by other methods. Most frequently, NMR spectroscopy, usually ^{1}H and ^{13}C (and, recently, solid-state techniques), is applied to-day.[35-39] However, this approach is expensive and time-intensive, requires highly skilled personnel, and not very suitable for the rapid analysis of large lots of samples. Alternatively, the control of the copolymer production is frequently based on the functional organic analysis using titrimetry.[27,28] In some cases, spectrophotometric measurement of the total content of carboxyl groups is used.[40] This provides rather high total accuracy of the determination of acidic, ion-exchangeable, or other functional groups, but does not always provide the required selectivity and sensitivity of the determination of comonomer admixtures.

However, analytical FTIR-spectroscopy is actively developing nowadays towards quantitative analysis and the significant expansion of the range of the studied materials. In addition, the instrumental arsenal of IR-spectroscopy has changed drastically over the last 5–7 years. All this leads to the increasing in the sensitivity of instruments of both the top and middle classes that are used to solve research and routine problems. Today, most typical detection limits are 10^{-3} to 10 wt. % with a relative standard deviation *ca.* 0.05–0.20.[41, 42] Portable, handheld, and compact instruments provide on-site and field analysis and mobile autonomous measurements. Thus, the development of a FTIR-quantitative procedure for PAN-fiber analysis seems topical.

In this paper, we present the results of the development of a simple procedure for FTIR-spectroscopic determination of the composition of PAN copolymers applicable to a wide range of state-of-the-art IR-spectrometers. We selected one of the most relevant products, a PAN fiber (the precursor of carbon fibers), and three of its main components, namely acrylonitrile, methyl acrylate, and itaconic acid.

Experimental

Instrumentation

We used FTIR spectrometers: Cary 660 FTIR and Cary 630 FTIR (Agilent Technologies, USA), Vertex 70 (Bruker Optik GmbH, Germany) and IR Prestige 21 (Shimadzu, Japan) equipped with standard transmission compartments. For the compact Cary 630 FTIR spectrometer, we used the configuration with windows made of ZnSe (spectral range 650–4000 cm^{-1}) and with open-cell transmission DialPath (optical path lengths 50, 100, and 250 μm) and Diamond ATR accessories. For Vertex 70, we used a fixed-angle (45°) GladiATR ATR compartment (Pike Technologies) with a diamond crystal. All the spectrometers provide the accuracy of measurement of wavenumbers of 0.05 cm^{-1} and reproducibility of 0.005 cm^{-1} according to NIST 1921.

For the transmission compartment, the film sample was attached to the holder ensuring that the sample was properly placed in the holder and aligned with an IR beam. To set the required distance from the bottom of the sample compartment, the positioning pin on the bottom of the holder was used.

Software

For Cary 660, we used Resolutions Pro software (Agilent Technologies, version 5.2.0 (CD 846)). For Cary 630, we used MicroLab PC software for data gathering. Data handling were made after the automatic export of the spectral data to Resolutions Pro software. For Vertex 60, data was gathered and handled using OPUS 6.5 software (Bruker Optik GmbH, version 6.5.27 (20090227), 2009) in MIR R&D mode. Shimadzu IR Prestige 21 was equipped with IRsolution software (Shimadzu, version 2.4).

Auxiliary equipment

Weighing of the reagents was carried out on an Ohaus Discovery DV114C analytical balance (Switzerland; precision, 0.0001 g). For the preparation of the solutions and sampling, Biohit Proline Plus mechanical automatic dispensers of 200, 1000, and 5000 ml (Axygen, USA; Biohit Group, Finland) were used throughout. All solutions were prepared in Class A glass volumetric flasks with volumes of 25–1000 mL (Labtekh, Russia). Other glassware (conical flasks, test tubes, etc.) was made from standard chemical-resistant laboratory glass. Working solutions of up to 2.0 ml were prepared in polypropylene microcentrifuge tubes of Eppendorf type, with a volume of 2.0 ml (Apexlab, Russia). Solutions, films, and fibers were dried in a SNOL 60/300 (Russia) drying oven with digital temperature control. Stirring was carried out using an IKA Topolino, MS-3000 (Biosan, Latvia; 0–3000 rpm) magnetic stirrer without heating and using a MSH-300 stirrer (Biosan, Latvia; 250 to 1250 rpm, 30–330°C) with heating.

Reagents and Samples

Deionized water (18.0 MΩ×cm) from a Milli-Q Academic water purification system (Millipore, France) was used throughout. Dimethylsulfoxide (DMSO, CAS # 67-68-5) and *N*,*N*-dimethylformamide (DMFA, CAS # 68-12-2) of cp grade (Reakhim, Russia) were used throughout.

Monomers of PAN fiber: AN (CAS # 107-13-1), MA (CAS # 96-33-3), and IA (CAS # 97-65-4) from Sigma-Aldrich were used throughout. Two films of samples (enterprise-level reference samples, M_w, 310 kDa; MWD, 1.89; data from the manufacturer) with the known content of IA and the MA/AN ratio ("PAN-I": IA, 1.11% w/w; MA/AN, 0.0378 and "PAN-II": IA, 1.10% w/w; MA/AN, 0.0368) from Composite Holding Company (Moscow, Russia) prepared according to[29, 30] were used. In addition, we used 5 test samples of PAN fibers (marked as PAN-21, PAN-29, PAN-30, PAN-34, and PAN-41; Composite Holding Company, Moscow, Russia), the content of components in which is known precisely by the reactor load (M_w 300 kDa; MWD, 2.00). These samples were thin films of a small size (0.5÷1) × (0.5÷1) cm. We analyzed 7 working samples of thermally unstabilized fresh PAN carbon fiber precursors (Composite Holding Company, Moscow, Russia, the parameters are as above for test samples) with approximately estimated contents of co-monomers. NMR ^{13}C analysis of all the films using a Bruker AVANCE 600 MHz spectrometer (ca. 100 mg of the fiber were diluted in 0.5 mL of deuterated DMSO for 12 h of signal accumulation) showed intense signals at 27–29 (=CH—CN), 34 (=CH_2), and 121 ppm (–CN); medium signals at 70.25 and 72.80 ppm (=CH–O–C(O)–); and weak signals at 44.73 (–C(H_2)–C(H_2)–COOR), 52.49 (CH_3–O), 60.68 (CH_2–O), and 173.86, 173.94, and 174.16 ppm (–C(O)O–). The signal at 34 ppm is attributed to the main polymer chain; the signals at 27–29 and 121 ppm correspond to AN; and 44.73 and 52.49 to MA. Medium signals at 70.25, 72.80 ppm are in good correlation with IA samples.

Procedure

If a film sample is rather large (1×1 cm) and flat, no further sample preparation is needed. Otherwise, the fiber or film sample of a PAN fiber (0.02–0.03 g) is placed in a 5-mL conical flask, 1.0 ml DMSO is added and the sample is transferred into an oven heated to 40°C. The mixture is carefully stirred manually until complete dissolution of the fiber (about 2 hours). The resulting solution was poured on optical CaF2 plates (0.5 ml per plate) and films were dried at 100°C at the oven for 5 min and then cooled to room temperature. The obtained films are carefully removed from the CaF2 plates and the film is cut resulting in flat and smooth pieces approximately the size of the holder: a 1×1 piece for the standard transmission cell or a 0.5×0.5 cm piece for the open-cell compartment.[43] The IR-spectrum for 1200–2300 cm^{-1} is recorded against a background spectrum (air).

Data treatment

All IR spectra were processed as follows. Transmission or ATR spectra were converted (using the conversion functions of the corresponding software) to absorption spectra in absorbance units. Next, a peak of CO_2 at 2400–2300 cm^{-1} was removed manually. Next, all the spectra were smoothed by 21–25 points and baseline-corrected using corresponding software.

For statistical data processing, we used Origin Pro 8.1 SR3 software (OriginLab Corp. MA, USA, version 8.1.34.90). The measurement results are presented in accordance with the requirements of ISO/IEC 17025:2005.[44] The correlation coefficients, confidence limits, standard deviations, relative standard deviations, limit of detection, and the limits of determination were calculated according to the rules of presentation of the results of chemical analysis according to the IUPAC recommendations 1998 and ISO 5725:1994.[45]

The calculations were made using the internal standard method to compensate unequal path lengths of the test sample and that of the external standard:

$$\frac{A_X}{A_{IS}} = \frac{k_X}{k_{IS}} \times \frac{c_X}{c_{IS}}, \qquad (1)$$

where X is the index denoting the unknown concentration of the component in the test sample and IS denote the values in the internal standard (the acrylonitrile peak at 2242 cm^{-1}), k is the absorption coefficient for the analytical wavenumber. These values for MA and IA were compared for the same values of the two external reference samples PAN-I and PAN-II, and the average of two measurements was calculated. The final concentration of acetonitrile as the main component was calculated from the sum of the percentage concentrations of two minor components. For each film sample, 5–13 replicate measurements were made for different spots of the sample, and the data were averaged for all these measurements.

For a more precise determination of IA and MA, an overdetermined Vierordt' equation system at four wavelengths[40, 41] was used for the determination of MA and IA from their composite peak in the range 1760–1680 cm^{-1}[46, 47]:

$$\begin{cases} \Delta A_{\mathrm{IA}} = A^{\nu_1} - A^{\nu_2} = l\left[c_{\mathrm{IA}}\left(k_{\mathrm{IA}}^{\nu_1} - k_{\mathrm{IA}}^{\nu_2}\right) + c_{\mathrm{MA}}\left(k_{\mathrm{MA}}^{\nu_1} - k_{\mathrm{MA}}^{\nu_2}\right)\right] \\ \Delta A_{\mathrm{MA}} = A^{\nu_3} - A^{\nu_4} = l\left[c_{\mathrm{IA}}\left(k_{\mathrm{IA}}^{\nu_3} - k_{\mathrm{IA}}^{\nu_4}\right) + c_{\mathrm{MA}}\left(k_{\mathrm{MA}}^{\nu_3} - k_{\mathrm{MA}}^{\nu_4}\right)\right] \end{cases}. \qquad (2)$$

Here, A is absorbance acquired from FTIR measurements. The maxima of $k_{\mathrm{IA}}^{\nu_1}/k_{\mathrm{MA}}^{\nu_1} \times \sqrt{k_{\mathrm{IA}}^{\nu_1} k_{\mathrm{MA}}^{\nu_1}} = f(\nu)$ and $k_{\mathrm{MA}}^{\nu_1}/k_{\mathrm{IA}}^{\nu_1} \times \sqrt{k_{\mathrm{IA}}^{\nu_1} k_{\mathrm{MA}}^{\nu_1}} = f(\nu)$ functions were used as the wavenumbers for Vierordt's method. For the overdetermined Vierordt's system, Eq.(2), ν_1 and ν_3 were at the maxima, and ν_2 and ν_4, at the minima of the absorption spectra of both components in the range of 1760–1680 cm^{-1}.

Results and Discussion

To determine the composition of the copolymer in the PAN fiber, the sample is usually re-formed by the dissolution in DMFA.[48-50] For calculations, the external standard approach is used using pre-prepared reference samples for which maximum accuracy is known, the ratio of components in the sample (independent data) or directly associated value. The mass fraction of itaconic acid in the polymer is usually determined by the measurement of the total content of carboxyl groups. This is done by spectrophotometry using the photometric reaction of formation of colored ion associates with Methylene Blue cationic dye[40]. This is a drawback, which results in the sophistication of the sample-preparation process and a decrease in the overall measurement precision. Moreover, as the exact thickness of the investigated films is unknown, to estimate the composition it is necessary to normalize all the spectra by a reference peak. As such, the peak of acrylonitrile as the main component of the PAN-fiber is used. Thus, these shortcomings and drawbacks required the development of a procedure based on FTIR measurements only and for more precise quantitative analysis.

Peak assignment

To select the conditions for the determination of the components of PAN fibres, we made the assignment of peaks in the samples of pure monomers and PAN fiber (Table 1). As an example, the spectrum of a film for the “PAN-I” standard sample is presented in Fig. 1B with the comparison with spectra of individual components Fig. 1A. As expected, the most intense peak in the whole spectrum is the peak of the stretching vibrations of the nitrile group of acrylonitrile (2242 ± 1) cm^{-1}, also it shows characteristic bands of CH– bonds (3100–2930 cm^{-1}) with rather low contribution from trace water (a wide band seen for IA sample, Fig. 1A). The second most intense peak is also a peak of the main component at 1450 cm^{-1} caused by CH flat aliphatic vibrations of AN, however both minor components have similar bands (Fig. 1B) and contribute to its intensity[24, 51], and, thus, it is non-preferable for quantification.

Working bands that can be used for the determination of methyl acrylate are the stretching vibrations of the carbonyl group at 1730 cm^{-1} (Fig. 1A) and several bands corresponding to C–O–C vibrations of esters (1300–1100 cm^{-1}).

The determination of itaconic acid can be carried out using bands at 1730 and 1710–1690 cm^{-1} (vibrations of carbonyl in unsaturated carboxylic acids), vibrations of OH– (1440–1390 cm^{-1}), –C–O– (1320 cm^{-1}), and R–OH groups (750 cm^{-1}), see Fig. 1.

All these peaks are present on the spectra of standard films of PAN and correspond well to the previously published data[1, 19, 29, 30]. All the bands assigned as most intense and characteristic for each of the three components are present on the spectra. However, the analysis of derivative spectra of PAN samples (Fig. 2) shows no symmetric peak, with the exception of the peak of the nitrile (2242 cm^{-1}) i.e. all peaks are not free from the overlaps from other components or peaks of the same component, which is supported by the discussion in the literature.[23, 24, 27, 52] This dictates a more careful selection of the conditions of the data processing and quantitative analysis by FTIR.

The feature of PAN-fibers, especially IA-stabilized, is a strong dependence of the peak shape and intensity of the thermal pre-conditioning.[53] All the spectra of tested samples show that, as expected from the conditions of the spinning process of the manufacturer, fibers are not stabilized, as they show no distinct peak at 2200 cm^{-1} (α,β-unsaturated nitrile groups due to hydrogenation, or tautomerization and isomerisation forming a ladder-like polymer structures);[20, 27] a shoulder peak at 1454 cm^{-1} is absent as well.

On the other hand, a sufficiently high resolution of the most information-bearing peaks, a low noise level in spectra, and a good reproducibility of the measurements, in particular, of the nitrile peak (2242 cm^{-1}), which must be used as a reference in the spectra normalization, is achieved. This has allowed us to start optimizing the available techniques to increase the precision of quantification. We selected the range of 2300–1200 cm^{-1} as the working range as it contains all the most intense and characteristic peaks and a flat background with a low level of noise (Fig. 1).

Solvent selection

An important point of existing approaches used in the studies of PAN fibers is the production of the film by dissolving the original PAN sample in an appropriate solvent and subsequent evaporation of the solvent. To our knowledge, DMSO and DMFA are used at this stage most commonly.[49, 50] DMFA is more frequently used for the dissolution of the films; however, its IR spectrum has the vibrations of the methyl group (3000 cm^{-1}), which does not interfere with the determination of the PAN-fiber comonomers. However, a peak of the amide group of DMFA (1700 cm^{-1}) does interfere with the characteristic peaks of IA and MA at 1740–1690 cm^{-1} and should be avoided.

On the contrary, the IR spectrum of DMSO does not have strong peaks in the selected working range, as its characteristic band of SO vibrations lies at 1050 cm^{-1}. In the case of DMFA, although the main peak of MA is intact (Fig. 3) there is a distinct increase in the absorption in the range 1710–1630 cm^{-1}, which is unfavorable for the determination of IA. Hence, the comparison of the solvent shows that DMSO is more advantageous for the procedure in question as it has lower overlap pattern with characteristic bands of IA, MA, and AN.

Film solvolysis

Next, the stage of dissolution/evaporation should not affect the IR-absorption spectra. However, our tests samples with known content of all the three components at their ranges common to industrial applications allowed us to compare the measurements of the same samples directly from the films prepared for FTIR measurements and for the samples re-dissolved in DMSO. For the working range, we obtained the spectra of the same samples (normalized to the internal standard peak of 2242 cm^{-1}) (*i*) without dissolution (original films) and (*ii*) for films obtained by re-dissolution. Fig. 4 shows the absorbance difference $A_{diss} - A_{orig}$, where A_{diss} is the normalized absorbance of the film prepared under re-dissolution and A_{orig} is the normalized absorbance of the original film. For all the five test samples, regardless of the IA and MA content, we observed the deviation from the expected value of zero (which means that the sample does not change under re-dissolution, and normalized spectra before and after the dissolution stage have the same absorbance).

Positive peaks of $A_{diss} - A_{orig}$ appear in the regions of 1700, 1660, 1400, and 1300 cm^{-1} and a distinct decrease reveals itself at 1550–1750 cm^{-1} (Fig. 4). This corresponds to an increase in the number of carbonyl groups of unsaturated acids (1690 and 1630 cm^{-1}) and in the concentration of carboxylate ion and and O–H groups (Table 1), i.e., to changes the composition of the polymer (obviously, due to the dissociation of itaconic acid and hydrolysis of the nitrile and methyl ester of acrylic acid). The synchronous growth of all peaks belonging to these different groups by the same value (by *ca.* 0.05) indicates that the results of a single process. A simultaneous decrease in the intensity of the peak at 1740–1730 cm^{-1} of carbonyl in methyl acrylate by the same factor is another evidence of this process.

Taking into account a higher concentration of MA compared to IA in PAN fibers[1, 28, 50], this leads us to a conclusion that this is a result of solvolysis leading to the transformation of methyl acrylate to acrylic anions. Thus, the dissolution of PAN fiber films has a substantial impact on the composition of functional groups of the polymer, which are selected for quantification, and sample preparation by dissolution/evaporation is quite destructive and affect the analysis results. Thus, it should be avoided or at least should occur under mild conditions in the case of quantitative determination of PAN copolymers.

As a result, in the following experiments, we substantially reduced the contact time with the solvent as well as the temperature and intensity of the dissolution. These conditions provided the negligible changes in the spectra of the films.

An alternative approach can be the use of ATR-FTIR for the quantification of the polymer composition as in this case, the requirements for sample preparation are quite simple, and the dissolution stage can be completely avoided. Unfortunately, the ATR-FTIR spectra of the test films showed very weak signals (absorbances no more than 0.03, which is at least 20-fold lower than for the transmission measurements), especially for the nitrile peak (i.e. very poor sensitivity of the main component). Thus, ATR-FTIR measurements provided the indentification of the major bands of the polymer, however showed nonreproducible quantitative results due to a change in the pressure from an ATR compartment screw and the work at the high-error shoulder of the error curve of the spectrometer used. Thus, we did not use the ATR-FTIR measurements in the following experiments.

Thus, the final sample procedure is based on the dissolution of the fiber in DMSO under the mildest possible conditions and we avoid it if the original film is good enough for transmission measurements.[43]

Simultaneous determination of methyl acrylate and itaconic acid

As mentioned above, the major peaks of the PAN-fiber spectrum are combination bands as MA and IA (or IA and AN) have several overlapping vibration bands. This is confirmed by asymmetrical derivative spectra at Fig. 2. Complete processing of the spectra obtained for the working range (baseline adjustment and data smoothing) allowed us to show that a pronounced peak at 1732 cm^{-1}

includes the contribution of both absorption bands of methyl acrylate and the groups of itaconic acid (Fig. 5A). This leads to overestimated results of the evaluation of the content of methyl acrylate from its peak at 1730 cm^{-1} by 10% (Table 2).

Deconvolution of the band at 1750–1680 cm^{-1} (using mixed Lorentzian–Gaussian functions) results in a stable solution of three overlapping peaks of 1732 cm^{-1} (almost coincident with the maximum of the composite peak), 1707 cm^{-1} (a nearly Gaussian peak), and 1625 cm^{-1} (a nearly Gaussian peak). The first peak corresponds to the carbonyl of metyl esters (MA), while two latter correspond to carbonyl of acids (IA) and carboxylate (IA). These peaks are clearly seen in the IR spectra of individual MA and IA (Fig. 1A and Fig. 5B, the shifts at their maxima is due to the influence of the polymer structure compared to individual compounds). The carboxylate peak at 1625 cm^{-1} is weak and does not interfere with the MA peak at 1732 cm^{-1}, while the IA carbonyl peak significantly interferes with the determination of MA by its carbonyl peak.

The simplest solution for MA determination is to use the wavenumbers greater than the maximum bandwidth (i.e. when 1740–1745 cm^{-1}) because the effect of IA to the quantification of MA at this shoulder area is minimal (Fig. 5A). The results of the data treatment show that, although leading to good results for medium quantities of MA, such an approach results in underestimation of MA for its high content in the polymers (PAN-21) and its overestimation if MA concentration is low (PAN-41), see Table 2. Thus, this cannot be recommended for the procedure.

Another approach can be based on the application of two wavelengths for the measurements: first IA is measured at 1695 cm^{-1} where the influence from MA is low. Next, IA content is used for the correction of the data of MA at 1732 cm^{-1}. This approach leads to a decrease of spectral overlap of acidic groups of itaconic acid and the improvement of analytical parameters (Table 2). The drawback of this approach lies in the addition of the error of the measurement of IA to the determination of MA but it still seems to be a good compromise.

Also, we found a more sophisticated version for the measurements, an overdetermined Vierordt's equation system at four wavelengths, to decrease the overall error.[46, 47] However, the estimation of the results show that this approach does not results in an increase in the precision and the results and the overall error of the measurements increases.

Performance parameters

The sensitivity and linearity of determination of minor components, MA nd IA, were estimated using the artifical mixtures of AN and IA, AN and MA, and three-component mixtures. The limits of detection of IA and MA are equal to 0.2 and 0.8 % w/w, respectively. The lower limits of quantification are 0.5 and 1.7 % w/w, respectively. The upper limits of quantification are 3.0% w/w for IA and 8% w/w (higher values were not tested in this study for MA). The coefficients of correlation are no lower than 0.96. The parameters obtained for all the IR spectrometers used in this study differ insignificantly.

These values of performance parameters show that the sensitivity of measurement is enough for the determination of components of PAN fibers in question, as the concentration ranges of IA are 0.7–2.5% and the range of concentrations of MA is 2–7%, so the procedure can be implemented for the majority of production mixtures.

The procedure is rapid and requires approximately 6–7 min total for a single sample, which is an advantage over the approaches based on FTIR/photometric approaches used in industry. The spectra of standard samples and calibration functions show a long-term stability: for a month, a change in the slope of the calibration for MA and IA did not exceed 2.5%. This can be useful for precalibrated measurements on-site with the test samples used for the calibration measured prior the measurements.

Analysis of test samples

Under the optimized conditions of sample preparation and data treatment, we determined all the components in five test samples with compositions known from the reactor load (Table 2). The samples were selected so they provide the same concentration of IA with significantly different concentrations of MA and AN. The IA concentration corresponded to the middle of the concentration range, which is the current optimum from the viewpoint of the target precursor properties.[19] The table shows that taking into account the inter-component effects of composite absorption peak of methyl acrylate discussed above leads to a good agreement of the results with the load data for all the five reference samples. Evaluation errors of measurements shows that the precision RSD of the determination of IA is 7–8%, of MA is 5–7% and acrylonitrile is about 1%. These values are consistent with the requirements for the methods for the quantification of PAN fiber and somewhat superior to existing approaches.[1, 18]

Next, we analyzed working PAN samples corresponding to various mixtures of the monomers and with approximate concentrations of the components calculated for the reactor load, Table 3. For most samples, a good agreement with the load-calculated results is shown, although the load results for samples no. 4 and no. 6 are at the boundary of our confidence intervals. Good reproducibility of measurements of all samples is obtained.

Noteworthy is that the precision and the results obtained for all the test samples for stationary laboratory spectrometers differ insignificantly from the results for a compact Cary 630 instrument.

This provides the possibility of on-site estimation of the composition of PAN fibers without transferring samples to a laboratory (except for the preparation of a film, if required).[43]

Conclusions

Thus, the procedure for the quantification of the main comonomers in PAN carbon-fiber precursors provides a sufficiently high precision and reproducibility along with a rather high sensitivity fitting the working ranges for the components. The approach is capable for the determination of all the main components by FTIR-spectroscopy as a single technique, thus providing rather rapid measurements for large lots of samples. This is also benefited from the possibility to use middle-class compact FTIR-spectrometers. High-quality spectra along with the rapidity provide the opportunity to check the quality of the samples (thermal pre-processing) and quantify the thermal changes and fully implement the data processing of and to select the best conditions for quantitative measurements. The precision of measurements of methyl acrylate and itaconic acid can be further enhanced by the application of PCA-based chemometric approaches that can be a subject of another research. The results of quantification of this type of PAN precursors can also be used to determine the composition of other PAN copolymers and similar polymers and in other practical tasks.

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Table 1. Major IR bands in the spectra of PAN fibers

Wavenumber, cm^{-1}	Group	Vibration type	Copolymer component	Band shape
3650–3550, 3200	–OH	ν_{OH}		Wide band due to intermolecular hydrogen interactions and water contribution
3100–3040	–C–H	ν_{as}	AN, MA, IA	A group of several narrow bands of different intensities
3040–3010	–C–H	ν_{s}	AN, MA, IA	
2930–2940	–C–H	$\nu_{C–H}$	AN, MA, IA	
2920	–OH		IA	weak
2850	–O–CH_3		MA	weak
2830–2800	–CH_3		IA	
2240–2243	CN	$\nu_{C–H}$	AN	strong
2200	α,β-unsaturated nitrile			Very weak or absent
2180	NC or enaminonitrile[24]	ν_{NC}		
2200–2100	SCN			SCN is the admixture in the fiber production
1870–1820	=CH_2	overtones	AN, MA, IA	Weak and wide
1730	Carbonyl group in α,β-unsaturated esters	stretching	MA	Strong, IA overlap
1710	Carbonyl group in α,β-unsaturated acids	stretching	IA	MA overlap
1620	Carboxylate anion	$\nu_{as\ C–O}$	IA	medium
1450	CH_2	δ_{CH} flat	AN, MA, IA	Strong, no visible shoulder peak
1440	O–H		IA	
1410	Carboxylate anion	$\nu_{s\ C–O}$	IA	
1390	O–H		IA	
1360	CH	$\delta_{C–H}$	AN, MA, IA	
1320	C–O–	$\delta_{C–O}$	MA, IA	
1250–1210	C–O	ν_{CO}	MA, IA	Three wide peaks
1180–1130	C–O-group in α,β-unsaturated esters and carboxylic acids		IA, MA	
1050	CH	δ_{CH} non-flat	AN, MA, IA	
950	CH	δ_{CH} non-flat	AN, MA, IA	
930–950	OH–	δ_{OH}	IA	
780	–C–CN	$\delta_{C–CN}$	AN	
750	ROH	δ_{OH}	IA	
700–730	CH_2– and CH_3–		MA, IA	

Table 2. The analysis of the test samples of PAN-fiber precursor with a known content of components (in % w/w) without sample preparation using the proposed conditions (*n* = 7, *P* = 0.95)

Data for	Component	PAN-21	PAN-29	PAN-30	PAN-34	PAN-41
Reactor load	IA	1.3 ± 0.1				
	MA	5.7 ± 0.1	3.5 ± 0.1	2.8 ± 0.1	2.8 ± 0.1	2.0 ± 0.1
	AN	93.0 ± 0.1	95.2 ± 0.1	95.9 ± 0.1	95.9 ± 0.1	96.7 ± 0.1
Procedure without (1730–1710 cm^{-1}) peak deconvolution	MA	5.9 ± 0.6	4.0 ± 0.4	3.5 ± 0.3	3.6 ± 0.4	3.0 ± 0.5
	AN	93 ± 1	95 ± 1	96 ± 1	95 ± 1	96 ± 1
MA measurements at 1740 cm^{-1}	MA	4.4 ± 0.2	3.2 ± 0.2	2.8 ± 0.1	2.8 ± 0.1	2.5 ± 0.2
	AN	94.3 ± 0.3	95.5 ± 0.3	95.9 ± 0.3	95.9 ± 0.4	96.2 ± 0.4
Final procedure	IA	1.2 ± 0.2	1.3 ± 0.2	1.4 ± 0.3	1.6 ± 0.4	1.5 ± 0.3
	MA	5.5 ± 0.2	3.7 ± 0.2	3.0 ± 0.1	2.8 ± 0.1	2.1 ± 0.1
	AN	93.3 ± 0.4	95.0 ± 0.3	95.6 ± 0.4	95.6 ± 0.5	96.4 ± 0.5

Remark: The precision of the sample load is provided by the manufacturer

Table 3. The results of the determination of the components in PAN samples with estimated content of components in the reactor load (in % w/w) (*n* = 13, *P* = 0.95).

Component	Data	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
IA	load	0.94	0.99	1.08	1.12	0.97	0.95	1.07
	found	0.9 ± 0.2	1.0 ± 0.1	1.1 ± 0.2	1.2 ± 0.4	1.2 ± 0.2	1.0 ± 0.1	1.1 ± 0.2
MA	load	5.7	5.4	5.6	5.5	5.0	5.3	5.3
	found	5.4 ± 0.4	5.5 ± 0.3	5.6 ± 0.5	5.9 ± 0.4	5.2 ± 0.4	5.6 ± 0.3	5.4 ± 0.3
AN	load	93.3	93.6	93.4	93.4	93.5	93.7	93.7
	found	93.7 ± 0.4	93.5 ± 0.4	93.3 ± 0.4	92.9 ± 0.5	93.6 ± 0.5	93.4 ± 0.4	93.5 ± 0.4

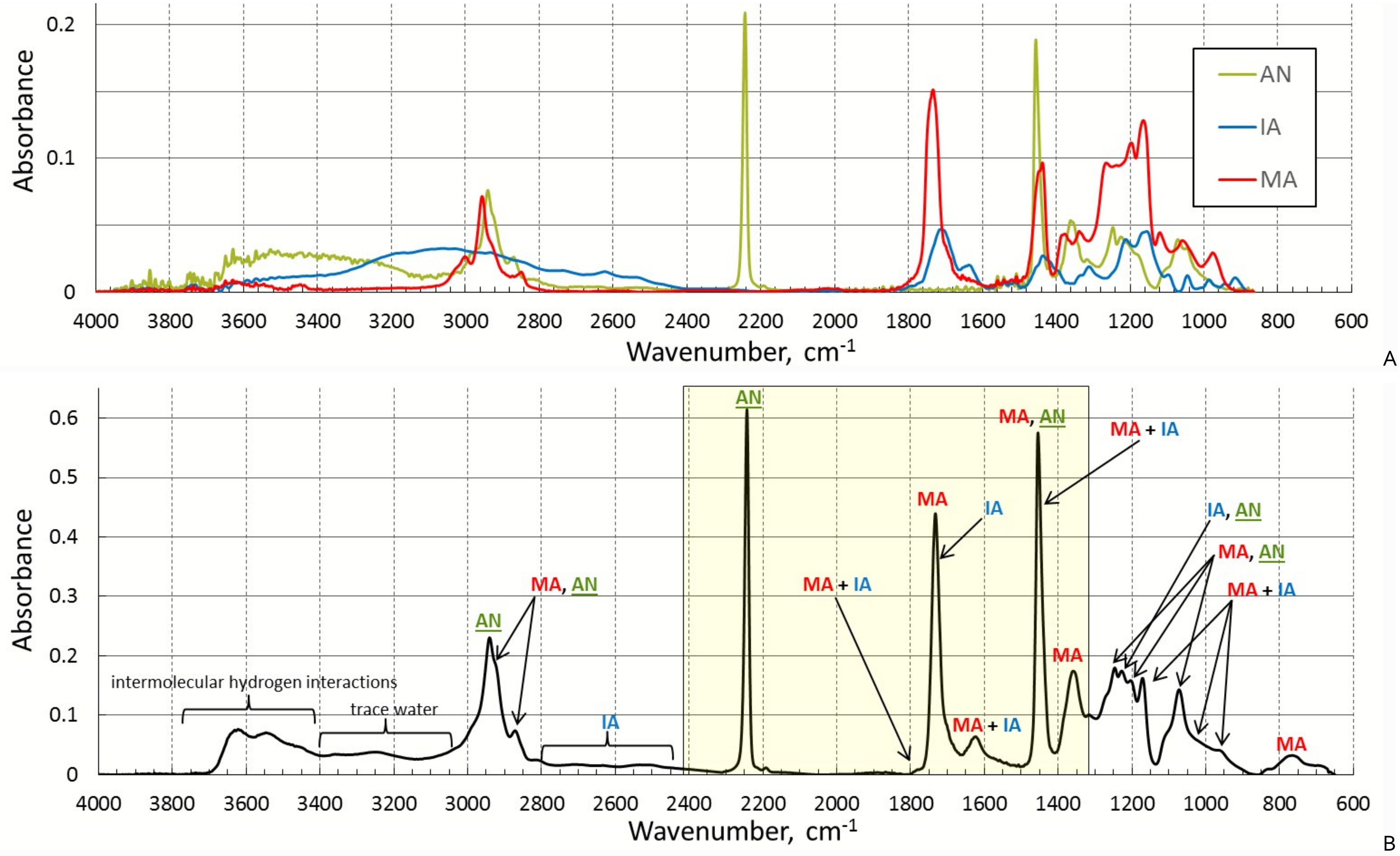


Fig. 1.The infrared absorption spectra of (a) individual co-monomers (the scale for MA is reduced for readability sake) and (b) the "PAN-I" standard sample. Spectra are recorded using Cary 630 (standard transmission accessory). Bands attributed to individual compounds labeled with appropriate abbreviations. The area used further in the procedure for the quantitative determination is framed.

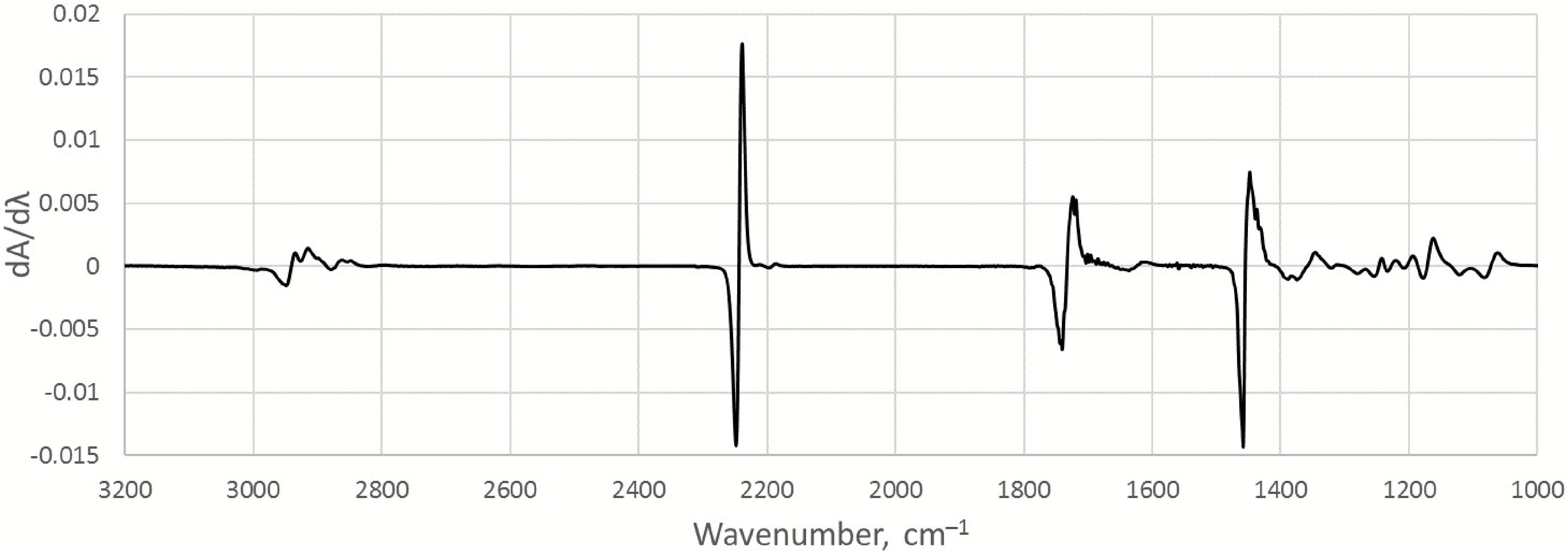


Fig. 2. The first derivative spectrum of the “PAN-II” standard sample using Cary 660 (standard transmission accessory).

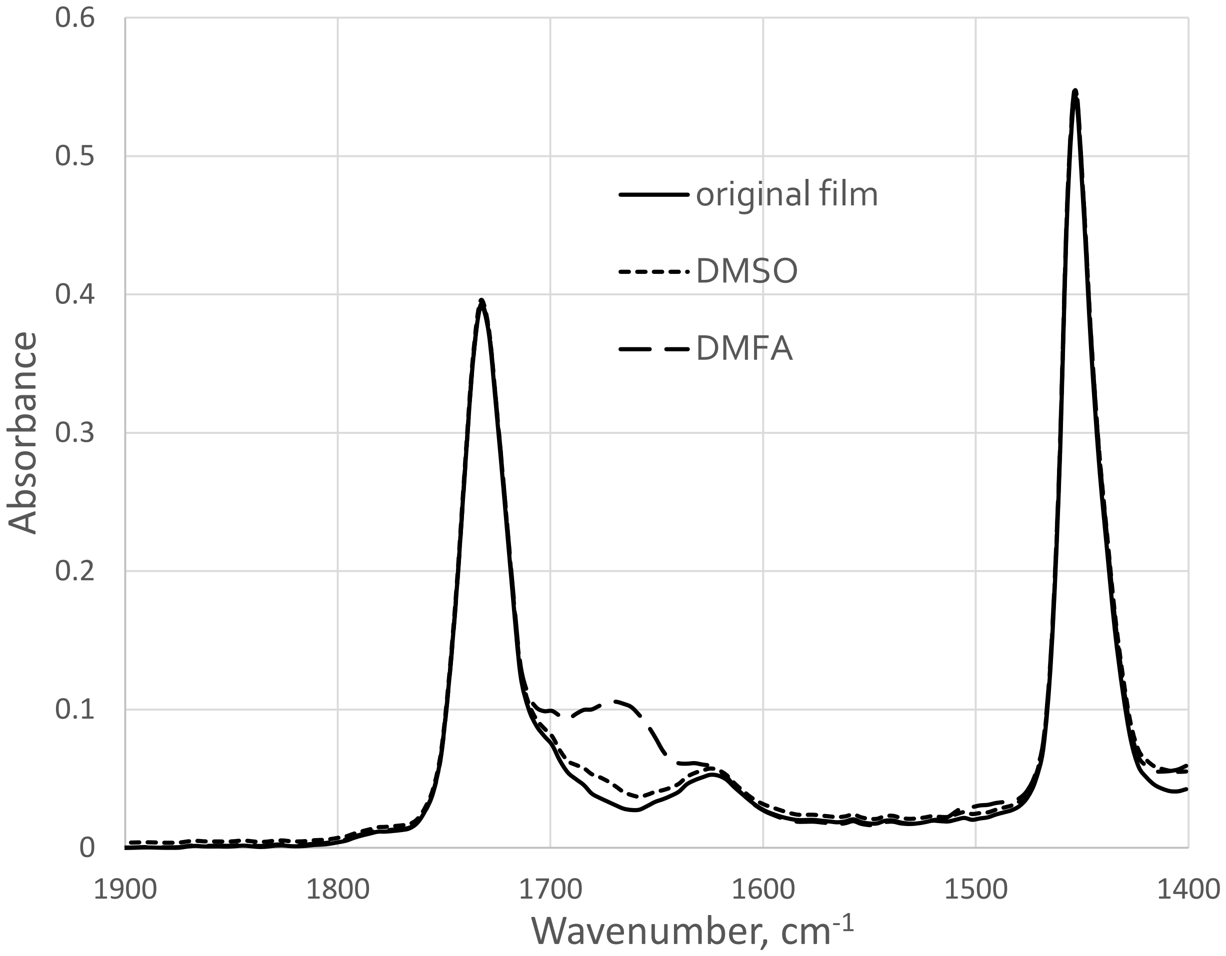


Fig. 3. The effect of the solvent on the characteristic range of IR-spectra of PAN fibers (“PAN-II” standard sample using Cary 660 with a standard transmission accessory

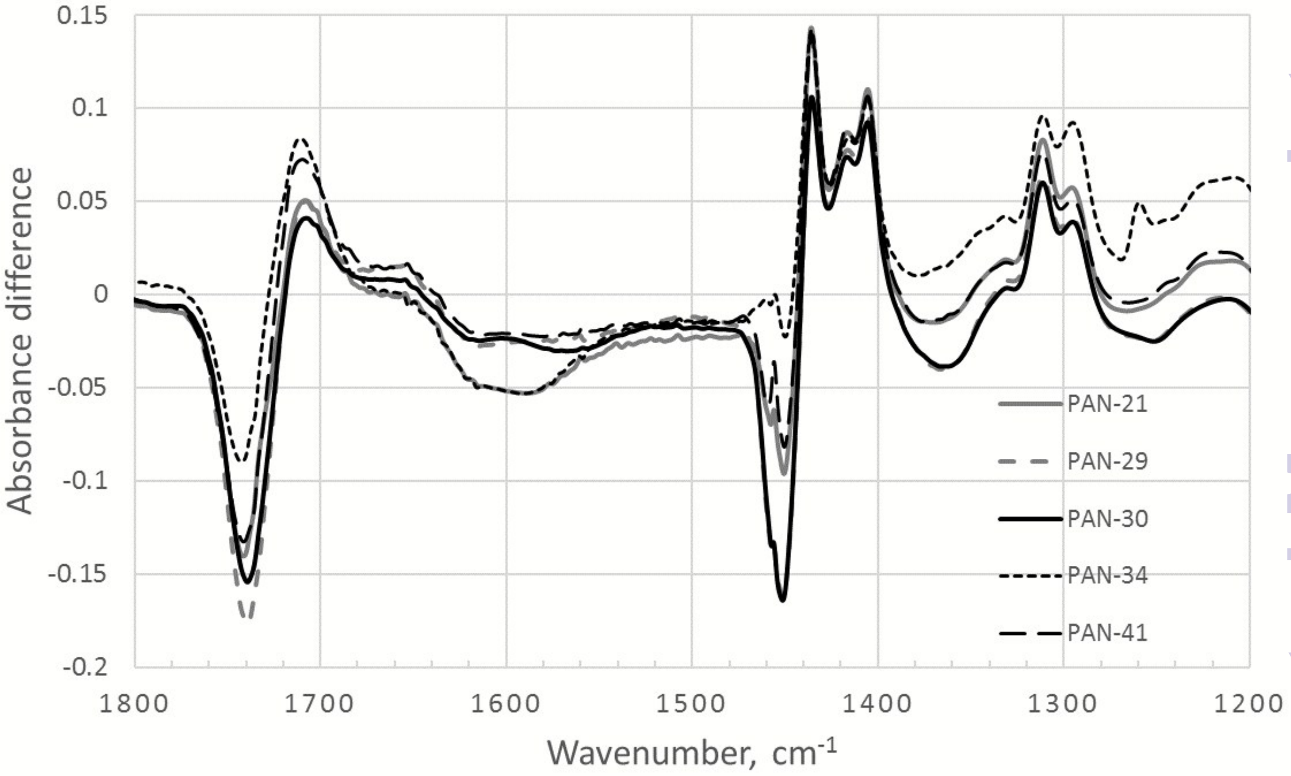


Fig. 4. The difference in absorbances in the spectra of test PAN samples obtained without re-dissolution of the fiber and its re-dissolution in DMSO.

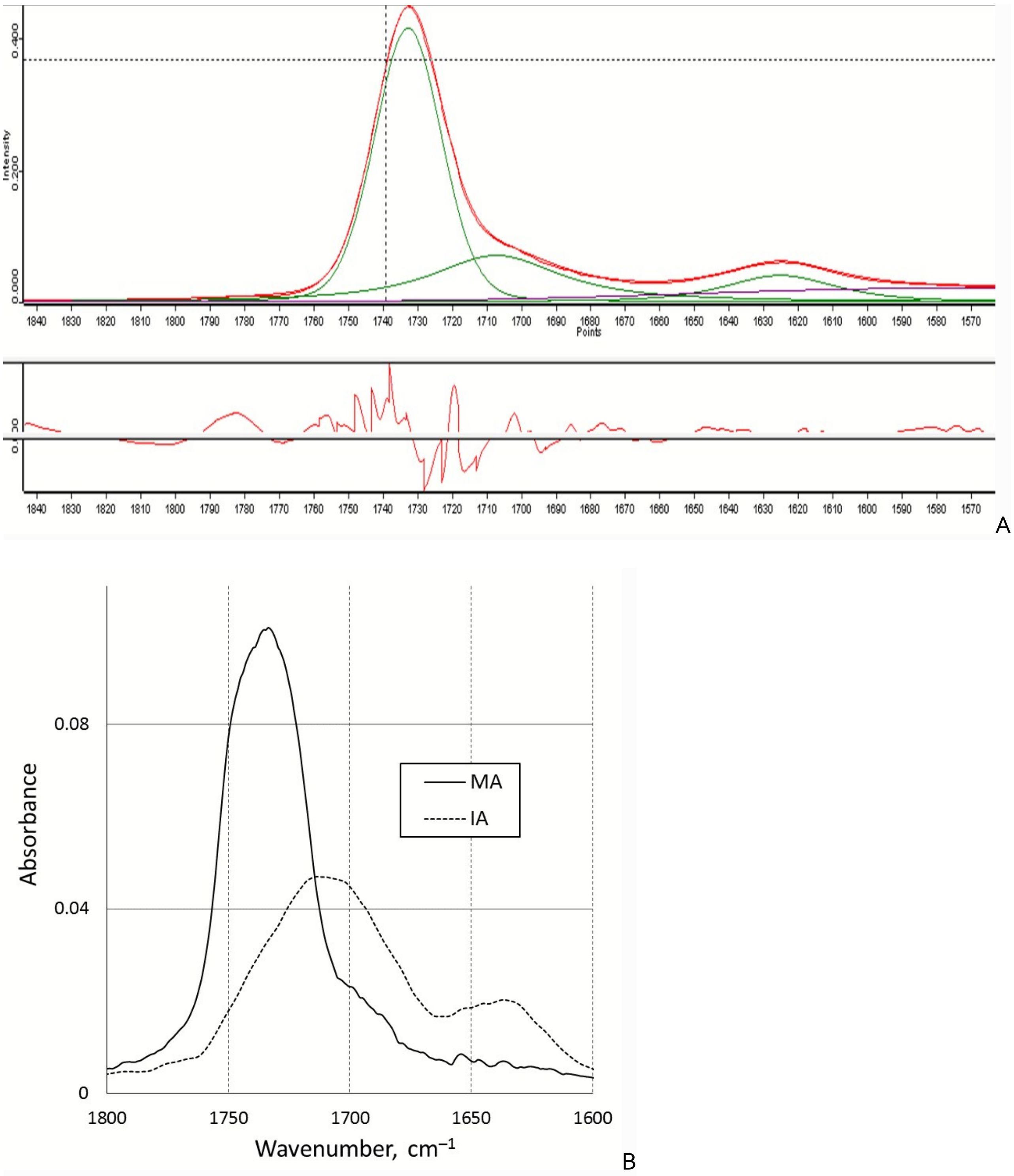
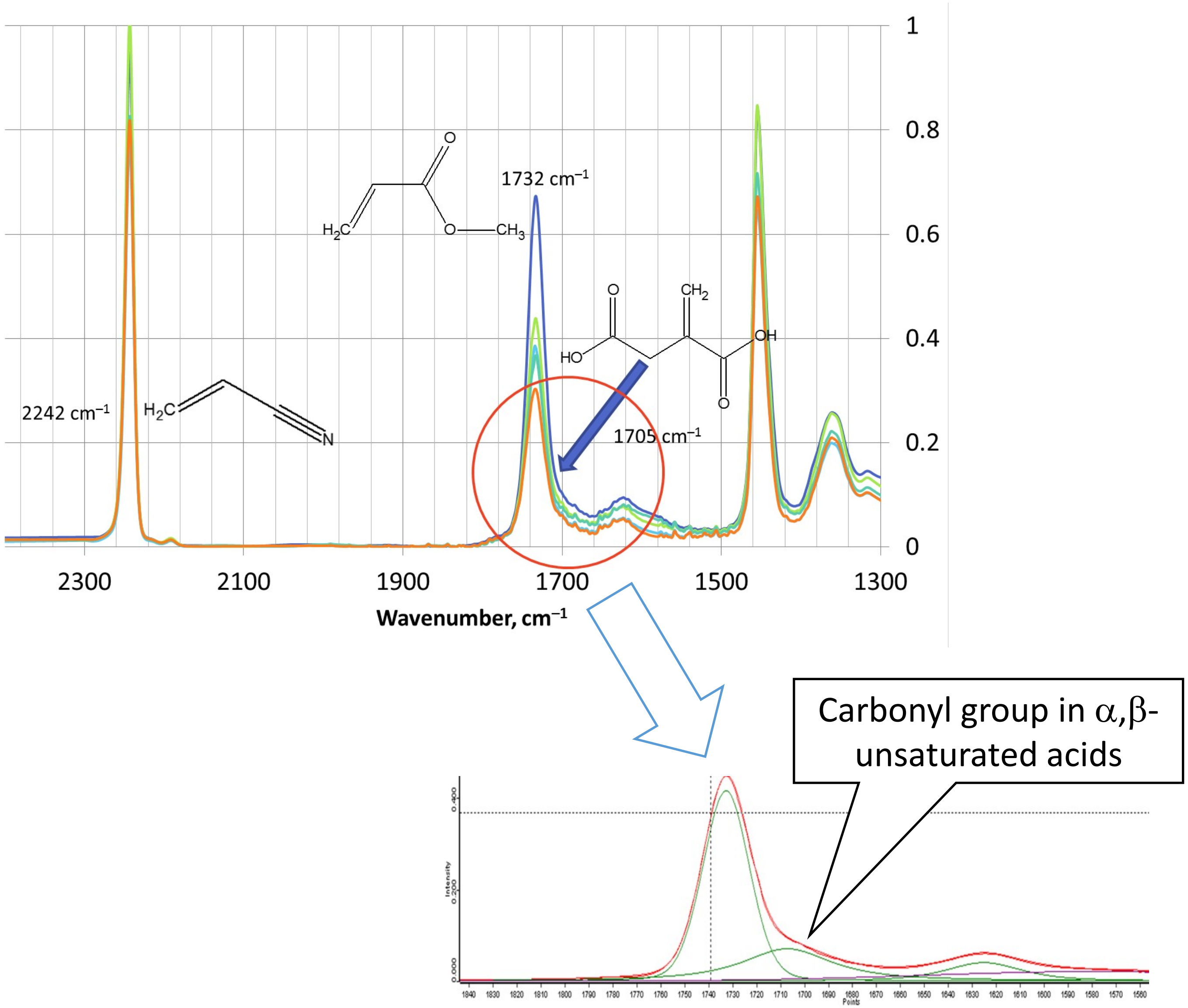


Fig. 5. (A) Deconvolution of the the peak at 1732 cm^{-1} using Lorentz–Gaussian functions for the determination of methyl acrylate and itaconic acid (a part of the operation screen of the OPUS software, Bruker Optic GmbH) and (B) the spectra of carbonyl peaks of methyl acrylate and itaconic acid obtained from individual compounds.



Carbonyl group in α,β-unsaturated acids