EXPERT KNOWLEDGE

TEST PROCEDURES

OF ELASTOMER COMPONENTS

SHORT VERSION

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TESTING CONSULTING DEVELOPING

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Chemical-Analytical Test Methods – Finding the Material DNA

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IR: Simple and Fast Method for Polymer Determination

Infrared spectroscopy (IR) uses invisible infrared radiation with a wavelength between visible light and microwaves. The infrared waves can only interact with polarizable bonds and trigger them to oscillate, resulting in radiation absorptions that stimulate different groups of molecules depending on the wavelength. The evaluation of these groups provides information about the contents of an elastomer. However, IR does not provide trace analysis (detection limit 2 to 5%). Whereas previously dispersive IR was used in the elastomer field, now only Fourier Transform Infrared Spectroscopy (FTIR) is used. With the help of the Fourier transformation of the measured values, the desired spectrum is obtained. This results in relatively short measurement periods with stronger signals. Elastomer spectrums contain complex mixtures, so that separation is not always possible. However, the significance can be increased by coupling different methods. Since most elastomers are black and therefore not transparent to light and infrared, pyrolysis FTIR or FTIR with ATR (attenuated total reflection) can help here. In the case of pyrolysis FTIR, the condensed vapor of a thermally decomposed elastomer sample is analyzed, while in the case of the ATR technique IR radiation passes through a special crystal (e.g. made of germanium), which is placed on the elastomer sample and penetrates it only for a few µm. The reflected radiation passes again through the ATR crystal and then hits the detector. Simplified, elastomers consist of the following four groups of substances: polymer, fillers, plasticizers/processing aids and carbon black. The first three groups can be found in the ATR spectrum, the pyrolysis spectrum can only detect the polymer and the plasticizers/processing aids. The wave numbers of important peaks (triggered by characteristic functional groups, e.g. C≡N nitrile group in NBR at a wave number of 2,235 cm-1) of the common polymers are known via databases, with which fast base polymer identification is possible. **Fig. 1** shows an example for an FTIR polymer analysis of an NBR-O-ring. The Y-axis shows the intensity of the absorption, while the X-axis shows the wavenumber (= reciprocal value of the wavelength) for display reasons.

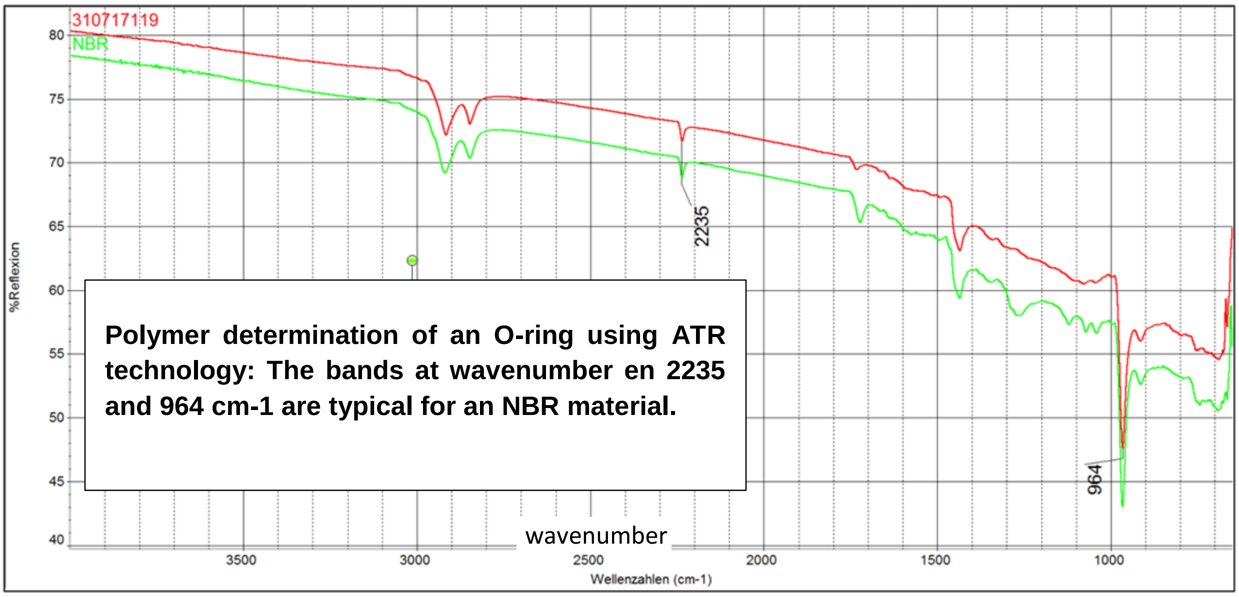

Fig. 1: FTIR polymer determination using the ATR method (Picture: O-Ring Prüflabor Richter GmbH)

The analysis of extracts is also of great practical importance. Hot extraction using a solvent mixture can be used to separate many important compound constituents from the rubber and thereby display the compound constituents more precisely than in ATR analysis or pyrolysis. This process is frequently used in quality assurance to compare different batches of a compound. **Fig. 2** shows a comparison of two batches of an NBR-70 formulation with large differences. In a failure analysis, the extract comparison of a failed seal with a new seal reveals which organic substances have diffused into the seal. FTIR analysis using ATR technology is also of practical importance in the chemical characterization of coatings. It can be determined,

for example, whether the O-rings sampled by the supplier are coated with the correct bonded coating (e.g. based on PTFE or VMQ).
Overall, FTIR analysis is a frequently used analysis method in elastomer technology. For simple QA tasks, basic chemical knowledge for the application is sufficient with the aid of good software. For more complex testing tasks (e.g. compound development, production or damage analysis), the operator should have a solid basic chemical understanding.

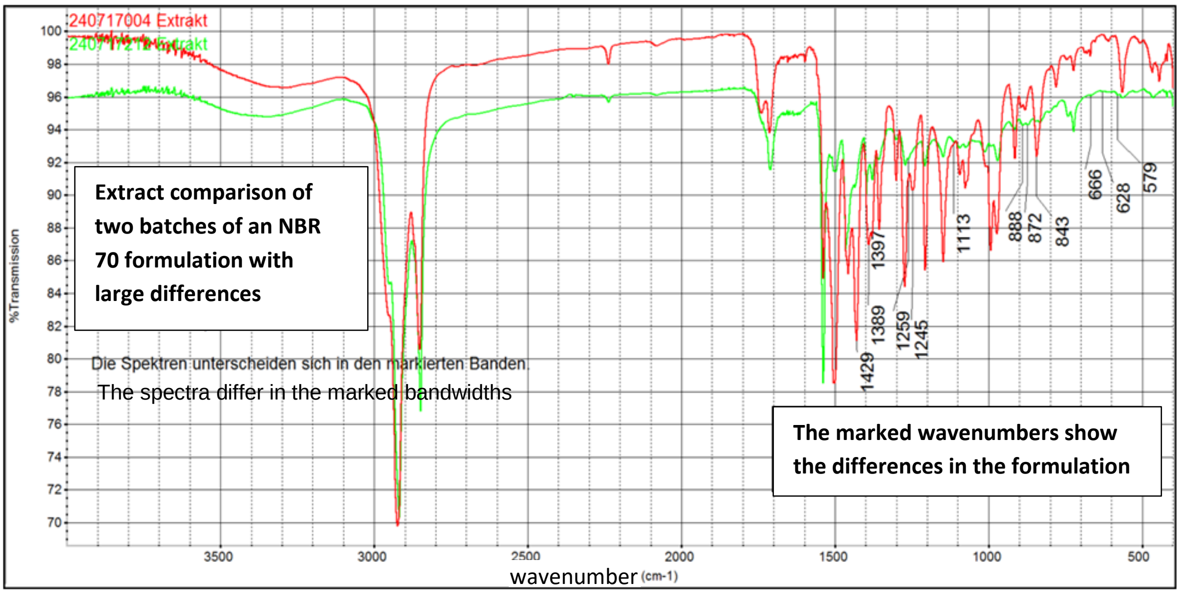

Fig. 2: Extract comparison of two batches of an NBR compound (Picture: O-Ring Prüflabor Richter GmbH)

GC-MS: For a Deeper Insight into the Elastomer Composition

Pyrolysis gas chromatography with mass spectrometry coupling (GC-MS) is used for this purpose. A gas chromatograph (GC) uses pyrolysis or thermal desorption to separate the components of a rubber compound. For this purpose, the sample is heated which, depending on the temperature, leads to outgassing of the volatile components or to decomposition (pyrolysis). The individual components travel through a long, thin, coated column - depending on their chemical nature - with an inert gas stream (helium, nitrogen or hydrogen) at different speeds and therefore arrive at the end of the column at different times. There, the individual molecules - still in the gas phase - are ionized and accelerated differently in an electric field according to their mass and charge. At the end they meet an analyzer (in the mass spectrometer MS). The signals can be compared with a database and the individual components identified. The detection limit of 10-10g is extremely low. Especially in damage analysis it can be very beneficial that even the smallest sample quantities of approx. 0.3 mg are sufficient for an analysis. Due to the low detection limit, the application area of GC-MS analysis in elastomer technology begins where FTIR analysis ends.
Compared to the FTIR analysis, the evaluation and interpretation is much more complex and requires a profound chemical education. The acquisition costs are also considerably higher than for an FTIR analyzer. As an instrument for quality assurance, this high-resolution analysis method is still used relatively little in elastomer technology. In critical applications or in cases

of failure that are difficult to explain, the GC-MS can be the decisive factor in problem identification, as it can reveal even the smallest differences in formulation that can result, for example, from the use of comparable mixing chemicals from different suppliers. However, the procedure can also eliminate the last uncertainties regarding batch fluctuations in suspected cases. **Fig. 3** shows a batch comparison of an FKM material with high correspondence. Each individual signal can be assigned to a chemical using a mass spectrometer.

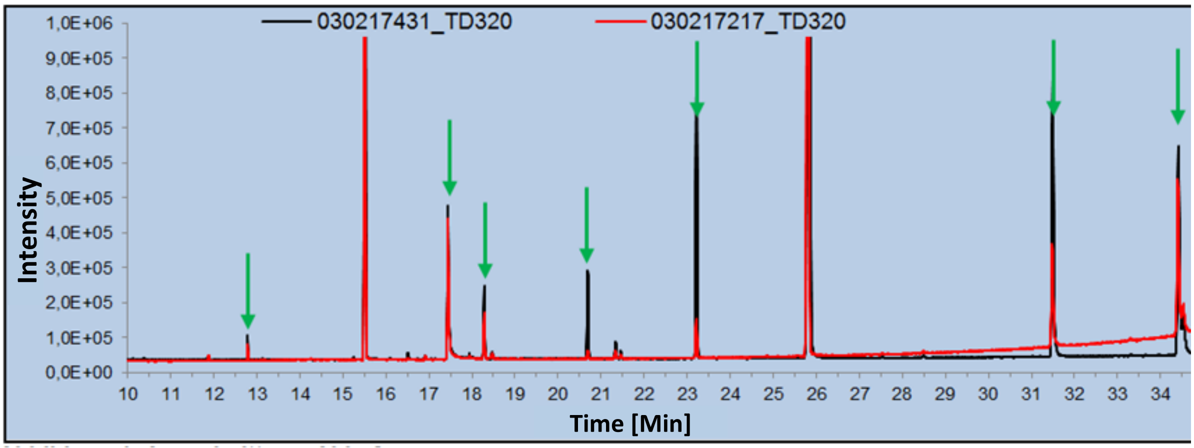

Fig. 3: Chromatogram of two batches of an FKM material (Picture: O-Ring Prüflabor Richter GmbH)

In the O-Ring Prüflabor Richter, GC-MS analysis is mainly used in failure analysis. It usually helps identifying which substances have diffused into the seal and were then the cause of the failure. Micro parts in particular react sensitively to plasticizers extracted from hoses or other rubber parts during operation. Impurities carried in can be identified. On swollen seals, the cause can be identified much more precisely than with the FTIR analysis. Sometimes it is also very helpful to prove that there has been no external contamination of the material and that therefore it has not caused the damage. The advantages of the GC-MS analysis are therefore the higher accuracy and resolution compared to the FTIR analysis, and also a quantitative analysis that can be carried out if required.