Lean manufacturing of polyurethane, assisted by near-infrared (NIR) and Raman spectroscopy

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Chemical manufacturing such as polyurethane production is characterized by a cost intensive production process combined with a negative ecological impact. These adverse effects can be significantly improved by using vibrational spectroscopy. This analytical technique can assist the operator of the plant to reduce costs and minimize the impact on the environment as is demonstrated in the present white paper.

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Polyurethane

Polyurethanes (PU) are a subclass of polymers with a wide range of applications as everyday products **[1]**. For example, most of the people who read this white paper will do it while seated. The soft component of the chair, which makes sitting so comfortable, is polyurethane. Polyurethane usage in chairs, and also in many other products, is based on its unique possibility to build foams. The foam building process can be influenced during the production process of this material. The size of the pores, density and other material properties of final product can be adjusted. Therefore, the properties of the final material can be customized in this way. Foams with relatively large pores are characterized trough a high resilience and elasticity, which enables the use as seats, sponges etc. Materials with middle-sized pores are characterized through excellent thermal insulation properties and are often used in the construction area. Microcellular PU foams are significantly harder and can be used for example as seals.

Due to the wide range of possible application fields global polyurethane production was estimated to be approximately 20 million tons, which resulted in a market size of approximately USD 55 billion in 2015 **[2,3]**. The final production of PU is a relatively simple chemical reaction (**Figure 1**). Isocyanate molecules react with polyol molecules in a condensation reaction. Polyols form bridges between isocyanate molecules, leading to polyurethane with a polymeric structure. The whole process can take several minutes.

The biggest challenge in this industry is located on the supply side of the PU factory, namely manufacturing of specific polyols and isocyanates. These production processes, which stand between refinery and PU factory, are known for their complexity. They can be cost, time, and energy-intensive processes. The reaction control as well as quality control of intermediates are still often based on empirical data or involve multiple analyzers. These instruments can be cost-intensive in daily operation due to the use of chemicals. On the other hand, this can be improved when using chemical-free analytical techniques such as near-infrared spectroscopy (NIRs) or Raman spectroscopy. Both techniques can be integrated directly into production processes and enable significant reduction of operating costs compared with the classical reaction or quality control systems. They can assist the operator to implement lean manufacturing principles and improve the quality of the product. The present White Paper summarizes briefly various application fields of both spectroscopic techniques in this industry branch as well as benefits of using these tools.

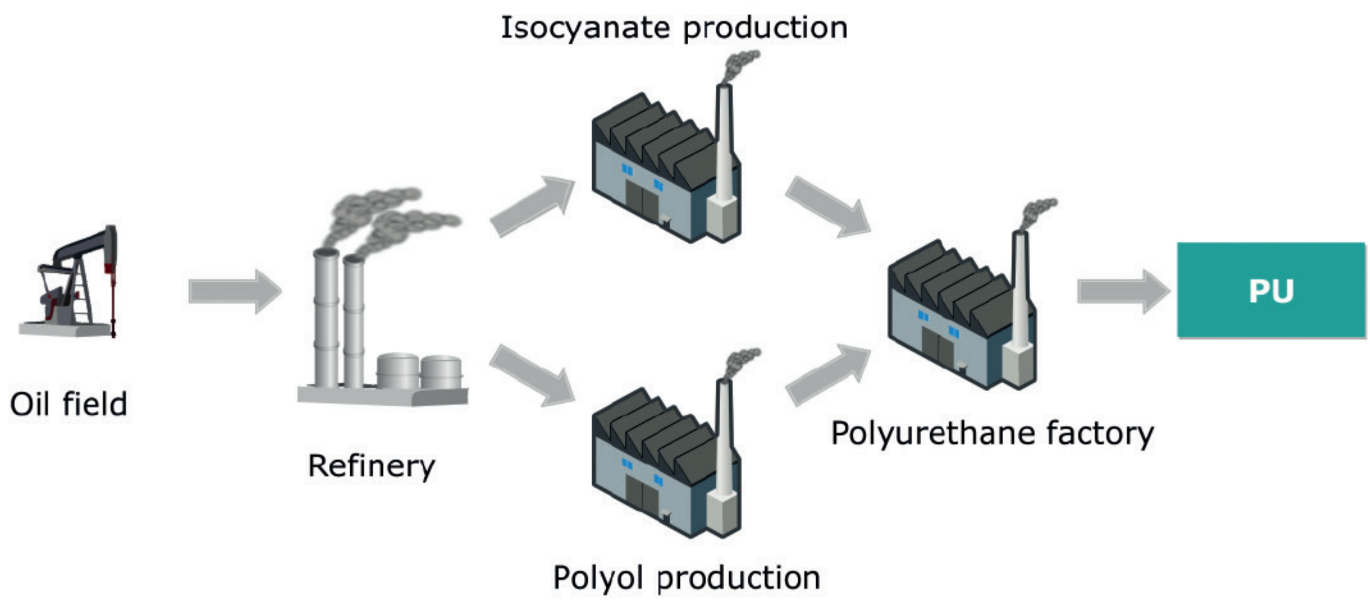

Figure 1. General description of the polyurethane manufacturing.

Manufacturing of polyols

Polyols are a broad class of organic compounds characterized by the presence of two or more hydroxyl groups **[1]**. They can be further separated into various subclasses. Two of them are widely used in polyurethane industry, namely polyester polyols and polyether polyols. Polyether polyols predominate in this market. Therefore, the present White Paper focusses only on the manufacturing process of this subclass of polyols.

The production starts with alkenes, which usually stem from the refinery (**Figure 2**). In the first step, pure alkenes such as ethylene or propylene or a mixture of both are oxidated to corresponding oxides. Both products, ethylene oxide (EO) or polypropylene oxide (PO) show similarity in their chemical properties. They readily react with water. This is industrially used for the production of glycols. However, in the production process of these oxides, this reaction is adverse, because it has an impact on the yield of the epoxide and lowers the quality of the product. Therefore, water content needs to be monitored during the whole production process. This is a challenging analytical task, because the moisture content is usually on a low ppm level. This problem can be solved using near-infrared spectroscopy (NIRS), which enables real-time monitoring of the moisture content and further quality parameters directly in the production process of epoxides. NIR spectroscopy is known for its excellent sensitivity to moisture content, which leads to limits of detection in a very low ppm range. Especially, dispersive NIR instruments, which are characterized by a very low noise level and, thus, a high signal-to-noise ratio compared to competitive technologies, can reach limits of detection around 10 ppm for moisture as it is required in this production process.

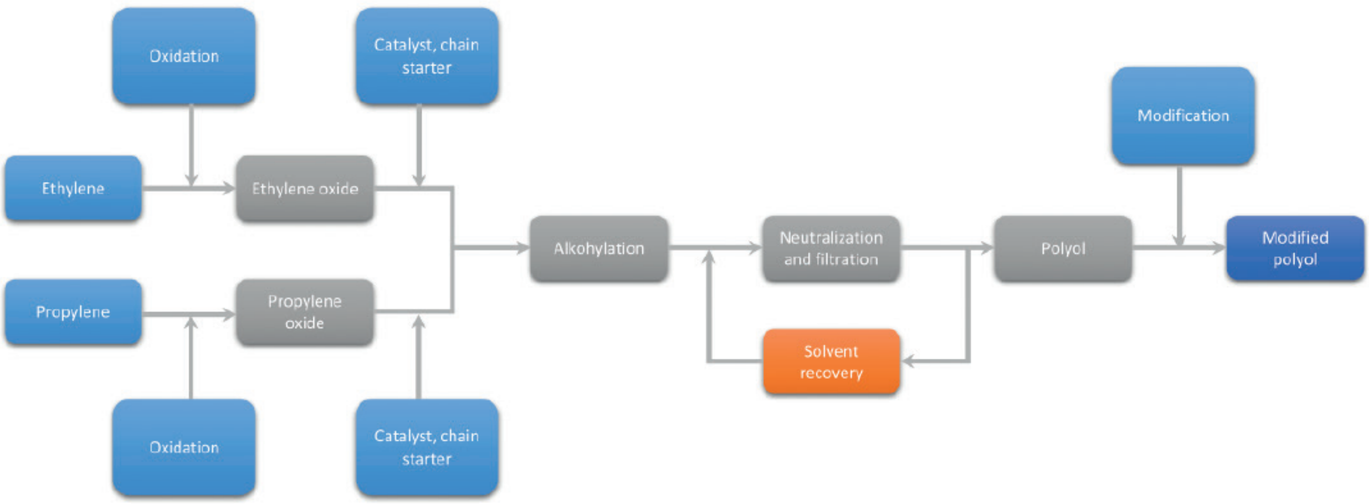

Figure 2. Schematic diagram of the manufacturing process of polyether polyols.

Subsequently, epoxides are alkoxylated in a three-step process namely pretreatment of catalyst and initiator and its reaction with PO, EO or EO/PO mixtures followed by posttreatment such as neutralization.

Especially the second process is very important one. It can be operated as a batch or semi-batch process with durations of up to several hours. The degree of alkoxylation as well as the hydroxyl value determine the property of the polyol and therefore also the property of the final polyurethane. Hence, it is important to monitor these quality parameters online during production. In this case, it is possible to utilize online NIR spectroscopy as a tool for process monitoring, as it was demonstrated in the Metrohm Application Note AN-NIR-007 «Near-infrared analysis of polyols: process monitoring in rough environments» **[4]**. This application note demonstrates that NIR can provide the results much faster than conventional method and enables significant time and energy-savings, which result in improvement of the plant profitability.

Furthermore, the solvents used in different processes can be recovered, in order to minimize operating costs. In this case, online NIR spectroscopy can be utilized for the online monitoring of the chemical composition of the solvent and therefore also the quality of the recovery process.

Finally, the produced polyol can be directly used for the production of polyurethane or modified prior to the final reaction e.g., through addition of other components such as solvents, solids etc. In this area, benchtop NIR systems are frequently utilized in the quality control of polyols as it was demonstrated in Metrohm Application Notes AN-NIR-006 and AN-NIR-035 **[5, 6]**. Additionally, the used analytical method can be developed according to ASTM or ISO norms **[7, 8]**.

Manufacturing of isocyanates

Isocyanate is a class of organic compounds characterized by a presence of an –N=C=O group **[1]**. Various isocyanates can be used as raw materials for polyurethane production, among others:

- Toluene diisocyanate (TDI)
- Methylene diphenyl diisocyanate (MDI)
- Hexamethylene diisocyanate (HDI)
- Isophorone diisocyanate (IPDI) and others.

Each compound has a different production process and it is beyond the scope of this White Paper to describe all industrially produced isocyanates. This manuscript will focus only on the production of MDI and TDI. These two compounds account for nearly 95% of the global polyurethane market (MDI 61% and TDI 34%) **[9]**. The manufacturing process of isocyanates like HDI, IPDI and others is slightly different but it is based on the similar chemical principles. Therefore, the applications of spectroscopic techniques presented in the current white paper can be slightly modified and used in the manufacturing process of these compounds.

All isocyanates are produced from various organic compounds, which usually stem from a refinery. The applications of spectroscopic techniques in refining are beyond the scope of the present White Paper. Therefore, the following description will start with the raw materials supplied by a refinery.

Manufacturing of MDI

The manufacturing process of MDI is shown in **Figure 3**. Different chemicals used in the production are usually provided by a third party company. Such a situation is a potential risk in almost all chemical production processes. A use of the wrong or mislabeled material can lead to damage of the whole plant and significant monetary losses through downtime and replacement of the plant components. Therefore, a verification of the incoming raw materials is indispensable for the efficient operation of the chemical plant.

A common and simple analytical solution in this case is the use of vibrational spectroscopy such as Raman or NIR spectroscopy. Especially, handheld Raman analyzers enable direct verification of the incoming materials without any sampling. The sample can be analyzed through the packaging material or through the flange inspection glasses, which are usually available on the trucks or rail tankers as well as on the pipes between the railway station and the plant. Further information about possible applications of handheld Raman spectroscopy for the identification of polymers and chemicals can be found in Metrohm Application Notes AN-RS-001, AN-RS-007 and AN-RS-008 **[10-12]**.

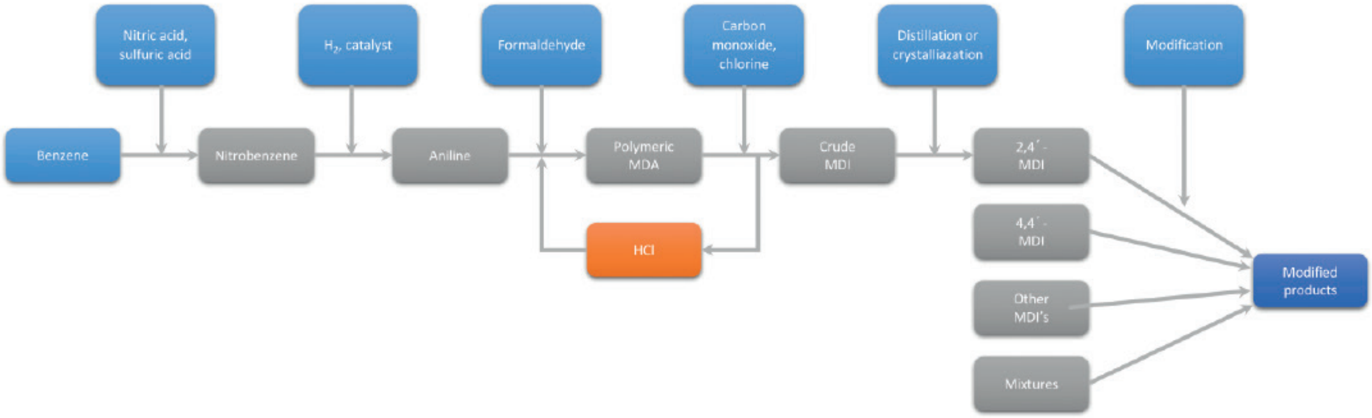

Figure 3. Schematic diagram of the manufacturing process of MDI. The part of production starting from the polymeric MDA is very similar to the final steps of HDI and IDPI production: instead of polymeric MDA, hexamethylene diamine and iophorone diamine are used in this case.

The production of MDI starts with the nitration of benzene using a mixture of nitric and sulfuric acids. This production step require constant monitoring of the quality of the acid mixture, which is a very challenging application due to high concentrations of acids. One of the possible solutions in this area is based on wet chemical methods. This requires additional safety measures for the operator and cost-intensive chemicals. On the other hand, the quality control can be simplified, when using an ATEX certified online NIR instrument, which is directly integrated into the production process. Specific acid resistant probes as well as dedicated sampling interfaces enable direct monitoring of the chemical composition of the acid mixtures in real time without any chemicals, sampling or safety measures.

Subsequently, nitrobenzene is hydrated to aniline, which is treated with aqueous HCl and formaldehyde solution and forms methylenedianiline (so-called polymeric MDA). The hydrochloric acid used in this step is usually a recycled byproduct of the subsequent manufacturing process. Its quality as well as a chemical composition of the HCl/formaldehyde mixture can be also monitored using online NIR system with a dedicated sampling interface and probe. Furthermore, a benchtop or offline NIR system can be used for the atline or inline quality control of polymeric MDA, namely for the determination of chemical composition, moisture content etc.

In the subsequent production step, the polymeric MDA reacts with a phosgene to a so-called crude MDI, which is a mixture of different MDI isomers. Usually, it is separated to single MDI isomers or specific mixtures in a distillation or crystallization process. Finally, the separated products can be optionally modified prior the use in the final polyurethane production. All these processes have some common challenges. Like many isocyanates, MDI tends to react with water, which forms undesirable byproducts, reduces the yield and lowers the quality of the product. Therefore, the moisture content has to be controlled along these production steps. This control can be also realized using online NIR instruments. Due to the well-known suitability moisture determination, NIR spectroscopy can be utilized for the real-time monitoring of the moisture content on the ppm level. Due to the well-known multi-parameter capabilities, this technique can additionally provide not only moisture content but also additional chemical and physical parameters such as isocyanate content, acid value, viscosity, purity of separated products, and others. Combined with the fact that this technique enables the analysis within a minute without using chemicals, this type of reaction monitoring enables a significant cost-saving in the daily quality control.

Manufacturing of TDI

The manufacturing process of TDI is summarized in **Figure 4**. It shows some similarities to the manufacturing of MDI. The first one is the continuous nitration of toluene using a mixture of nitric and sulfuric acids. The related analytical tasks as well as solutions were described in the section above.

In contrast to the nitration of benzene, nitration of toluene is usually a two-stage continuous process. Due to the use of toluene instead of benzene, it leads to mixture of different chemicals, mainly different dinitrotoluene isomers (DNT). Quite often it results in a 80/20 mixture of two isomers: 2,4- and 2,6-dinitrotoluene (DNT). This isomer mixture can be further processed and is the basis of 80/20 TDI. Slightly different process conditions lead to a 65/35 mixture, which is used for the production of 65/35 TDI. However, these isomers can be also separated into single components, if required e.g., for the production of 2,4-TDI or 2,6-TDI. In both cases, online NIR spectroscopy enables the possibility to monitor online chemical composition of DNT mixtures as well as of the purity of the distillated DNT fractions. One single online NIR analyzer can be used for the monitoring of up to nine product streams of the distillation unit.

The produced DNT or DNT mixtures are further processed using a catalytic hydrogenation to toluenediamine (TDA). This product is often contaminated by a presence of unwanted 2,3- and 2,5-isomers from the previous process, which need to removed using distillation. At this stage, benchtop NIR spectroscopy utilized atline or online NIR spectroscopy enable fast identification of purity of the desired fraction, which can shorten and simplify the distillation process and reduce significantly its duration.

The subsequent phosgenation of TDA to TDI is very similar to the previously described phosgenation of MDI. A byproduct of this reaction, hydrochloric acid, can be also be recycled and used in other production processes. After neutralization and distillation, pure TDI products can be modified in a similar way as MDI products. Therefore, the use of NIR spectroscopy in both steps leads to the same benefits for the plant operator as described before for MDI.

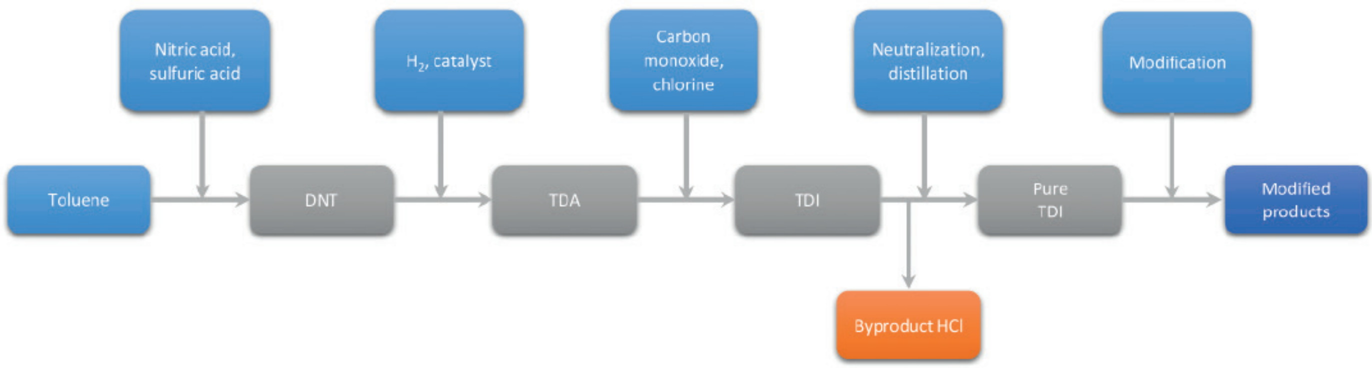

Figure 4. Schematic diagram of the manufacturing process of TDI.

Manufacturing of polyurethane

As mentioned before, the chemical reaction between isocyanate and polyol is usually a very fast process. However, even in this case, the use of NIR spectroscopy can lead to improvements of the product quality and consistency while minimizing reaction time. Online NIR spectroscopy was successfully utilized for the quality control of prepolymers **[13]**. Furthermore, this technique was used for the monitoring of the polymerization reaction, as it is demonstrated in Metrohm Process Application Note AN-PAN-1041 **[14]**. When measuring samples in transmission mode, NIR spectroscopy can be used for the improvement of reaction-injected molding or monitoring of curing online. Additionally, NIR can be utilized for the determination of the quality of the end product. In this case, NIR can assist in determination of physical properties, residual components (monomers), and other parameters. When using dedicated benchtop analyzer with probes, this technique can assist in optimization of reaction conditions in a small R&D reactor prior to scale-up.

General aspects in quality control of incoming raw materials, intermediates, and final products in the polyurethane industry

All mentioned production processes can be utilized by a single company, which forms a cluster of different plants. However, these manufacturing steps are also frequently distributed between different dedicated plants operated by multiple independent enterprises, which are often located in the same industrial area. This specialization adds an additional requirement to the previously mentioned quality control of the incoming materials. It is insufficient to verify only the identity of the incoming materials. In this case, it is also important to verify the quality, which is usually defined through multiple chemical and physical parameters such as acid and hydroxyl numbers, moisture content, and others.

This is a typical application field for the benchtop NIR instruments, which enable a combination of qualitative and quantitative analysis in a single step without any sample preparation. The main advantage of using NIR spectroscopy can be identified through the comparison of traditional» quality control and quality control using NIR spectroscopy (**Figure 5**). Traditional QC labs operate multiple instruments. Analysis of five parameters requires five instruments with five operating procedures. Some of these quality control procedures require sample preparation and chemicals and the analysis takes up to one hour. Furthermore, the lab technician needs to be trained to use these instruments. On the other hand, the lab manager can avoid this complexity using an NIR analyzer. One NIR analyzer can determine multiple quality parameters in a single operating procedure without any sample preparation or chemical waste within a minute. An operator can be trained to use the system within five minutes. This simplifies significantly quality control and reduces dramatically the costs of the daily quality control. A brief description of parameters, which can be determined in quality control using NIR spectroscopy in the polymer industry in general as well as in PU more specifically are summarized in Metrohm Application Bulletin AB-414 **[13]**.

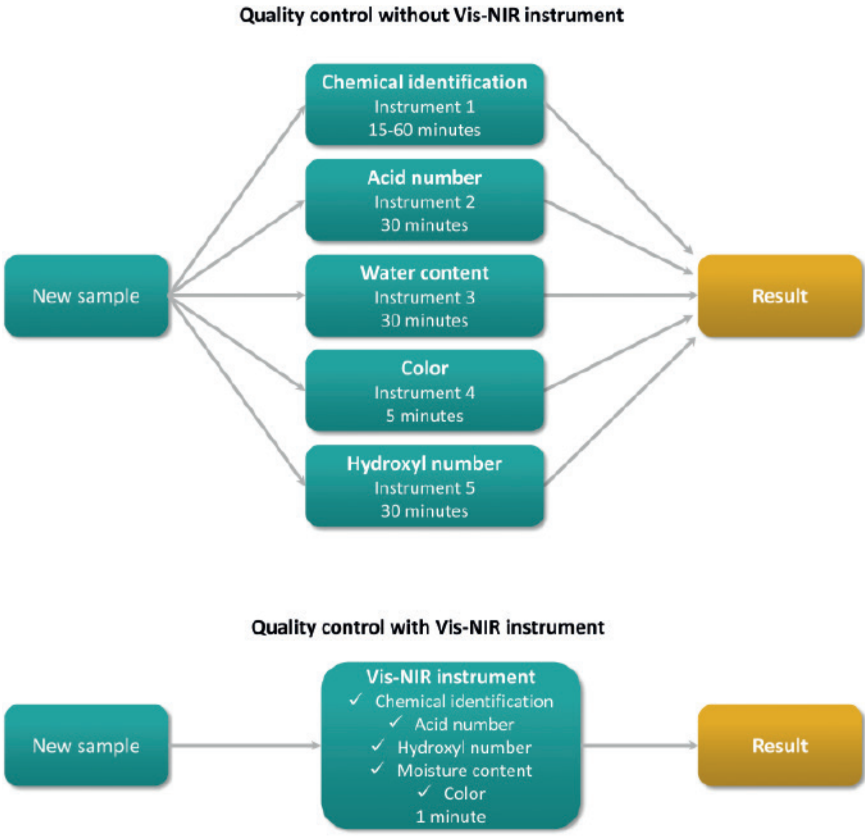

Figure 5. Quality control of polyurethane raw materials with and without Vis-NIR.

Spectroscopy as a tool for lean manufacturing

Lean manufacturing is a systematic approach to reduce waste during production without sacrificing productivity **[15]**. This approach stems originally from Japanese automotive industry. Combined with a Kaizen, a philosophy of continuous and never-ending improvement, this approach is quite often utilized as a management tool in a modern customer-orientated enterprise.

The Japanese word «muda» is used for the waste related to the production process. It means «futility, uselessness, or wastefulness». Waste are various processes, activities, and features, which do not add value to the final product. For examples, a fifth wheel on a car is muda. Continuous analysis of the performance of the production combined with the identification and reduction of muda gives the operator the possibility to improve the quality of the products and to reduce the costs of the manufacturing process.

Muda can be classified using a 7s model, which describes seven types of waste (**Figure 6**). These types of waste are:

- **Transportation.** For example, each movement of material from one location to another, which does not add value to a product, requires resources and can cause damage.
- **Inventory.** Stored components require space, packaging, and need to be transported. This increases costs compared to just-in-time manufacturing.
- **Motion.** For example, movement of machines or excessive travel between workstations does not add value to the product.
- **Waiting.** This is the waste of time, e.g., through waiting for components, response from another department, etc.
- **Over-production.** Excess needs to be stored, requiring again space and therefore also money.
- **Over-processing.** For example, additional work, which is not needed in the present step.
- And finally **defects:** quality issues, which require reprocessing or even disposal of the produced material.

Figure 6. 7s model.

Spectroscopy can be utilized as a tool for assisting the plant operator in the reduction of some types of waste, as is described below.

Transportation

A typical transportation problem is related to quality control or reaction monitoring. The operator needs to take a sample and bring it to the analysis location such as a QC labor or at-line lab. This type of waste can be eliminated by using online NIR, which brings the lab to the sample instead of bringing the sample to the lab.

Motion

The example above is also related to waste in the form of motion. Someone has to bring a sample to the lab. In large industrial parks, the distance to the lab can be very long. The use of benchtop NIR atline or online NIR minimizes the motion.

Waiting

As soon as the sample arrives in the lab it is integrated into the existing analysis workflow, namely:

- Sample preparation. In contrast, instead of wasting time for the sample preparation, the sample can be analyzed as-is using NIR or Raman spectroscopy.
- Sample analysis. Instead of analyzing multiple parameters on multiple analyzers, where each analysis can take up to one hour, multiple quality parameters can be determined in a single NIR measurement within a minute.
- Release. The lab manager needs to study multiple reports from all used analysis techniques and verify that the results are inside specification. A single report for multiple quality parameters combined with sophisticated operating procedure for QC as is realized in Metrohm Vision Air software simplifies paperwork and minimizes possible human errors.

Waiting can be also further minimized when using online NIR spectroscopy. The complete analysis can be performed directly in the production process within a minute. In contrast, classical sampling in process, atline, or offline analysis and release etc. can take up to one hour. This waiting of one hour, especially in processes with high consumption of energy, leads to a significant monetary loss, which can be eliminated using process analysis techniques such as NIR and Raman spectroscopy.

Inventory

The classical analysis of incoming raw materials, intermediates and final products costs time and can create waste as motion and transportation (distance to the lab) as well as waiting for results of analysis. Especially the last one can be problematic in case of incoming raw materials. It is not unusual that samples for QC of raw materials are low prioritized. The duration of waiting for the release by the QC department in this case can be hours or longer. Quite often, it is days, sometimes weeks. This means that the material needs to be stored, which requires space and is again linked to money. This situation can be significantly improved when using easy-to-use handheld analyzers, such as handheld Raman systems, directly in the warehouse. The advantage is that the identification of the incoming good can be immediately performed directly in the warehouse without sampling. The report can be sent to the QC manager for release, which shortens significantly the duration of the analysis and therefore also of the storage period.

Defects

The main problem with defects is the fact that they are usually identified at the end of the production process and no one knows where and which error occurred. This happens often when the operator does not control the process sufficiently, e.g., when the quality of the intermediates is not monitored. It is not unusual that an out-of-spec situation of a product occurs at the beginning of the production without being identified. This out-off-spec intermediate is subsequently processed until the final step, which generates costs. The possibility to avoid such monetary losses is the implementation of instruments for online reaction monitoring or atline quality control. However, the implementation of QC for intermediates is often associated with waste types «over-processing», «waiting», «motion» etc. Furthermore, such quality control generates additional costs due to the use of analysis methods, which require sample preparation and chemicals. Expenses for these chemicals play usually a significant role in the annual budget and limit the willingness to perform quality control of intermediates.

On the other hand, these analytical tasks can be solved using spectroscopic techniques mentioned in this White Paper. Due to the possibility of chemical-free analysis without sample preparation, the operating costs of such systems are negligible compared to wet chemical methods. The only one cost factor is the investment in the technique and its implementation into the existing process. However, through the significant cost-saving in the daily use the payback period is usually less than one year, which is extremely short.

An additional benefit of using spectroscopic tools, among others NIR and Raman spectroscopy, is their green nature. Both techniques do not require sample preparation and therefore chemicals. The only one chemical waste is the sample itself. However, only 2 milliliter of sample are needed for the analysis. This chemical-free analysis provides the operator a possibility to achieve ecological goals.

Summary

The present White Paper provides an overview about application possibilities of NIR and Raman spectroscopy in the production of polyurethane raw materials. It demonstrates that both techniques can assist the operator with the implementation of lean management principles while reducing costs and improving quality of the products. The implementation of these techniques in the specific production process as well as method development can be supported by your local Metrohm representative.

General application possibilities

Task	Solution
Raw material identification	Qualitative analysis using Raman spectroscopy through packaging materials
Raw material identification and verification of the specifications	Qualitative analysis using NIR spectroscopy combined with quantitative analysis for the determination of: • Moisture content • Particle size • Color properties • Chemical indices
Quality control of polyols	Quantitative analysis using NIR spectroscopy for the determination of: • Hydroxyl value, primary and secondary hydroxyl number • Acid number and total acid number • Moisture content • Solid content • Residual oxides • EO/PO ratio • Solvent content • Color, color index and further color related properties
Quality control of isocyanates	Quantitative analysis using NIR spectroscopy for the determination of: • Isocyanate content (NCO value) • Acid number and total acid number • Moisture content
Quality control of acid mixture	Quantitative analysis online using NIR spectroscopy for the determination of: • Nitric acid • Sulfuric acid • Hydrochloric acid • Moisture content
Solvent recovery	Quantitative analysis online using NIR spectroscopy for the determination of chemical composition of the recovered solvents
Reaction monitoring	Real-time end-point determination through determination of multiple quality parameters using ATEX certified online NIR systems
Control of the purification processes such as distillation	Real-time monitoring of multiple quality parameters in up to nine product streams using ATEX certified online NIR systems
Quality control of polyurethanes	Quantitative analysis online using NIR spectroscopy for the determination of • Physical properties • Residual components (monomers) • Percent linear expansion • Curing

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