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White Paper

Sample preparation in viscometry of polymer solutions

Executive summary

Proper sample preparation is essential for accurate viscosity measurements of polymer solutions. Even if the viscometer is functioning properly, errors in sample prep - such as during weighing, dispensing the solvent, dissolving the polymer, or temperature control - can affect the final result.
This guide describes the main steps in sample preparation, explains where errors can occur, and discusses methods that can improve accuracy and repeatability. The information is based on practical laboratory experience and follows the principles used in commonly **referenced standards** such as **ISO 1628, ISO 307, ASTM D4603, and ASTM D789.**

The following sections cover the key aspects of sample preparation that influence the accuracy and repeatability of polymer solution viscometry:

- Factors affecting measurement uncertainty
- Polymer concentration
- Sample and solvent quantification
- Manual and automated sample preparation
- Volumetric and gravimetric methods
- Dissolution, stirring, heating, and grinding
- Polymer degradation
- Safety considerations

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1. Introduction

Viscometry of polymer solutions using glass capillary viscometers is widely used for quality control of technical polymers and plastics. It provides information about the degree of polymerization, which is important for both processing and final product properties. Dilute solution viscosity is commonly measured for polyesters and polyamides (condensation polymers) during production, processing, and recycling. The method is also used, although less frequently, for polymers such as PMMA, PVC, polycarbonate, and polyolefins.

Commonly referenced standards include **ISO 1628 (Parts 1-6), ISO 307, ASTM D2857, ASTM D4603, and ASTM D789.** Figure 1 shows a viscometry system used for the measurement of polyamides, polyesters, and polyolefins.

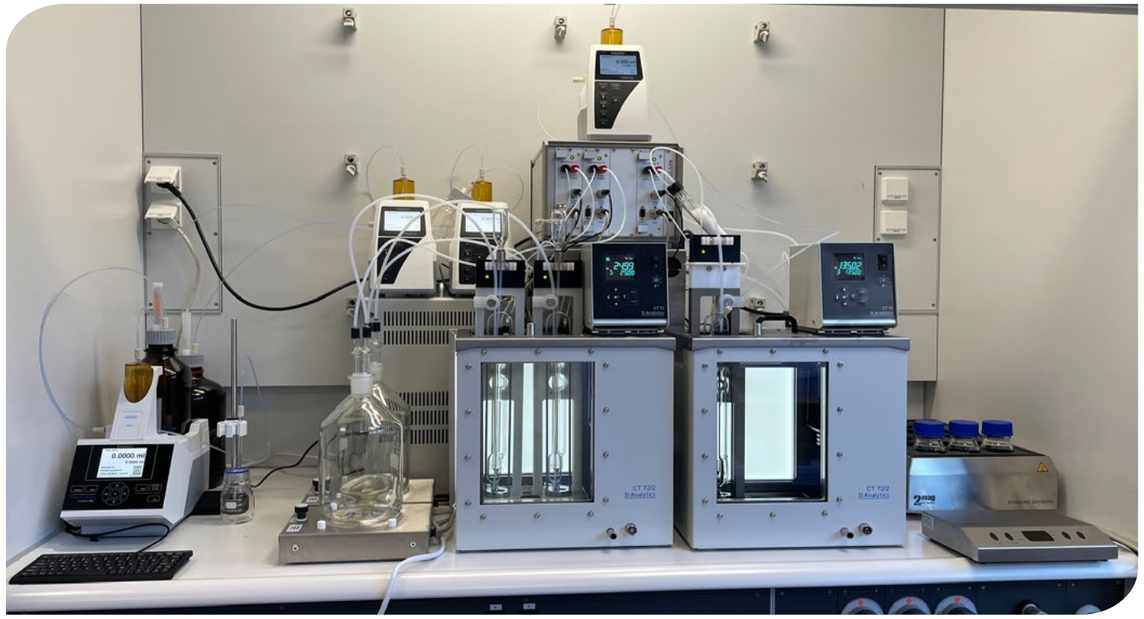


Figure 1: Viscometry measuring system AVS® 370, positioned in a fume hood at KraussMaffei Extrusion GmbH, Hannover.[1]

The sample preparation setup shown in Fig. 1 includes: A burette for automated solvent dosing located on the left side, and a heated stirrer on the right side, required for PE/PP dissolution at elevated temperature. A fume hood is recommended due to the hazardous solvents used in these applications.

The measurement uncertainty of the final results (e.g., relative viscosity, viscosity number, or intrinsic viscosity) has been evaluated in several round robin studies. Compared with kinematic viscosity measurements, which are performed using the same capillary viscometers for applications such as petrochemicals and pharmaceuticals, polymer solution viscometry generally has higher measurement uncertainty. The primary reason is that polymer solutions must be prepared before measurement, and the quality of this preparation has a major influence on the result.

The most important factors include:

- **Polymer concentration:** The concentration must meet the value specified by the applicable standard. Deviations from the target concentration typically result in a similar percentage error in the final viscometry result.
- **Complete dissolution and polymer stability:** Polymers may degrade, particularly when elevated temperatures or aggressive solvents are required. Dissolution can take several hours, and all sample material must be completely dissolved before measurement. The solution should be inspected to ensure that no undissolved particles remain.

The following sections describe the key steps in sample preparation, the methods and equipment commonly used, and the critical points where errors can occur.

[1] Published with permission.

2. Achieving accurate polymer concentration

2.1 Concentration variables in polymer viscometry

The concentration of a polymer solution is commonly expressed as the mass of polymer dissolved in a defined volume of solution. This is referred to as mass concentration and is typically reported in units such as g/ml, g/dl, g/L, or mg/ml.

Other concentration definitions are also used in polymer analysis. Table 1 summarizes the concentration parameters referred to in this guide.

	Name	Formula	Description	Unit
(1)	Mass concentration	$c_P = m_P / V$	c_P: polymer concentration m_P: polymer mass V: volume of solution	g/ml, g/dl, g/l, mg/ml
(2)	Mass concentration, based on solvent volume	$c_P = m_P / V_S$	V_S: volume of solvent	g/ml, g/dl, g/l, mg/ml
(3)	Mass fraction of polymer	$w_P = m_P / m$	m: total mass of solution	/

Table 1: Concentration parameters used in polymer analysis

2.2 Quantifying the sample portion: balance and weighing

The sample portion is determined by weighing. An analytical balance is required for dilute solution viscometry methods such as **ISO 1628 (Parts 1–5), ISO 307, and ASTM D4603.** In these methods, the sample mass typically ranges from 50 to 500 mg.
The applicable standards also specify the required weighing accuracy. In many cases, the sample mass must be measured to the nearest 0.2 mg, requiring an analytical balance with a readability of 0.0001 g. To achieve this level of accuracy, the balance should be equipped with a draft shield and placed on a stable, vibration-free surface, away from drafts and electromagnetic interference. Figure 2 shows a typical analytical balance used for polymer viscometry sample preparation.

Figure 2: Typical analytical balance, required to weigh sample portion in dilute solution viscometry

2.3 Quantifying solvent in standard sample preparation

Volumetric flasks are the standard laboratory equipment used to prepare polymer solutions to a defined volume. The final volume includes both the solvent and the dissolved polymer, rather than the solvent alone. This approach corresponds to the mass concentration defined in Table 1, row (1).
Sample preparation is typically performed as follows: First, the weighed polymer sample is transferred to the volumetric flask. Next, approximately 50% to 80% of the required solvent is added. After the polymer has completely dissolved, additional solvent is added carefully until the solution reaches the graduation mark of the flask (Figure 3).

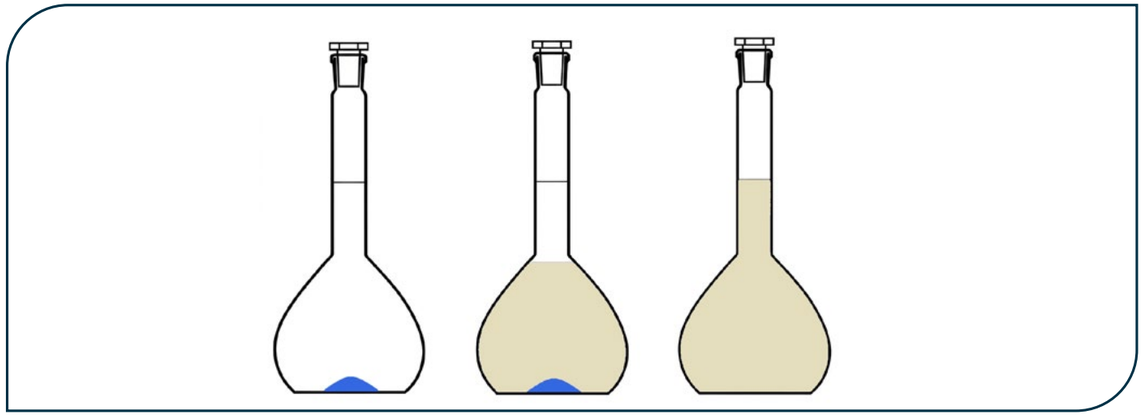


Figure 3: Three-step sample preparation using a volumetric flask. After the polymer has completely dissolved, the solution is brought to the graduation mark with solvent.

2.4 Key considerations for manual volumetric sample preparation

The following sections describe important aspects of manual sample preparation for polymer viscometry that can affect concentration accuracy and, ultimately, the measurement result.

Sample Weight / Weighing

When preparing samples as described above, the required test portion depends on the target concentration and the volume of the volumetric flask. For example, ISO 307 specifies a concentration of 0.5 g/dl for polyamide (PA).
Using a 50 ml volumetric flask requires exactly 250 mg of polymer to achieve this concentration.

Obtaining this precise mass can be challenging when the polymer is supplied as pellets or other granular material. It may be necessary to repeatedly add or remove individual pellets until the required mass is achieved. If the measured mass differs from the nominal value (250 mg), the actual mass must be used when calculating the solution concentration. The target concentration of 0.5 g/dl is achieved only when the polymer mass is 250.0 ± 0.2 mg.

Additional requirements are specified in the standards. For example, polyamide readily absorbs moisture. ISO 307 therefore recommends that samples are dried before weighing. Weighing should also be completed quickly to minimize moisture uptake from the air.

2.4 Key considerations for manual volumetric sample preparation

Sample Weight / Weighing

In many cases, the test material is not pure polymer but contains other components, such as fillers or glass fibers. Because the concentration refers only to the polymer content, the additive content must be considered when calculating the required sample mass. For example, if a material contains 10% glass fibers and the target polymer mass is 250 mg, the total test portion must be 277.8 mg, calculated as:

250 mg ÷ (100 − 10) × 100 = 277.8 mg

Detailed calculation methods and additional examples are provided in the applicable standards.

Use of magnetic stirring bars

Up to this point, the discussion has focused on obtaining the correct polymer mass. Accurate solvent volume is equally important for achieving the required polymer concentration.

If a magnetic stirring bar is used, it should be removed before the final fill to the graduation mark. To avoid loss of polymer solution adhering to the stirring bar, the bar should first be moved to the neck of the flask using an external magnet and rinsed with solvent so that any remaining solution flows back into the flask. The stirring bar should only then be removed.

This **procedure is straightforward for aqueous solutions** but becomes more difficult when hazardous solvents commonly used in polymer analysis are involved. Later in this guide, automated sample preparation systems are discussed as a way to simplify this process.

Use of pipettes or burettes instead of volumetric flasks

Some viscometry standards, such as ASTM D789 for concentrated polyamide solutions, specify the volume of the pure solvent rather than the total solution volume. In these methods, volumetric flasks are not used. Instead, the solvent volume is measured using a pipette or burette. This approach corresponds to the concentration definition given in Table 1, row (2).

Because measuring solvent volume with a pipette or burette is simpler than preparing solutions in volumetric flasks, some laboratories use this approach even when standards specify concentration based on the total solution volume, effectively ignoring the volume occupied by the dissolved polymer.

To illustrate the effect of neglecting polymer volume, consider a target concentration of 0.5 g/dl and assume that both the solvent and dissolved polymer have a density of 1 g/ml. A solution prepared with 100 ml of solvent and 0.5 g of polymer has a total solution volume of 100.5 ml. As a result, the actual concentration is approximately 0.5% lower than the target value, producing a similar bias in the final viscometry result.

This difference may not be significant when results are compared only within the same laboratory, as repeatability is generally unaffected. However, it becomes important when comparing results between laboratories or when compliance with a specific standard is required.

2.4 Key considerations for manual volumetric sample preparation

Influence of temperature on volumetric solvent quantification

Because all liquids expand or contract with temperature, the accuracy of volumetric dosing depends on the temperature of the solvent or solution. Approximate thermal expansion coefficients for common solvents are listed in Table 2.

Solvent	$y / 10^{-4}K^{-1}$
Sulfuric acid (96%)	5.5
Phenol / 1,2-Dichlorobenzene (50:50)	8.5
Formic acid 90%	8
m-Cresol	8
Chloroform	8

Table 2: Approximate thermal expansion coefficients for common solvents

The resulting concentration error is approximately **0.05% to 0.09% for every 1 °C difference** between the sample preparation temperature and the viscosity measurement temperature.

To minimize this source of error, the final step of volumetric sample preparation - bringing the solution to the graduation mark – needs to be done at a temperature close to the measurement temperature. For example, the ISO 307 standard specifies a range between 23 °C and 27 °C for the final step of volumetric sample preparation - namely, filling the solution to the scale mark - for the final filling when the measurement temperature is 25 °C. This maximum temperature difference of ±2 °C limits the concentration uncertainty due to thermal expansion to approximately 0.11% when using sulfuric acid as the solvent.

2.5 Automation of sample preparation

Manual sample preparation using volumetric flasks is the reference method specified in most polymer viscometry standards. It requires only basic laboratory equipment and minimizes the risk of systematic errors because no automated devices are involved.

However, many laboratories have adopted automated sample preparation to improve efficiency, consistency, and operator safety.

The main advantages include:

- Volumetric flasks have a fixed volume, requiring the sample mass to be weighed very precisely to achieve the target concentration. This can make sample preparation time-consuming and increases the potential for weighing errors.
- When magnetic stirring is required, removing the stirring bar and bringing the solution accurately to the graduation mark can be labor-intensive, particularly when hazardous solvents are used.

Volumetric sample preparation using automated burettes

Automated piston burettes equipped with sample preparation software can simplify these procedures. Based on the measured sample mass, the software calculates the required solvent volume so that the target concentration is achieved without requiring an exact nominal sample mass.
Xylem Analytics piston burettes include software with calculation routines for polymer solution preparation.

When calculating the required solvent volume, the software accounts for the volume of both the solvent and the dissolved polymer. This calculation requires the density of the polymer.

For dilute solution viscometry, the polymer occupies only a small fraction of the total solution volume. Therefore, a literature value for polymer density is generally sufficient, as uncertainty of this value has only a minor influence on the final concentration. In some cases, the appropriate density value is specified directly in the applicable standard (for example, ISO 307).

Figure 4: Xylem burette Titronic® 500, used for polyamide solution preparation. The burette is available with special dosing units suitable for corrosive and high-viscosity solvents such as concentrated sulfuric acid

2.5 Automation of sample preparation

Gravimetric sample preparation using special balances

In addition to volumetric flasks, pipettes, and burettes, some automated sample preparation systems determine the required amount of solvent by weighing rather than by volume. The conventional approach is referred to as Weight by Volume (w/v), while the latter is known as Weight by Weight (w/w) because both the polymer and the solvent are quantified by mass.

With the w/w method, the composition of the solution is initially expressed as the mass fraction (w), as defined in Table 1, row (3). The mass fraction is a dimensionless quantity, typically expressed as a percentage (%). It can be converted to the mass concentration (cp) by multiplying it by the density (ρ) of the solution:

$$c_P = w_P \cdot \rho \quad \text{(Eq. 1)}$$

Strictly speaking, ρ should be the density of the final solution. However, for most applications it can be approximated sufficiently by the density of the solvent, which is available from standards or the literature.

Note: The relationship between these concentration parameters is described here because mass concentration (g/dl) is sometimes incorrectly equated with weight percentage (%). This is only valid when the density ρ is exactly 1 g/ml. At other densities, the numerical values differ.

The primary advantage of the w/w method is that mass measurements are independent of temperature, whereas volume measurements are affected by thermal expansion. As a result, w/w sample preparation can provide improved repeatability and, in some cases, greater concentration accuracy.

2.5 Automation of sample preparation

However, polymer viscometry standards specify concentration as weight by volume (w/v). This convention is based not only on historical practice but also on the fundamental work of Einstein (1906) and Staudinger (1930), which showed that the **viscosity** of a polymer solution is **related to** the **volume fraction of** the dissolved **polymer**.

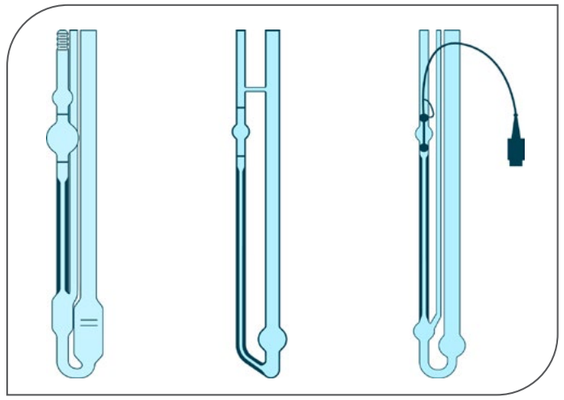
When using the w/w method, the mass concentration must therefore be calculated from equation 1 using the solution density. Any **error in the density value** introduces a **systematic difference** compared with the **volumetric reference method**. For example, the density of solvent mixtures can vary significantly with composition, as in phenol/1,2-dichlorobenzene (50:50 w/w) mixtures or sulfuric acid with different water contents.

Another disadvantage of the w/w approach is the increased hardware complexity. Automated gravimetric dosing requires a balance integrated with software that continuously monitors the solvent mass during dispensing to determine the correct endpoint. By comparison, volumetric dosing with an automated burette is mechanically simpler.

Despite these limitations, gravimetric solvent dosing offers an advantage for certain applications involving volatile solvents such as dichloromethane or chloroform. Solvent losses caused by evaporation during or after dispensing can be compensated by weighing, improving dosing accuracy. However, the lowest risk of solvent loss is still achieved with volumetric flasks, making the reference method superior for these applications.
The advantages and limitations of the different sample preparation approaches are summarized in Table 3.

	Manual, volumetrically Volumetric flasks Weight by Volume (w/v)	Automated, volumetrically Solvent quantified by burette Weight by Volume (w/v)	Automated, gravimetrically Solvent quantified by balance Weight by Weight (w/w)
Reference method	✓	✓	–
No influence of temperature on dosing quantity	✕	✕	✓
Complexity / price	Simple / cheap	Simple / affordable	Complex / expensive
Ease of use	–	+	(+)
Accuracy	+/-	+	+
Repeatability	+/-	+	++
Comparability to reference method	++	+	(–) density of solvent must be known precisely
Accuracy in case of volatile solvents	+	–	+

Table 3: Sample preparation: Comparison of different ways of solvent quantification.[2]



[2] Quantity of test specimens is always determined by analytical balance.

3.Dissolution of test specimen: stirring, heating, and optional grinding

As discussed previously, polymers typically require time to dissolve after the solvent has been added. To accelerate dissolution, stirring or shaking is generally required, with magnetic stirrers being the most common choice in laboratories. Dissolution time depends on both the polymer and the solvent. For example, polyamide granules require approximately 1 hour to dissolve in 90% formic acid at room temperature, but about 4 hours in 96% sulfuric acid due to its higher viscosity. Sample form also affects dissolution time, with granules or shredded plastic requiring longer than finely ground powder.

The applicable standards often specify the required dissolution temperature. For example, PET requires elevated temperatures for complete dissolution. ASTM D4603 specifies a dissolution temperature of 110 °C and a dissolution time of 15 to 45 minutes. Because elevated temperatures can promote polymer degradation, the dissolution time should be limited to the range specified in the standard. Grinding the sample can further reduce dissolution time because powders dissolve more rapidly than pellets or granules.

3.1 Grinding

The details of grinding are beyond the scope of this guide. However, the following points should be mentioned here.

Grinding PET

Grinding is commonly used during PET sample preparation. PET is often highly crystalline, which slows dissolution. Reducing the particle size can significantly shorten the dissolution time. Because PET is relatively elastic, cryogenic grinding is generally required. Cooling the sample with liquid nitrogen makes the material brittle, allowing efficient grinding. Suitable laboratory mills are commercially available from several manufacturers.

Representative Sampling

Grinding also improves sample representativeness in dilute solution viscometry. Typical test portions are only 150–250 mg, consisting of just a few pellets. If these pellets are analyzed directly, the test portion may not accurately represent the bulk material.
This is particularly important for processed polymers, where different regions may have experienced different degrees of degradation and therefore have different molecular weights. Even virgin PET pellets can exhibit molecular-weight variations. During solid-state polycondensation (SSP), a radial molecular-weight gradient develops, with the outer regions of the pellet having a higher molecular weight than the core. As a result, intrinsic viscosity (IV) measurements can vary depending on pellet size. Grinding a larger quantity of material before sampling produces a more representative test specimen.

3.2 Stirrers

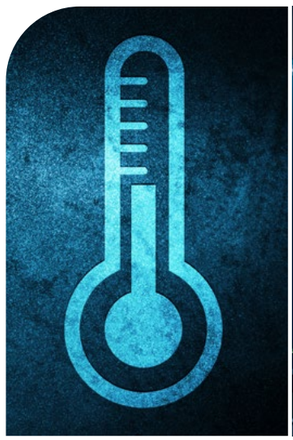
Magnetic stirrers are the most commonly used devices for dissolving polymer samples. When dissolution can be performed at room temperature, multi-position magnetic stirrers allow several samples to be prepared simultaneously. Laboratory shakers may also be used, although they are less common.

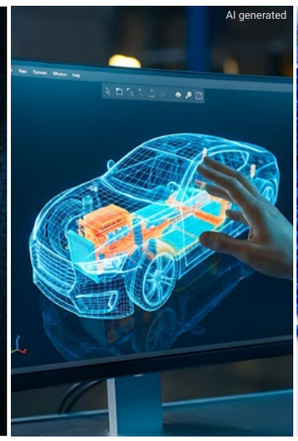
When elevated dissolution temperatures are required, either an oil bath or a magnetic stirrer equipped with a heating block may be used. Heated magnetic stirrers are available from a limited number of manufacturers and generally provide more convenient handling of sample bottles than liquid baths.

3.3 Possible causes for polymer degradation

Several factors can contribute to polymer chain degradation during sample preparation.

- **Temperature and dissolution time** should remain within the limits specified by the applicable standard.
- **Solvent quality is also critical.** Condensation polymers, such as polyesters, can undergo hydrolysis if water is present in the solvent, particularly at elevated temperatures. For this reason, ISO 1628-5 and ASTM D4603 specify maximum moisture contents for the solvent. Because hydrolysis is acid-catalyzed, ASTM D4603 also recommends the addition of a hydrogen chloride scavenger.
- **Oxidation** should be considered for polyolefins. Polyethylene (PE) and polypropylene (PP), measured according to ISO 1628-3 at 135 °C, are susceptible to oxidation at the required dissolution temperature. Consequently, the standard specifies the addition of an oxidation inhibitor to the decalin solvent.
- **Shear stress** can also degrade polymers, although this is uncommon and is primarily relevant for cellulosic materials such as paper, pulp, and cotton dissolved in bis(ethylenediamine) copper(II) hydroxide (CuEN). In these applications, sample preparation should follow the standard carefully, as excessive stirring and oxygen exposure can degrade the cellulose chains.





3.4 Safety precautions

Many polymer viscometry methods require hazardous solvents. All applicable laboratory safety procedures and local regulations must therefore be followed. The recommendations below are intended only as a supplement and are not a substitute for laboratory safety requirements.

- **Personal protective equipment (PPE)** should always be worn.
  → Safety glasses
  → Laboratory coat
  → Appropriate chemical-resistant gloves
  → Additional PPE, such as safety shoes or a face shield, when required
- **Sample preparation at elevated temperatures**
  Hot surfaces and heated solvents present additional hazards. When using an oil bath, the temperature should be controlled with an independent control thermometer. Care should be taken to ensure that the sample bottle is never heated above the boiling point of the solvent, particularly when hazardous solvents are used.
- **Hazardous and volatile solvents**
  Sample preparation involving volatile or hazardous solvents should always be performed in a properly functioning chemical fume hood.

Contact

This content was created from:
Dr. Andreas Eich
Product Manager Viscometry
andreas.eich@xylem.com
Xylem An alytics Germany Sales GmbH & Co. KG, SI Analytics
Erich-Dombrowski-Straße 4
D-55127 Mainz
Germany

For questions or comments, please contact Dr. Andreas Eich.

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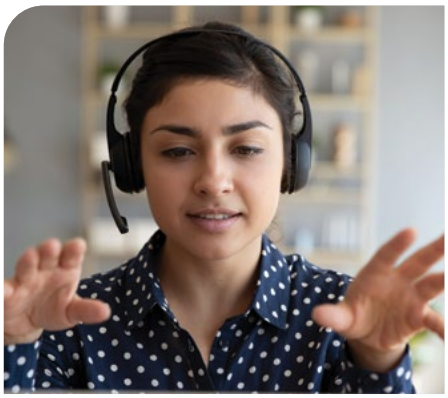

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SI Analytics
xylem

Xylem Analytics Germany Sales GmbH & Co.
Am Achalaich 11
82362 Weilheim
Germany

Phone: +49 881 183-0
Fax: +49 881 183-420
Info.XAGS@xylem.com
www.xylemanalytics.com

xylem