



Pulp and Paper Industry

Dependable online, inline,
and atline solutions for your
papermaking needs

**PUSHING
THE
LIMITS
TOGETHER**

 **Metrohm**
Process Analytics

Monitoring your process 24/7



**Maximize profitability,
comply with regulations,
and stay safer**

Metrohm Process Analytics understands the challenges our clients face and creates tailored solutions for them. In the past 45 years, we have developed and installed over 10,000 industrial process solutions all over the world. We assist in decision-making and combine our extensive experience in sampling and analysis with our expertise in chemistry, software development, and engineering to create the ideal analyzer for your process needs.

The Metrohm Process Analyzers take the famous Metrohm laboratory solutions a step further. Fully automated, online, and customizable analyzers facilitate process monitoring across a wide array of industries. Drawing on our core competencies in titration, spectroscopy, ion chromatography, and electrochemistry, we leverage our applications knowledge to create reliable solutions for process analysis that optimize efficiency, decrease chemical consumption, and create a safer work environment.

Benefits of online monitoring in the pulping process

In the pulp and paper industry, the Kraft process is the dominant pulping process used to turn solid wood into sheets of paper. It is full of complex processes and aggressive chemicals but it has the highest chemical recovery efficiency compared to other pulping processes.

HARSH SAMPLES AND SAFE MEASUREMENTS

The first step for pulping paper consists of saturating wood chips with white liquor (a mixture of sodium hydroxide «NaOH» and sodium sulfide «Na₂S») to break down the lignin and cellulose linkages. This mixture is cooked at high temperatures in pressurized digesters forming a liquid stream consisting of pulp solids and black liquor. Next, the mixture is washed and the resulting pulp is sieved, rinsed, and bleached to produce paper as a final product.

The main objective of the subsequent process is recovering the resulting liquors from the prior washing step to reuse in future pulping processes. Chemical recovery is a key process as it does not only allow the reuse of chemicals (saving costs, reducing environmental impact) but it also provides additional utilities (steam, power) throughout the pulping process.

After the first washing step, a significant amount of the now «weak» black liquor (~15 wt% solids) continues to the chemical recovery loop into multiple evaporators. Here, the excess water from weak black liquor is evaporated to increase its solids content.

The now «strong» black liquor (>65% solids) enters the recovery boiler, where sodium sulfate «Na₂SO₄» is reduced to sodium sulfide «Na₂S». Then, the green liquor (containing mostly Na₂S and sodium carbonate «Na₂CO₃») is sent to the causticizing plant to react with lime «CaO» and regenerate white liquor for the pulping process. Thus, the recovery cycle is completed.

OPTIMAL CHEMICAL RECOVERY CYCLE FOR A SUCCESSFUL PULPING PROCESS

Optimizing the pulping process can lead to significant cost reductions, safer working environments, reduction of waste and rework, and product quality improvements.

This can be done by monitoring the composition of the white and green liquors in «real-time». Therefore, in order to optimally run the chemical recovery process, constant quality checks and analyses should be performed.

KEY PARAMETER:

DIRECT MEASUREMENTS WITH TITRATION, ION CHROMATOGRAPHY, AND SPECTROSCOPY:

- Effective «EA», Active «AA», and Total Alkali «TTA» in pulping liquors (white, green, and black liquor)
- Carbonate «Na₂CO₃» in green liquor
- Hydroxide «NaOH» in pulping liquors
- Sulfide «Na₂S» in green liquors
- CE% (causticizing degree) in Caustic plant
- and more ...



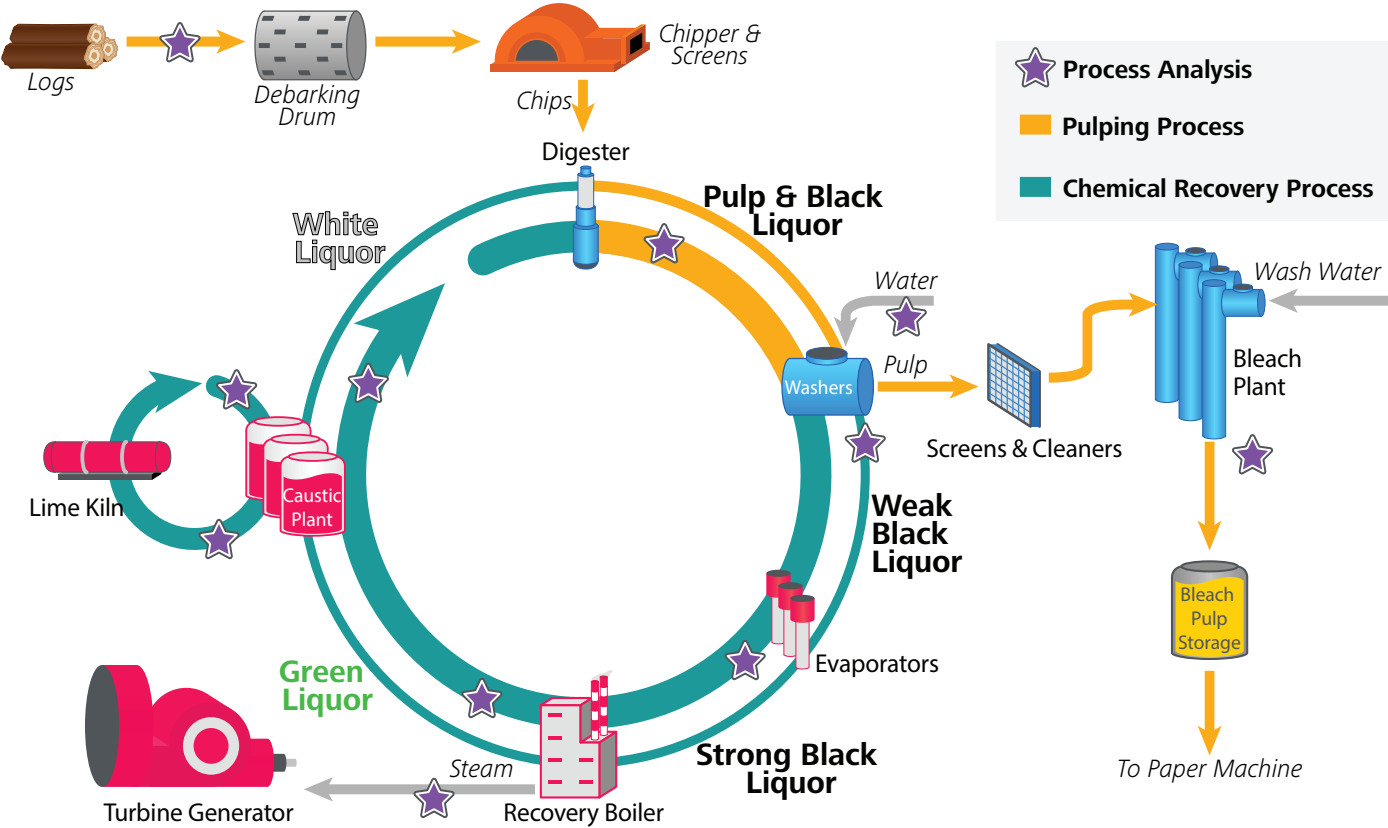
Chemical Recovery Process using online analyzers

In the **Kraft recovery cycle**, the constant monitoring of multiple parameters is necessary for maintaining the optimal recovery process, improving reaction yield, and enhancing process optimization. However, process samples are very hot and corrosive (like white liquor), increasing the risk of accidents when sampling manually.



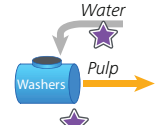

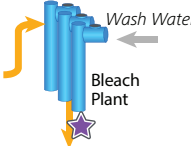







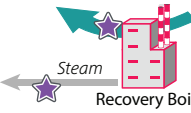


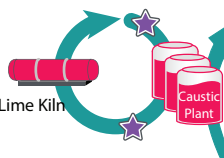


It is also important to consider that variations in one part of the cycle will result in disturbances in the downstream unit operation. In turn, these disturbances can create further variations, causing a downward spiraling effect. Additionally, laboratory analysis contributes to long response times between the sampling and the analysis results. In

cases involving significant process changes, this also undermines the recovery efficiency.

Metrohm Applikon, with the brand of Metrohm Process Analytics instruments, is able to offer several applications solutions for the pulp and paper industry. Process analyzers from Metrohm are designed to offer fast, reliable, accurate measurements in a rugged housing, 24/7 to ensure processes are always running within specifications. Online analysis with industrial process analyzers lessens the need for highly-skilled technical employees and saves time by automating measurements directly at the sample point.



IMPORTANT PARAMETERS RELATING TO PULP AND PAPER ANALYSIS

Process segment	Process Analysis Technology	Key parameters	
		Incoming goods:	
		<ul style="list-style-type: none">- Moisture- Brightness- Wood species	<ul style="list-style-type: none">- Acetic acid- Resin
		Process water:	
		<ul style="list-style-type: none">- Organic acids or sulfur species in process water	
		Wash water:	Pulp:
		<ul style="list-style-type: none">- Calcium and Magnesium in brine	<ul style="list-style-type: none">- Residual H₂O₂ in bleaching
		Pulp:	
		<ul style="list-style-type: none">- Lignin content- Kappa number- Cellulose content	<ul style="list-style-type: none">- Total organic material- Liquor and crude tall oil- Resin content
		Pulping liquors:	
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%
		Pulping liquors:	Black liquor:
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%- REA- Solid content
		Pulping liquors:	
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%
		Pulping liquors:	
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%
		Steam:	
		<ul style="list-style-type: none">- Trace impurities in steam	
		Pulping liquors:	
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%
		Pulping liquors:	
		<ul style="list-style-type: none">- EA, AA, and TTA- Carbonate- Hydroxide	<ul style="list-style-type: none">- Sulfidity- CE%

Preconditioning

Solution provider for all types of challenges



SAMPLE PRECONDITIONING AND INTEGRATED SYSTEMS FOR CHALLENGING SAMPLE STREAMS

Besides the chemical analysis, sample preparation, preconditioning, and location of the analyzer are deciding factors for the success of inline, online, and atline analysis. Metrohm Process Analytics can provide a comprehensive solution for almost any application: an analyzer in combination with sample preparation or even a complete package with a shelter, piping, wiring, and interfacing. This allows seamless startup and integration of the instrument on site.

Metrohm Process Analytics can engineer and supply virtually any «unit operation» for sample preconditioning. With more than 45 years of experience, we can provide a complete and exact solution for almost any application. Projects range from one analyzer in combination with simple sample panel preparation to complete complex turn-key packages.

On site, only the necessary utilities and the sample stream need to be connected, saving significant time and energy in the start up phase of the instrument.

Analyzers tailored to your requirements

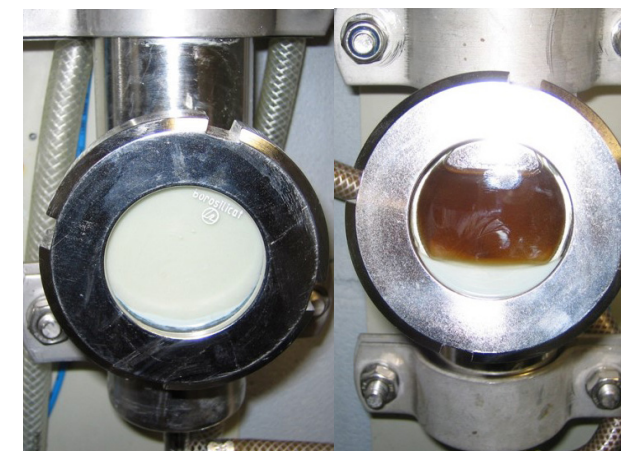
«Sample preparation and preconditioning of the sample stream are deciding factors for the success of online and atline analysis»

RELIABLE SETTLERS TO REMOVE SOLIDS BEFORE ANALYSIS

In online and inline analysis, where the most representative analytical data is collected right at the process point, sampling and sample preparation are at least as important as the analyzer itself.

Metrohm Process Analytics has vast experience in this area, capable of offering custom-made sampling systems from pressure reduction and filtering to degassing and cooling.

In the Kraft process, any analysis in the process is a challenge since the sample stream is corrosive, full of solid particles, and at elevated temperatures. Thus, there are risks of accidents when sampling manually.



Settlers installed on-site before and after the filtering step.



A customized sampling panel designed according to your process needs is part of the full solution to overcome such challenges. With Metrohm Process Analytics, your sampling panel will be designed with settlers to remove solid particles, include automatic temperature controllers, and will be built as a closed system to avoid dangerous spillages and fumes. Some of the benefits that Metrohm Process Analytics provides you with our sampling preconditioning panels are:

- IP66 enclosure for harsh environments and in plant operation
- Ability to monitor multiple sample streams from any part along the process
- Automatic temperature control to avoid fluctuations in the results and maintain safe temperatures in the sample stream
- Closed system for added safety
- Stainless steel materials to ensure chemical resistance to harsh sample streams

Smart programming for multiparameter analysis

«Real-time» process control to optimize multiple parameters (e.g., liquor quality) enables improved liquor reutilization, reduced equipment maintenance, and increased recovery and causticizing efficiency. In pulp mills, alkali determination is commonly made through ABC-tests either in the laboratory (every hour) or online (**every 30 minutes**) with our 2060 Process Analyzer.



Intuitive software designed to program and control the analyzer with various analysis applications (e.g., tiamo, vision, ...)

Reliable reference method to build an optimal calibration model of your sample stream

Reagent cabinet integrated with (non-contact) level detection to increase analyzer uptime

2060 Process Analyzer

Near-infrared spectroscopy «NIRS» is a *secondary* technique, meaning it requires a prediction model (obtained by a primary method such as titration) if quantification of samples is desired.

Titration-based methodologies can complement online NIRS which offers 24/7 reagentless automated measurements **every 45 seconds** with no need to carry samples to the laboratory. A single NIRS process analyzer can be connected to **up to nine sampling points**, offering a competitive cost-per-sampling point. Depending on your needs, either the NIRS XDS Process Analyzer, the 2060 Process Analyzer, or a combination of both analyzers can be implemented.



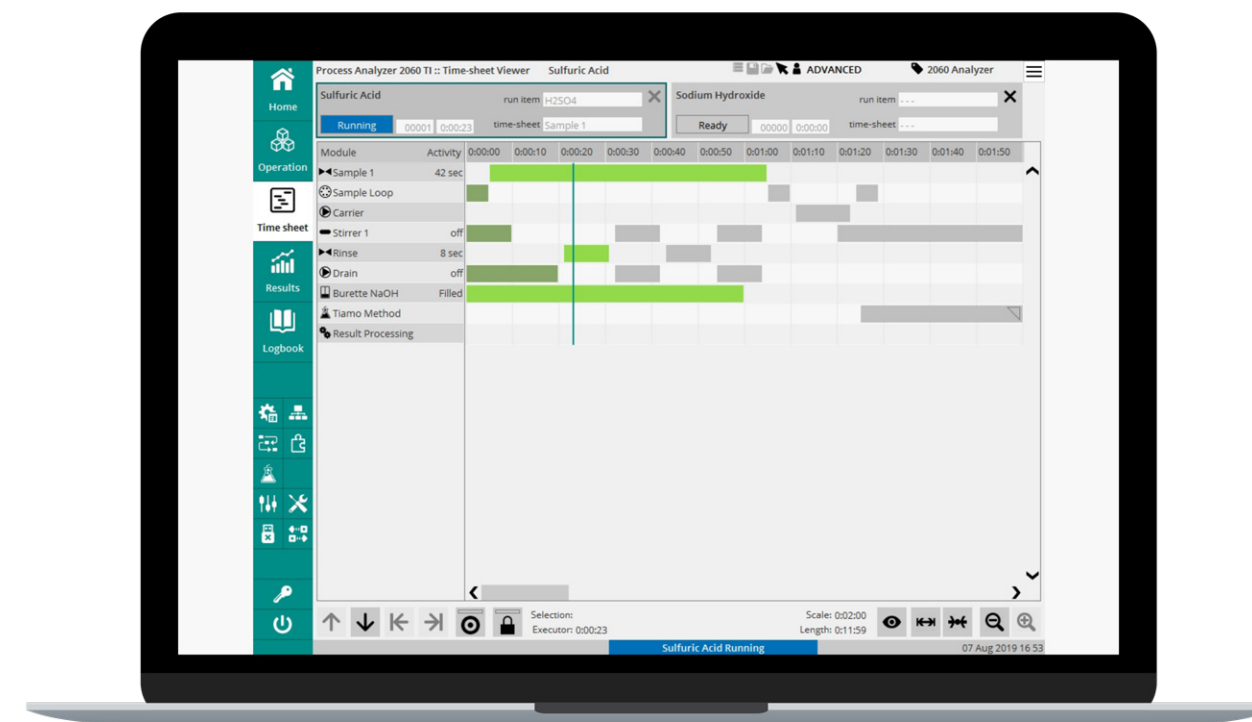
Multiplexing capability of NIR systems – More savings per measurement point and results

No reagents – No chemical waste

Wide scan range (800 to 2200 nm) that enables a wide range of applications

Fast analysis results around the clock (24/7)

NIRS XDS Process Analyzer



UNIQUE SOFTWARE FOR AUTOMATION AND «REAL-TIME» CONTROL

Our **2060 software** is more than your average instrument software. It was designed to efficiently program and control the analyzer for any industrial application. Using so-called «time programming sheets», the analyzer program execution is displayed in a clear graphical timeline representation. Alarms can be programmed to monitor the current status of the analyzer and the date can be communicated using a variety of process communication protocols (e.g., Modbus or Discrete I/O).

When the NIRS XDS Process Analyzer and the 2060 Process Analyzer are used in combination, both analyzers are connected to the same 2060 software. All analysis results are processed by the 2060 software and directly sent to the plant's programmable logic controller (PLC) or distributed control system (DCS) every 45 seconds (for NIRS) or twice per hour (for titration, as per customer needs).

OUR «ALL-IN-ONE» SOFTWARE ALLOWS:

- **Performing routine analysis**, with operation methods, time sheets, and displaying trend charts.
- **Automation** by programming, connecting to sensors, and activating pumps or valves.
- **Process communication** via analog or digital protocols.
- **Remote support** so our engineers can access remotely for diagnostics and maintenance.

This complete solution enables fully automatic diagnostics of the chemical recovery process – around the clock, seven days a week. When the analyzers detect an erroneous result, the 2060 software has been designed to send automatic feedback to the process and take action (e.g., re-measure a sample, or start a cleaning cycle if necessary).

Multiparameter analysis –

Titration and spectroscopy in full synergy

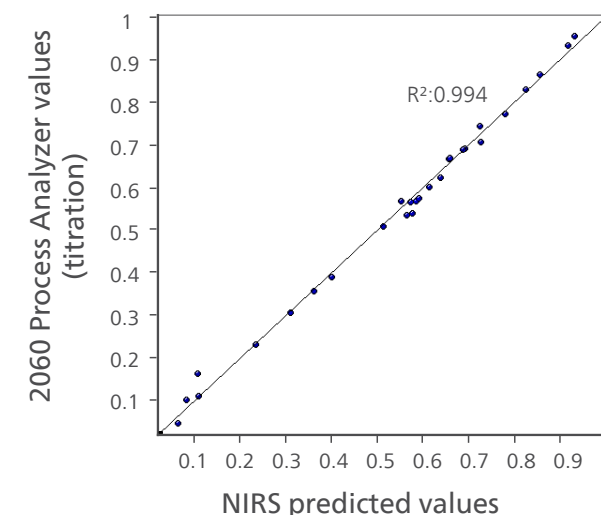
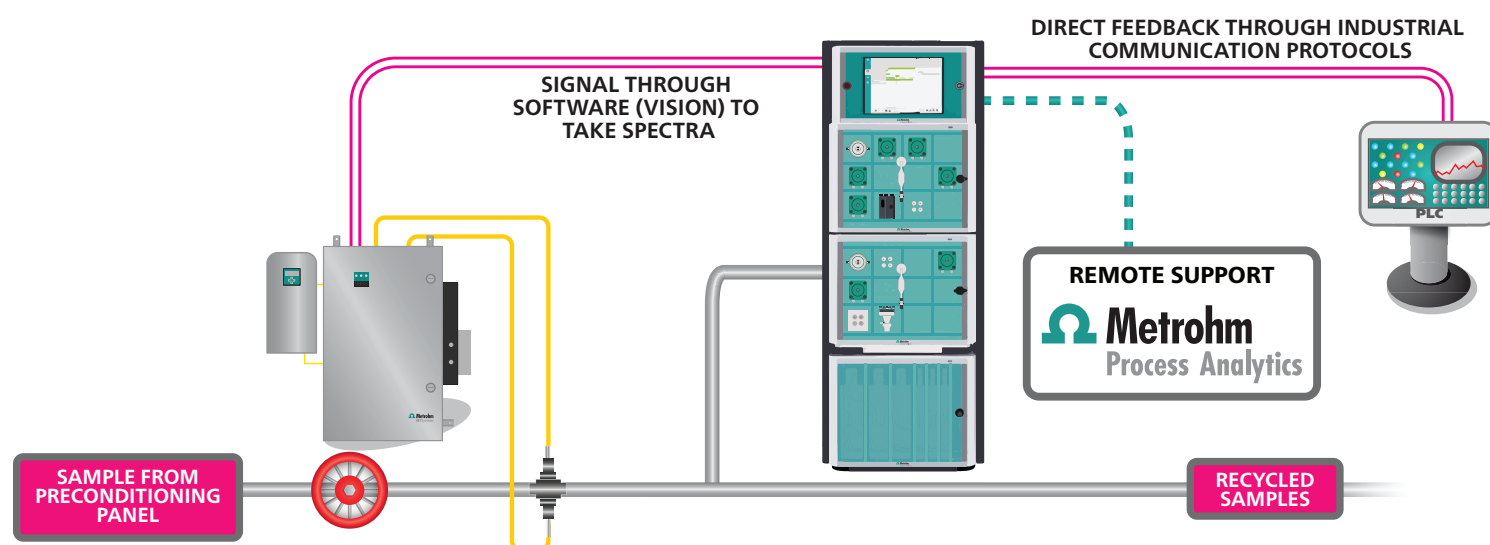
COMPLEMENTING NIRS WITH ONLINE TITRATORS

Precise and reproducible results are obtained when the samples themselves are consistent. To do so, a preconditioning system mounted on a panel has to be used to treat the samples, by removing solid matter, or by ensuring all samples are at the same temperature before the analysis.

Instead of manual measurement in a separate laboratory, the prefiltered sample is sent to the analytical system to perform the multiparameter analysis. This system consists of a flow-through cell for the NIRS analysis, and a reaction vessel in the 2060 Process Analyzer for the titration measurements.

For ABC-tests, white and green liquors flow through the analysis system sequentially after cleaning intervals. There are three current practices to identify the sample:

- The user sends a discrete I/O signal to notify the 2060 software which liquor is flowing, assigning the correct prediction model for NIRS and the correct titration method.
- The NIRS Process Analyzer performs an identification step to determine the type of liquor which is actually flowing in the pipeline. It applies the correct prediction model to then inform the 2060 software which titration method to use.
- The 2060 Process Analyzer controls the sample streams on the conditioning panel and the sequence of liquors is programmed within the 2060 software.

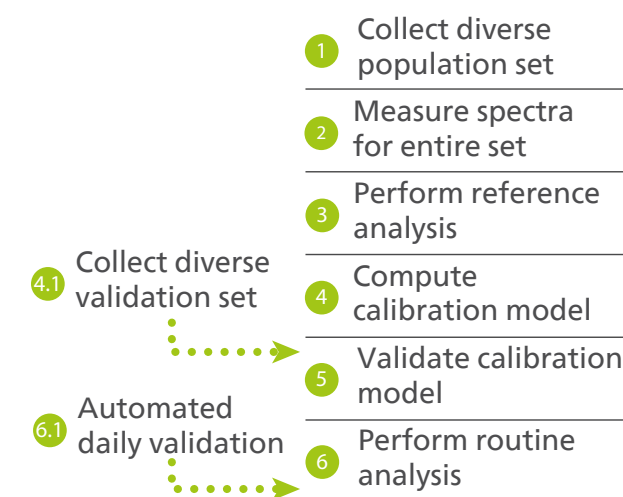


Calibration set for the TTA model. Titration data versus NIRS values for the determination of TTA on Green Liquor.

EASY MODEL BUILDING

For any quantitative determinations using NIRS, a calibration model is needed to link NIRS spectra to results from primary methods such as titration. Therefore, model building can be a hurdle when implementing NIRS online, but Metrohm Process Analytics has the right solution to avoid complications. At the time of commissioning, the online 2060 Process Analyzer uses titration analysis to generate reference values to be used in the NIR prediction model.

This process is also fully automated: the NIRS analyzer acquires a spectrum at the same time as the titration measurement is performed, and reference values are associated to the corresponding spectra. There is no need to transport samples to the laboratory and no errors are introduced by entering manual values. With one titration performed every 30 minutes, users receive 96 data points in 48 hours, which is highly sufficient for building a robust prediction model with NIRS.



Validation and calibration overview using Metrohm Process Analytics analyzers.

VALIDATION

Processes must be continuously monitored and plant safety guaranteed. Downtimes are associated with high expenditures and costs and these inconveniences cannot be tolerated in such highly controlled processes as the recovery cycle. Thus, regular validation routines are needed to ensure that the NIRS analyzer is performing correctly and according to specifications. This validation process can be fully automated within the 2060 software by combining NIRS and titration analysis.

The 2060 software compares the titration results with the NIRS data and if they deviate beyond user-defined limits, it will take action, e.g., by recalibrating the NIR spectrometer. Meanwhile, a notification will be sent e.g., to change the lamp bulb of the spectrometer. By doing so, there is a continuous automated validation of the NIRS spectrometer, which prevents the generation of incorrect or falsified results.

Applications

Multiple analytical choices for the pulp & paper industry



Online or atline analysis of pulping liquors

The 2060 Process Analyzer is suitable to analyze white, green, and black liquors with multiple sample lines, outputting results for closed loop control. For atline analyses, the 2060 Process Analyzer is typically used for multiple sampling points and parameters that do not require fast response times nor frequent analysis.

Titration is the method of choice for the pulp and paper mills meeting the industrial requirements for online/atline high quality and reliable analysis. ABC-tests (according to SCAN-N30:85 method) are widely used to determine Alkali (active «AA», effective «EA», and total titratable «TTA»), carbonate, sulfide and causticizing degree (CE%).



2060 Process Analyzer for analysis of pulping liquors

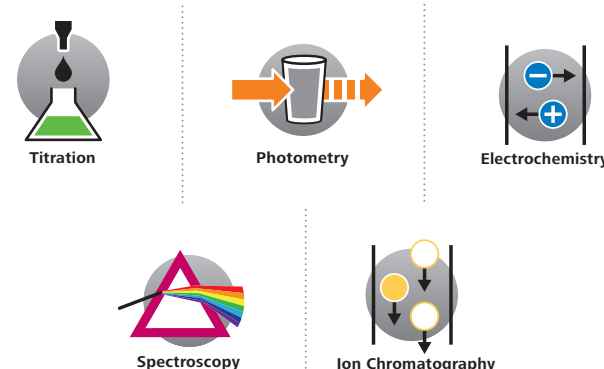
CUSTOMIZED SOLUTION DEPENDING ON YOUR NEEDS WITH METROHM PROCESS ANALYZERS

Reducing manual sampling lowers costs and increases the safety of plant operations. With subsidiaries located worldwide, you can rest easy knowing we can support you locally, wherever you are.

Benefits of Metrohm Process Analyzers in a pulp mill:

- **Cost reductions** (lime purchase, utilities, maintenance) by process optimization
- **Increase the degree of reduction efficiency** and CE%
- **«Real-time» feedback** to the process to avoid over- or underdosing reagents (e.g., lime)
- **Avoid hazardous sampling** and laboratory analyses

Following, a portfolio of possible analyzer solutions with their respective list of parameter analysis is presented for the pulp and paper industry using Metrohm Process Analytics.



Sulfate measurement by thermometric titration

Sulfate concentration can be easily measured with thermometric titration. Metrohm is currently the only manufacturer on the market offering online thermometric titration, and the 2060 Process Analyzer is ideal for this application. Combined with the ABC titration results, this gives a perfect indication for the degree of reduction and information about the recovery boiler efficiency as a reactor.

- Enthalpy change of the reaction is monitored
- Robust probe is resistant to aggressive samples
- No sensor calibration or maintenance required
- Fast and accurate results: Thermoprobe response time of 0.3 s with a resolution of 10^{-5} K

Process Application Notes for the Pulp & Paper Industry

ABC Titration: Analysis of alkali, carbonate, hydroxide, and sulfide in Pulping Liquors. [AN-PAN-1004](#)



Maximum flexibility for multiple wet chemistry techniques. The 2060 Process Analyzer for Thermometric analysis

Applications

Multiple analytical choices for the pulp & paper industry



Alkali determination by NIRS

Online NIRS solutions gradually have gained ground against the dominant wet chemical analytical strategies in the pulp and paper industry. Currently, ABC-tests are widely used to determine Alkali (active «AA», effective «EA», and total titratable «TTA») in white and green liquors, from which sodium carbonate (Na_2CO_3), sodium sulfide (Na_2S), causticizing efficiency (CE), and recovery efficiency (RE) are derived. Online monitoring with NIRS can go a step beyond and provide fast, precise, and reliable results allowing real-time control of the chemical recovery process.

Quantification Parameters: Accuracy

	White Liquor [g/L]	Green Liquor [g/L]
AA	0.5	0.6
EA	0.4	0.3
TTA	0.5	0.4
Na_2CO_3	0.6	0.5
Na_2S	1	1

Dedicated Process Solutions for the Pulp & Paper Industry

Brochure: Pulp and Paper Industry – Optimizing Chemical recovery in Pulp Mills with online spectroscopy (NIR). [8.000.5330](https://www.metrohm.com/en/products/na/2000/2000-5330)



Spectroscopic applications for papermaking

For fast, reagent-free, nondestructive analyses, near-infrared spectroscopy can be used. Metrohm Applikon offers two NIRS lines: the XDS and PRO. The NIRS Analyzer PRO can be configured for contact and noncontact measurements, while the XDS can handle up to 9 measuring points. These analyzers come with a wide portfolio of fiber optics and probes ready to handle any sample.

Suitable parameters for NIRS:

- Kappa number
- Lignin content
- Kraft pulp yield
- Tall oil
- Coatings
- Moisture
- Resin
- Brightness
- Wood species
- Hardwood/Softwood ratio
- Component analysis (clay, TiO_2 , fillers, ash, etc.)



NIRS XDS Process Analyzer

Other important parameters

Metrohm Process Analytics offers much more than what can be outlined here. We also offer complete process solutions for other areas, such as analysis of Ca and Mg in brine in the production of Cl_2 for bleaching. The 2060 Ion Chromatograph (IC) is suitable for measuring either organic acids or sulfur species in process water or even trace impurities in steam in order to protect the turbines from excessive scaling, for example:

- Ca and Mg in brine in the production of Cl_2 for bleaching
- Organic acids or sulfur species in process water
- Trace impurities in steam

No matter what application, our turn-key process solutions from Metrohm Process Analytics are indispensable when it comes to increasing throughput and saving money in your plant.



2060 IC configured to analyze trace impurities in pulping mills

Metrohm Process Analytics Quality Service – Service you can rely on



Metrohm Quality Service encompasses more than just analyzer service

Metrohm Quality Service is primarily about trust. Trust that someone will be there for you when you need advice, service or support. Our support continues with your decision to implement a Metrohm solution. We are available, with all of our expertise, to address any issue that may arise over the course of your Metrohm system lifetime. Issues we address include:

- Modifications or extension of current methods
- Integration of new system components
- Transfer of a system and requalification at a different location
- Decommissioning obsolete systems in conformity with applicable regulations

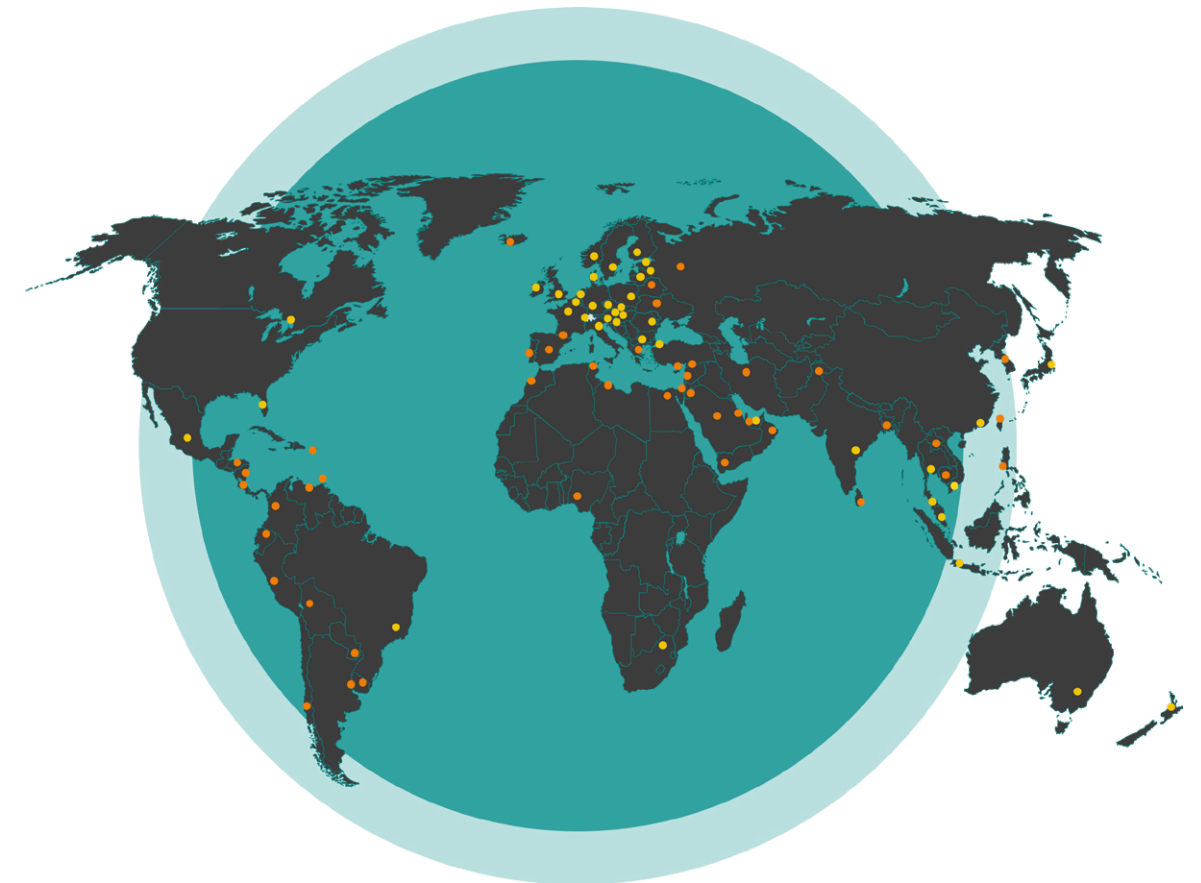
Whatever the challenge, we'll offer you a safe and efficient solution.

Analytical Instrument Qualification (AIQ)

Metrohm's Analytical Instrument Qualification meets all requirements mandated by many regulators. AIQ is more commonly known as IQ/OQ.

In regulated environments of some industries, commissioning and use of analytical process analyzers in accordance with applicable regulations is mandatory. However, meeting these requirements systematically can be challenging.

Metrohm can assist you with this process. We have developed a modular system for the installation and qualification of your Metrohm process analyzers in strict accordance with the current regulations and can provide documentation as required.



Metrohm Quality Service is available worldwide

Metrohm Process Analytics is present in more than 50 countries. Every subsidiary has its own service organization, spare parts warehouse, and trained Service Engineers. Distributors are either equipped with the same infrastructure or receive service and repair support from our Regional Support Centers (RSC), or directly at our headquarters in the Netherlands.

Wherever you need us, we're there to help.



A high standard for us – and a promise to you

The high standards we maintain are also a promise to you. Regardless of when or where in the world you rely on our services, these services are performed to the same exacting standards. The core elements of our global service promise are:

- Clearly defined system maintenance
- Implementation with specially developed diagnostic instruments
- Uniform maintenance agreement with clearly defined services tailored to customers' needs
- Training and courses with customized user-specific content
- Uniform documentation of all services executed

