Metrohm International Headquarters

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Application Bulletin

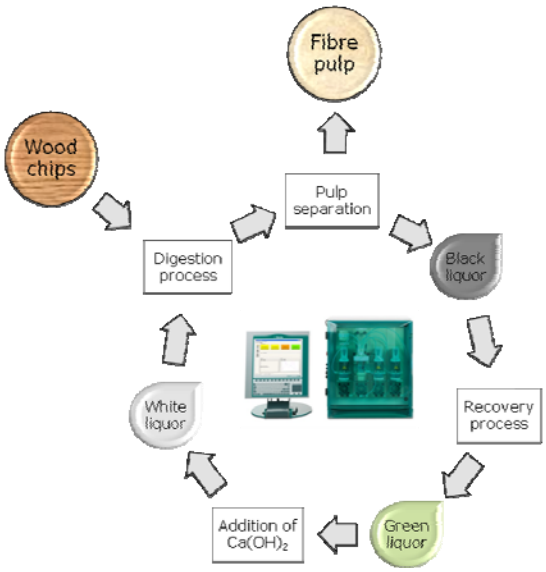
Of interest to:	Paper & pulp, card board, wood, process, production, potentiometry, titration, liquor, white, green, black, total, effective, active, alkali, sulphate, sulphide	

ProcessLab for paper & pulp: Analysis of white, green and black liquors

General information

The paper and pulp production is a well established industrial process which has been adapted over time to fit today`s needs. Resource management has become vital in a constantly changing market. Quality and a high yield are here the key words to achieve a maximum price for the end product. Strong competition on the markets constantly forces production to optimize conditions.

In contrast to this are the input costs on and the market price of the value added chain. The gap between buying and selling is the profit, which needs to be optimized by effectively and quickly amortizing investments.



Closer process control

As the liquors used for the wood fiber digestion process are recycled and it is of utmost importance to constantly monitor this material flow. The classic approach is to sample on site followed by an analysis in the central QC lab. This way the process can be kept within specifications but in many cases the feedback times are too long in order to closely control the process. ProcessLab fills this gap by being placed directly in the process area (e.g. boiler house) performing the analytical task using the same technology as in the laboratory.

Our solution

Samples analyzed on site and results are immediately available to optimize the process. To offer more flexibility ProcessLab is used for many different sampling locations of **white, green and black liquor**. The included touch screen allows a simple selection of the correct sample and method without any other complex functions involved. On request, additional or different parameters are implemented. Optionally results are transmitted to the PCS where they are available for monitoring of the production chain.

Significance and use

The core of the paper and pulp production process is the digestion of the wood fibers. In order to separate the cellulose from the unwanted lignin (Lignin provides structural integrity to the wood) the wood pulp is cooked for several hours at approximately 150 °C. This digestion is carried out using **white liquor**, which is an aqueous mixture of sodium sulphide and sodium hydroxide. This slowly splits up the bonds between the lignin and cellulose and subsequently destroys the structural integrity.

When finished, the cellulose fibers and remaining cooking liquor are separated in the so called blower. Here a sudden pressure reduction causes volatile substances to evaporate and condense (mainly turpentine). The liquid residue is now screened to separate the cellulose from the liquor by using different types of sieves and centrifuges. The remaining cellulose is now shipped or directly further treated to produce the final product – pulp, paper or card board.

The cellulose separated liquor contains now lignin and many other contaminative ingredients and is called the **black liquor**. It is then, in various intermediate steps, reduced to a dry content of around 60 – 80 % before feeding it into the recovery furnace where it is burned. The remaining smelt on the bottom of the boiler is again dissolved in water and normally stored in a tank. The now forming solution of sodium carbonate and sodium sulphide is known as **green liquor**. The addition of calcium hydroxide converts the green liquor again into **white liquor** which is used for the initial digestions process.

ProcessLab benefits

- Closer process control
- Located directly in the production of the mill
- Robust in setup and design, flushable with instrument air – IP 54
- Simple integration into process control
- Very low response times
- Optimization of process window
- Flexible and modular concept

The ProcessLab analyzer is very flexible and can be adapted very easily to any specific needs. Additionally a reagent cabinet is available and ProcessLab can be placed on top of it – this means sufficient space for all reagents, which makes ProcessLab even more practical.

Wet part setup & system overview

Module A

Module B

Operating unit

Application details

The procedures described are based on a titrimetric determination of alkaline, hydrogen sulphide and sulphate content in **white, green and black liquors**. Often these methods already exist in the central lab – thus they can be easily adapted for ProcessLab and allow a full comparability of results obtained in the laboratory and in the process area.

Depending upon the situation on site additional parameters may be integrated. The flexible concept allows an almost seamless integration into every process condition.

Analytical procedures & calculations

Total, active and effective alkali content (total alkalines, OH^- + HS^-, OH^-)
A suitable amount of sample is measured in the loop sampling system and transferred into the determination vessel. Water is added until the electrode and reference system are completely submerged in sample solution. The stirrer is switched on and the titration carried out using 1 mol/L HCl with the previously evaluated parameters. The resulting endpoints are evaluated and used for the subsequent calculation of the results.

$$\text{First EP: } OH^- + S^{2-} + 2\,H^+ \rightarrow H_2O + HS^-$$
$$\text{Second EP: } CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
$$\text{Third EP: } HS^- + HCO_3^- + 2\,H^+ \rightarrow H_2S\uparrow + CO_2\uparrow\, H_2O$$

Notes

This reaction produces H_2S during the determination, titration parameters should be chosen in such a way (more slowly) so that excess hydrogen sulphide can degas from the solution. A soft stream of air may accelerate this process.

The endpoints will be around pH 11, pH 8.5 and pH 4 – in some cases, depending upon the specific chemistry, the determination is carried out with fixed endpoints. In this case the electrode should be calibrated using the described buffers of pH 4, pH 7 and pH 9 or similar.

Hydrogen sulphide content (HS^-)

The amount of sample is measured using the Dosino loop sampling system from the previously with sample filled determination vessel. After the sample has been measured and transferred back into the vessel. Then 50mL of sodium hydroxide and 5 mL ammonia solution are added to produce a strongly alkaline media which is a requirement for the later reaction to take place. Under strong stirring the sample is now titrated using 0.1 $AgNO_3$. The endpoint volume is used for the further calculation of the result.

$$\text{First EP: } HS^- + OH^- + 2\ Ag^+ \rightarrow Ag_2S\downarrow + H_2O$$

Notes

The ammonia solution added results in a more flaked precipitation and simplifies later vessel rinsing and cleaning.

It is recommended to use KNO_3 as electrolyte to avoid precipitation of AgCl in the electrode

For reduction of titrant consumption half the sample size may be used.

When two endpoints are observed this is possibly due to polysulphides present. They are destroyed by adding a known amount of sample (usually 1 – 2 mL) to a hot solution of 10 mL sodium sulphite. This solution is now used as sample with a reduced amount of 40 mL sodium hydroxide instead of 50 mL. The practice shows that this is handled depending upon the plant and processes.

Sulphate content (SO_4^{2-})

50mL formaldehyde solution and 50 mL acetone are added into the determination vessel. The sample, which has been already measured prior to the addition of formaldehyde and acetone, is now transferred to this mixture. The pH is now automatically adjusted to pH 3.0 using the perchloric acid. The resulting solution is then immediately titrated using the lead perchlorate as titrant. The resulting endpoint is then used for calculation of the result.

$$\text{First EP: } SO_4^{2-} + Pb(ClO_4)_2 \rightarrow PbSO_4\downarrow + 2\ ClO_4^-$$

Notes

This determination uses a so called ion selective lead electrode which needs a soft polish from time to time. This should be the first measure when curves obtained start to differ from the usual curve shape.

For reduction of titrant consumption half the sample size may be used.

General remarks

The described methods reflect the best case of our experiences – certain procedures may be carried out differently depending upon type of process and used raw material.

Generally a relative standard deviation of approximately 1% can be reached with these procedures.

Filtering of the raw sample may be considered as solids can influence the precision and accuracy of the results.

*Reagents**

All analyses
- Deionized water

Total alkali, effective and active alkali
- Hydrochloric acid, c(HCl) = 1 mol/L
- Suitable buffer solutions, pH 4 and pH 9

Hydrogen sulphide
- Silver nitrate, $c(AgNO_3)$ = 0.1 mol/L
- Sodium hydroxide, c(NaOH) = appr. 1 mol/L
- Ammonia hydroxide, $w(NH_3)$ = appr. 25 %
- Alkaline sodium sulphite solution, $c(Na_2SO_3)$ = 0.5 mol/L in 1 mol/L NaOH

Sulphate content
- Lead perchlorate, $c(Pb(ClO4)_2)$ = 0.05 mol/L
- Perchloric acid, concentrated
- Acetone, analytical grade
- Formaldehyde, w(HCHO) = appr. 15 %

* The reagents listed generally agree with those as specified in SCAN-N 30:85, SCAN-N 31:94 and SCAN-N 6:85. Depending upon local regulations or specific applications different ones may be used.

Accessories used

- 2x 2.875.0510; ProcessLab base L Touch
- 1x 2.878.0120; ProcessLab Extension module R
- 2x 6.7201.210; ProcessLab MDM Controller with 2 measuring amplifiers
- 1x 6.7202.000; ProcessLab I/O Controller

- 1x 6.7202.100; ProcessLab Digital input 4 DI 24 V DC
- 4x 6.7202.200; ProcessLab Digital output 4 DO 24 V DC

- 1x 6.7203.000; ProcessLab blind plate wet part module
- 7x 6.7203.100; ProcessLab Dosino mounting device
- 2x 6.7203.200; ProcessLab sensor connection
- 4x 6.2104.030; Electrode cable 2m
- 7x 2.800.0010; Dosino 800
- 3x 6.3032.210; Dosing unit 10 mL
- 2x 6.3032.220; Dosing unit 20 mL
- 2x 6.3032.250; Dosing unit 50 mL

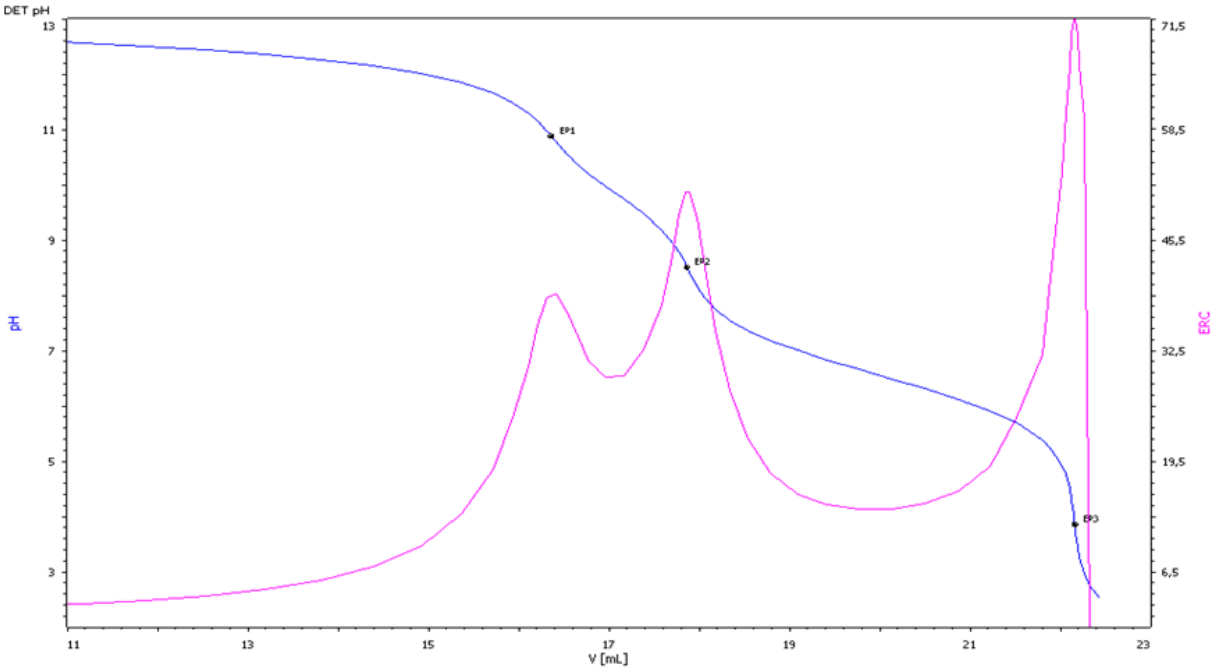
- 2x 6.7204.000; ProcessLab vessel mounting with stirrer
- 2x 6.7204.120; Measuring vessel 40 – 150 mL for 875

- 5x 6.7205.020; ProcessLab peristaltic pump 120 mL/min
- 4x 6.7205.030; ProcessLab peristaltic pump 320 mL/min

- 2x 6.7206.040; Sample loop 10 mL var. compl. for 875

- 1x 6.0259.100; Unitrode
- 1x 6.0502.170; Pb ISE
- 1x 6.0750.100; LL ISE Reference
- 1x 6.0255.100; Profitrode
- 1x 6.0451.100; Combined Pt ring electrode

Curves and results



Curve discussion

- Typical curve of the so called ABC* titration (Total, effective and active alkali)
  *__A__cid __B__ase __C__hemistry

Calculations

Process-relevant analytical parameters

Monitored parameter		Green liquor	White liquor	Black liquor	Commonly used units*
Total alkali		X	X		c(alkalines) = mol/L
Active alkali		X	X		$c(OH^-) + c(HS^-)$ = mol/L
Effective alkali		X	X		$c(OH^-)$ = mol/L
Hydrogen sulphide		X	X	X	$c(HS^-)$ = mol/L
Sulphate		X	X		$c(SO_4^{2-})$ = mmol/L

* Sometimes results are calculated in a different unit, like e.g. corresponding amount of g/L NaOH.

Result calculations

$$\text{Total alkali} = \frac{EP3 * c(HCl)}{Sample\_size[mL]}$$

$$\text{Effective alkali } (OH^-) = \frac{EP1 * c(HCl)}{Sample\_size[mL]}$$

$$\text{Active alkali } (OH^- + HS^-) = \frac{((2 * EP1) - (2 * EP2) + EP3) * c(HCl)}{Sample\_size[mL]}$$

$$\text{Sulphate } (SO_4^{2-}) = \frac{EP1 * c(Pb(ClO4)_2}{Sample\_size[mL]}$$

$$\text{Hydrogen sulphide } (HS^-) = \frac{EP1 * c(AgNO_3)}{2 * Sample\_size[mL]}$$

Several properties may be derived from the analysis results

$$\text{Sulphidity} = \frac{2[HS^-]}{[OH^-] + [HS^-]}$$

$$\text{Degree of causticizing} = \frac{[OH^-] - [HS^-]}{[OH^-] - [HS^-] + 2[CO_3^{2-}]}$$

$$\text{Degree of reduction} = \frac{[HS^-]}{total\_sulphur}$$

References

SCAN-N 30:85; Total, active and effective alkali in white and green liquors

SCAN-N 31:94; Hydrogen sulphide ion concentration in white, green and black liquors

SCAN-N 6:85; Sulphate content in white and green liquors

Tappi T 625 cm-85; Analysis of soda and sulphate in black liquor

* SCAN methods are test methods created by the Scandinavian Pulp, Paper and Board testing committee.

** TAPPI is the **T**echnical **A**ssociation of the **P**ulp and **P**aper **I**ndustry which is a registered non-profit organization which provides also standards to this industry.