


Round Robin  
Lignin content determination in lignin samples

Fredrik Aldaeus




### Background

#### "Total lignin content"?

- Total lignin content = Native lignin + lignin degradation products  
or
- Total lignin content = Total mass - "impurities" (moist, carbohydrates, inorganics, extractives, etc.)  
or
- Total lignin content = Alkali dissolved lignin  
or
- Total lignin content = Klason lignin + acid soluble lignin


2011-01-28  
2

Fredrik Aldaeus "Round Robin - Lignin content determination in lignin samples"

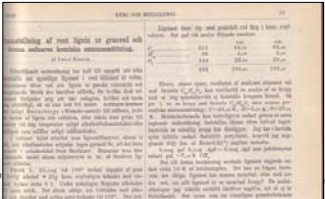


### Johan Peter Klason (1848-1937)


- Professor 1890–1913 in chemistry and chemical engineering at the Royal Institute of Technology (KTH), Stockholm, Sweden.
- "Framställning af rent lignin ur granved och denna sednares kemiska sammansättning" [Teknisk Tidskrift, 1893]



"Preparation of pure lignin from sprucewood and its chemical composition"



in lignin samples"



### Background

#### Acid hydrolysis method (Klason method)


Pre-hydrolysis → Hydrolysis → Filtration → Retentate → Gravimetry  
 • 72% H<sub>2</sub>SO<sub>4</sub>      • 121 °C, 1 h      Klason lignin

Filtrate → UV spectroscopy  
 • Vacuum, 15 min      acid-soluble lignin

• 30 °C, 1 h

• Dilution to 3% H<sub>2</sub>SO<sub>4</sub>

Chromatography  
 carbohydrate composition



### Background

#### Acid hydrolysis method (Klason method)

Pre-hydrolysis → Hydrolysis → Filtration → Retentate → Gravimetry  
 • 72% H<sub>2</sub>SO<sub>4</sub>      • 121 °C, 1 h      Klason lignin

Filtrate → UV spectroscopy  
 • Vacuum, 15 min      acid-soluble lignin

• 30 °C, 1 h

• Dilution to 3% H<sub>2</sub>SO<sub>4</sub>


1 min?

Necessary?

Ion chromatography  
 carbohydrate composition

2011-01-28  
5

Fredrik Aldaeus "Round Robin - Lignin content determination in lignin samples"




### Background

#### Evaluated alternative methods

Steps in protocol	Standard metod	Alternative method #1	Alternative method #2
Pre-hydrolysis with concentrated acid	1 h	no	no
Hydrolysis in autoclave (time at 121 °C)	1 h	1 min	no
Hot filtering	yes	yes	yes

2011-01-28  
6

Fredrik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Background Evaluated samples

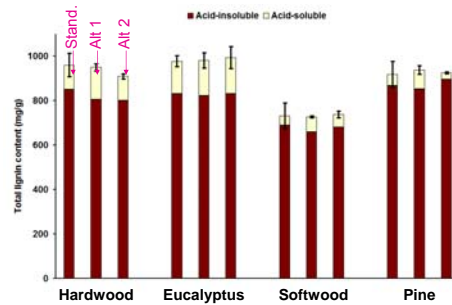
- Black liquor – Hardwood
- Black liquor – Eucalyptus
- Black liquor – Softwood
- LignoBoost lignin – Hardwood
- LignoBoost lignin – Eucalyptus
- LignoBoost lignin, unwashed – Softwood
- Indulin AT – Pine

2011-01-28  
7

Fredrik Aldehus "Round Robin - Lignin content determination in lignin samples"



## Background Lignin content in lignin samples

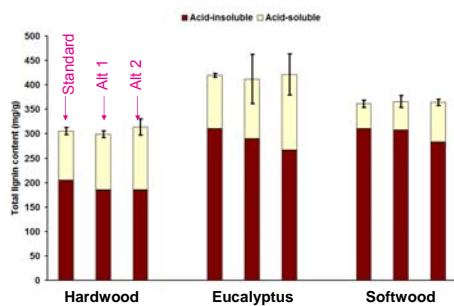


2011-01-28  
8

Fredrik Aldehus "Round Robin - Lignin content determination in lignin samples"



## Background Lignin content in black liquors

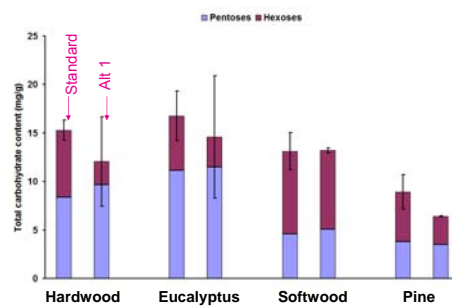


2011-01-28  
9

Fredrik Aldehus "Round Robin - Lignin content determination in lignin samples"



## Background Carbohydrate content in lignin samples

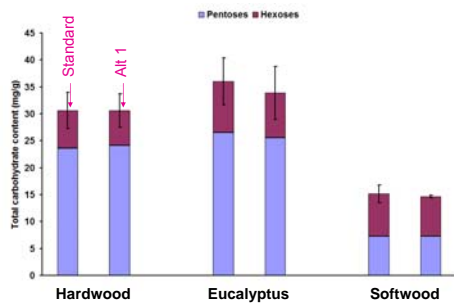


2011-01-28  
10

Fredrik Aldehus "Round Robin - Lignin content determination in lignin samples"



## Background Carbohydrate content in black liquors



2011-01-28  
11

Fredrik Aldehus "Round Robin - Lignin content determination in lignin samples"



## Background EWLP 2010



2011-01-28  
12



## Round Robin results Evaluated protocols

Steps in protocol	Procedure 1 "Standard metod"	Procedure 2 "Alternative method #2"
Pre-hydrolysis with concentrated acid	1 h	no
Hydrolysis in autoclave (time at 121 °C)	1 h	no
Hot filtering	yes	yes

2011-01-28  
13

Frederik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Round Robin results Evaluated samples

- KLHM = hardwood kraft lignin (birch/aspens)
- KLSM = softwood kraft lignin (pine/spruce)
- Orgsolv = organosolv lignin (spruce)
- Soda = soda lignin (wheat straw)
- ESEL = residue after enzymatic treatment of steam explosion (poplar)

2011-01-28  
14

Frederik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Round Robin results (tentative) Total lignin contents (with 95% confidence limits)

- **KLHM**  
Procedure 1 = 960 ± 24 mg/g  
Procedure 2 = 935 ± 56 mg/g  
Difference = -24 ± 40 mg/g
  - **KLSM**  
Procedure 1 = 970 ± 37 mg/g  
Procedure 2 = 950 ± 58 mg/g  
Difference = -21 ± 46 mg/g
  - **Orgsolv**  
Procedure 1 = 820 ± 32 mg/g  
Procedure 2 = 802 ± 67 mg/g (n=8)  
Difference = -20 ± 47 mg/g
  - **Soda**  
Procedure 1 = 731 ± 23 mg/g  
Procedure 2 = 782 ± 48 mg/g (n=8)  
Difference = 51 ± 34 mg/g
  - **ESEL**  
Procedure 1 = 877 ± 29 mg/g (n=6)  
Procedure 2 = 891 ± 78 mg/g (n=6)  
Difference = 14 ± 51 mg/g
- n = 9 unless otherwise stated!*

2011-01-28  
15

Frederik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Round Robin results (tentative) Coefficients of variation

- *CoV = average / standard deviation*
- **Procedure 1**  
Total = 3 – 5 %  
AIR = 3 – 6 %  
ASL = 18 – 51 %
- **Procedure 2**  
Total = 7 – 10 %  
AIR = 7 – 12 %  
ASL = 42 – 51 %

2011-01-28  
16

Frederik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Conclusions

- Hydrolysis may be omitted  
– *should be tested for each sample type!*
- Simplified procedure especially good for screenings  
– *high throughput!*
- Filtering procedure still a problem

2011-01-28  
17

Frederik Aldaeus "Round Robin - Lignin content determination in lignin samples"



## Round Robin results (tentative) KLHM

Lab	Procedure 1			Procedure 2			Diff Total
	AIR	ASL	Total	AIR	ASL	Total	
1	907	86	992	852	105	957	-36
2	843	73	916	879	128	1007	91
3	827	101	928	851	107	958	30
4	857	81	939	907	99	1006	67
5	877	75	952	777	46	823	-129
6	875	95	969	857	86	944	-26
7	976	38	1013	982	27	1009	-5
8	844	127	972	810	25	835	-136
9	846	109	955	761	117	878	-77
Average	872	87	960	853	82	935	-24
Stdev	45	25	31	67	39	73	
Stdev (pooled)							56
CoV	5%	29%	3%	8%	48%	8%	
n	9	9	9	9	9	9	9
tinv	2,3	2,3	2,3	2,3	2,3	2,3	2,1
conf 95%	35	19	24	52	30	56	40

Round Robin results (tentative)  
KLSM

Lab	Procedure 1			Procedure 2			Diff Total
	AIR	ASL	Total	AIR	ASL	Total	
1	985	42	1027	917	27	944	-83
2	919	29	948	962	27	989	41
3	913	41	954	920	40	960	6
4	905	52	957	946	24	969	12
5	912	34	946	881	14	895	-51
6	941	57	997	963	34	998	0
7	983	77	1060	996	65	1061	1
8	888	73	961	925	22	947	-14
9	825	59	884	758	29	787	-97
Average	919	52	970	919	31	950	-21
Stdev	49	17	51	69	14	76	
Stdev (pooled)							65
CoV	5%	33%	5%	7%	46%	8%	
n	9	9	9	9	9	9	9
tinV	2.3	2.3	2.3	2.3	2.3	2.3	2.1
conf 95%	38	13	39	53	11	58	46

Round Robin results (tentative)  
Orgsol

Lab	Procedure 1			Procedure 2			Diff Total
	AIR	ASL	Total	AIR	ASL	Total	
1	766	65	832	647	45	692	-139
2	705	95	800	739	91	830	30
3	739	71	810	722	114	836	26
4	718	64	781	702	58	759	-22
5	747	63	810				
6	751	71	822	797	15	812	-11
7	858	55	913	910	48	958	45
8	753	88	842	684	110	794	-48
9	692	82	774	657	79	736	-38
Average	748	73	820	732	70	802	-20
Stdev	48	13	41	86	35	80	
Stdev (pooled)							62
CoV	6%	18%	5%	12%	49%	10%	
n	9	9	9	8	8	8	8
tinV	2.3	2.3	2.3	2.4	2.4	2.4	2.1
conf 95%	37	10	32	72	29	67	47

Round Robin results (tentative)  
Soda

Lab	Procedure 1			Procedure 2			Diff Total
	AIR	ASL	Total	AIR	ASL	Total	
1	716	24	740	780	28	807	67
2	707	28	735	741	35	776	41
3	705	31	736	773	24	797	61
4	658	26	683	798	27	824	141
5	699	27	726				
6	674	33	707	729	37	766	59
7	745	28	773	851	21	871	98
8	662	44	705	637	43	680	-26
9	692	82	774	657	79	736	-38
Average	695	36	731	746	37	782	51
Stdev	28	18	30	71	19	58	
Stdev (pooled)							45
CoV	4%	51%	4%	10%	51%	7%	
n	9	9	9	8	8	8	8
tinV	2.3	2.3	2.3	2.4	2.4	2.4	2.1
conf 95%	21	14	23	60	16	48	34

Round Robin results (tentative)  
ESEL

Lab	Procedure 1			Procedure 2			Diff Total
	AIR	ASL	Total	AIR	ASL	Total	
1	878	21	899	935	17	952	53
2	802	36	838	921	30	951	113
3	845	27	872	853	28	881	9
4	831	24	854	935	17	952	98
5	872	23	895	766	12	778	-117
6							
7							
8	865	40	906	820	11	831	-75
9							
Average	849	29	877	872	19	891	14
Stdev	29	8	27	70	8	74	
Stdev (pooled)							56
CoV	3%	27%	3%	8%	42%	8%	
n	6	6	6	6	6	6	6
tinV	2.6	2.6	2.6	2.6	2.6	2.6	2.2
conf 95%	30	8	29	74	9	78	51