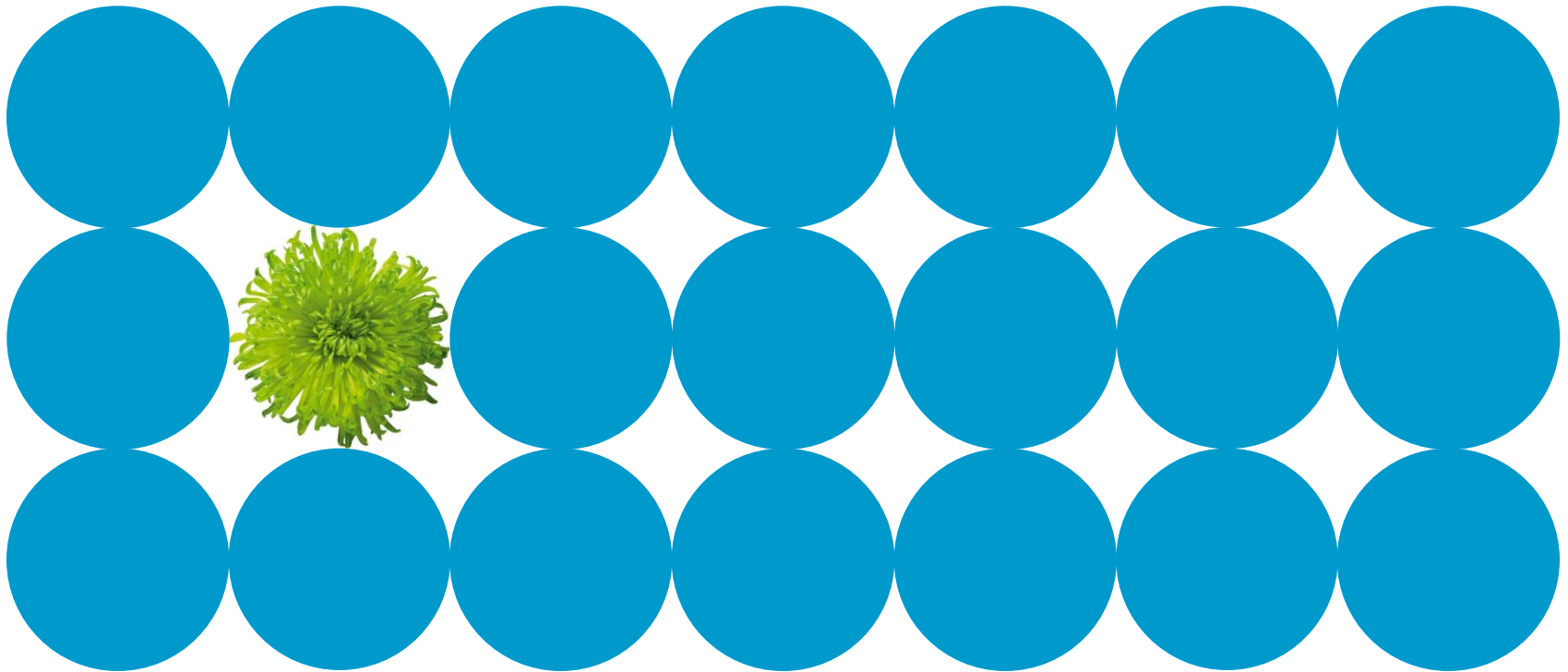


# COAL-TAR PITCH X-RAY FLUORESCENCE APPLICATION DEVELOPMENT – OUR EXPERIENCE FROM COOPERATION WITH A PITCH SUPPLIER



**Katarzyna Mirek-Sliwa, Lorentz Petter Lossius**

The 17th Norwegian X-Ray Conference, 10-12 September 2012 Kristiansand

# PITCH IN CARBON ANODES for ELECTROCHEMICAL PRODUCTION OF ALUMINIUM METAL

Hydro uses coal tar pitch as a binder in a large scale production of anodes. The pitch is a by-product of metallurgical coke handling in steelworks and is a multi-component mixture of mostly polyaromatics.

The carbon anode we use is a carbon aggregate with 15-0 mm grains, 1/3 is less than 0.25 mm and this part has 95% of the surface area. The pitch binder is the cement in this paste.

The anode weighs 1200 kg, and the binder is 14%, or 170 kg per anode. A mid-size aluminium plant uses 200 000 anodes per year.



---

Coal tar pitch pictures from google.com

# PITCH IN CARBON ANODES for ELECTROCHEMICAL PRODUCTION OF ALUMINIUM METAL

Pitch is quite expensive and due to industrial consolidation there is now less than a handful of producers. Hydro runs controls on suppliers' certificates versus specs.

Monitoring Na and some other trace elements is crucial in this, and XRF is an important analysis. We see that the increasing content of impurities observed in the raw materials used in aluminium production over past decade have an effect on the final aluminium metal quality.



# ISSUES WITH XRF PITCH APPLICATION

As we know from round robins and other interlaboratory studies, labs do not analyse the same. In 2010 the Hydro laboratory in Årdal decided to run a development study to determine how close we can come to suppliers reported results by copying an XRF method.

The suppliers, called **Supplier 1 and Supplier 2** in the following, has been quite helpful and positive about harmonizing with Hydro, and we succeeded in exchanging the basic information about supplier's measuring program.

Pitch softens with heat, and the sample can measured only once. We have limited time available for the application.



# FUNDAMENTAL INFORMATION EXCHANGE

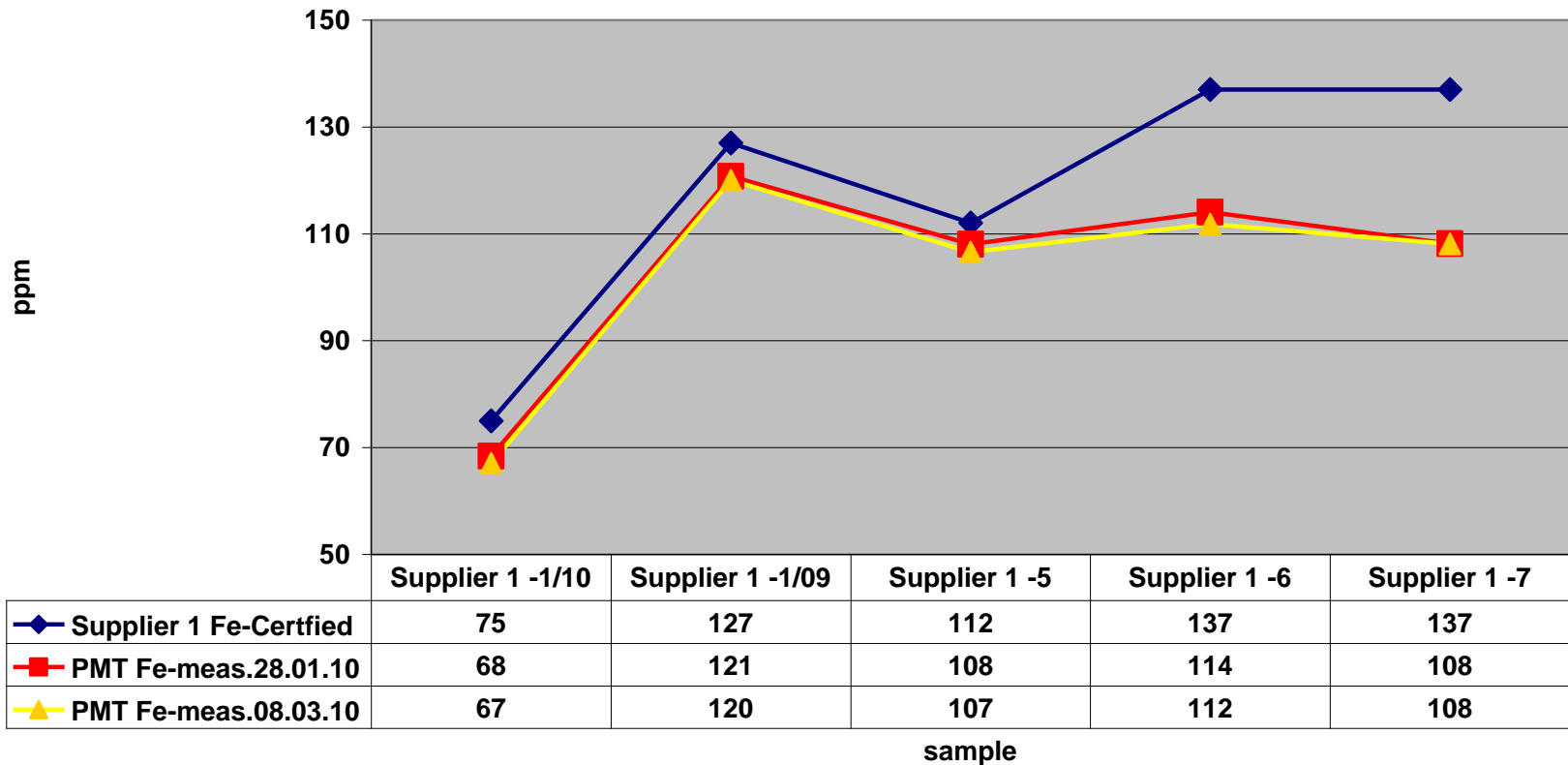
In order to establish an XRF pitch application adjusted to the supplier's application Hydro needs this fundamental knowledge about the method:

- Calibration standard set
  - Alcan Pitch 02-07 (AP02 etc,)
- Measuring conditions
  - set the same (kV, mA) as for supplier application
- Sample preparation method
  - supplier presses only pitch material, Hydro uses boric acid baking
- Total measuring time per sample and amount of measured elements
  - supplier's time is 16 minutes, Hydro's - firstly 40 minutes (January 2010)→ (March 2010) 15-18 minutes for the same amount of elements
- Other relevant information
  - Zn overlaps Na
  - sample surface might be blurry after pressing

# RESULTS OF HYDRO MEASUREMENTS

## COMPARISON AGAINST SHIPMENT CERTIFIED VALUES FROM SUPPLIER 1

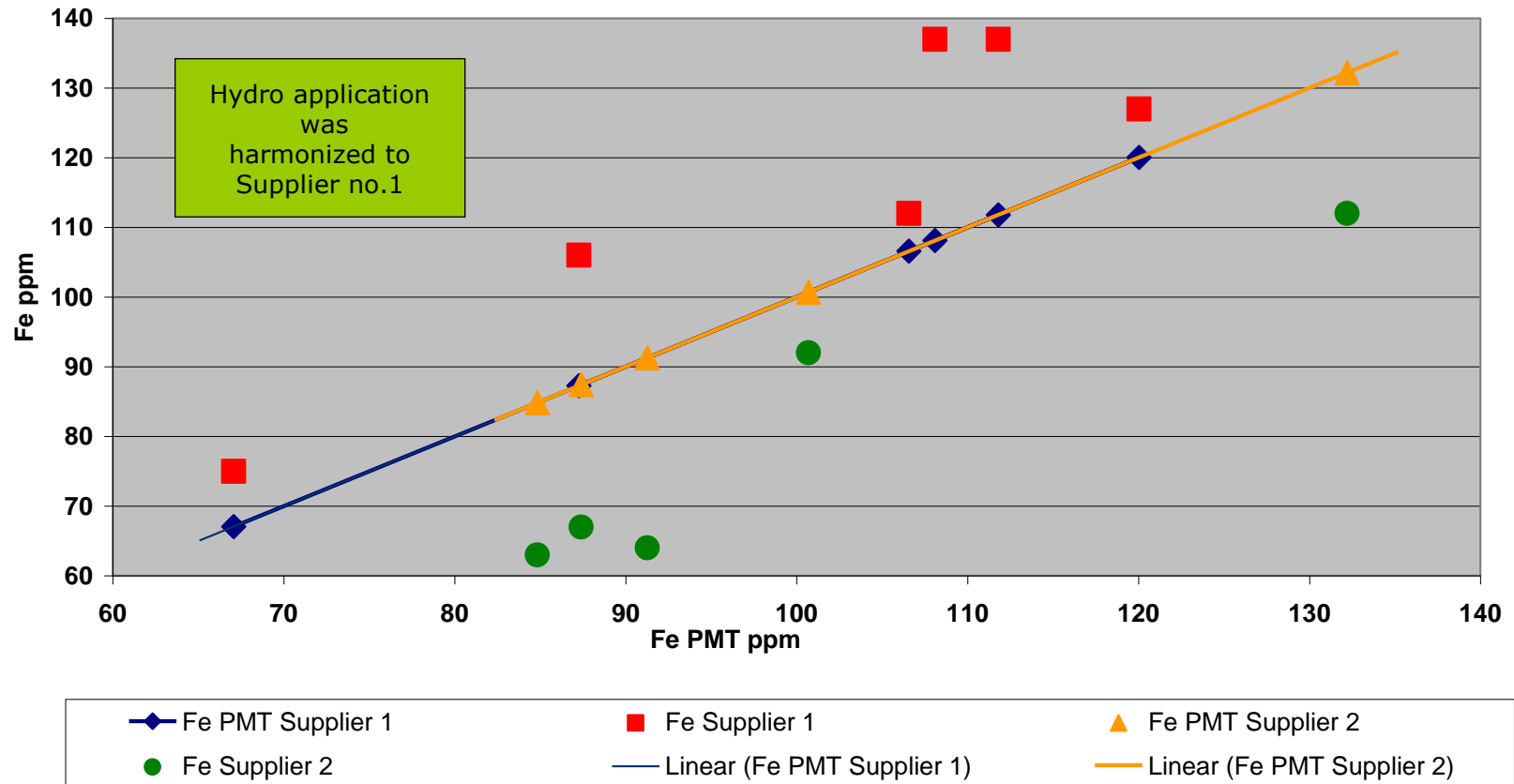
Iron - blue line is the Supplier 1 shipment certificate and these samples were also analysed twice by the Hydro application in January and March 2010 ( red and yellow lines) - at this time Hydro was systematically lower for Fe.



# RESULTS OF HYDRO MEASUREMENTS

## COMPARISON AGAINST SHIPMENT CERTIFIED VALUES FROM BOTH SUPPLIERS

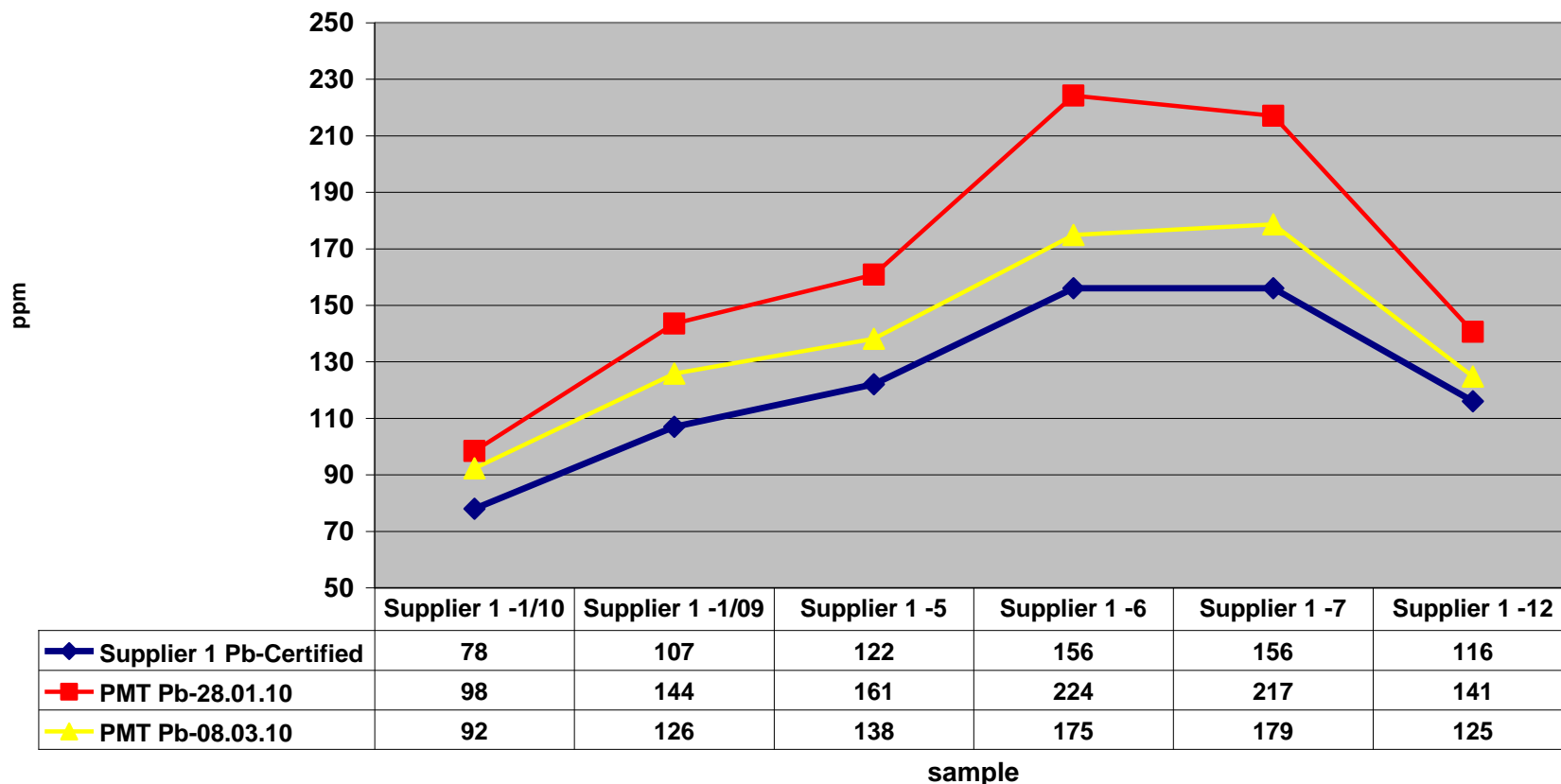
Iron - PMT results as the straight line compared with red Supplier 1 and blue Supplier 2 showing calibration differences when measuring the same samples (08.03.2010)



# RESULTS OF HYDRO MEASUREMENTS

## COMPARISON AGAINST SHIPMENT CERTIFIED VALUES FROM SUPPLIER 1

Lead - blue line is the Supplier 1 shipment certificate and these samples were also analysed twice by the Hydro application in January and March 2010 (red and yellow lines) - at this time Hydro was systematically higher for Pb

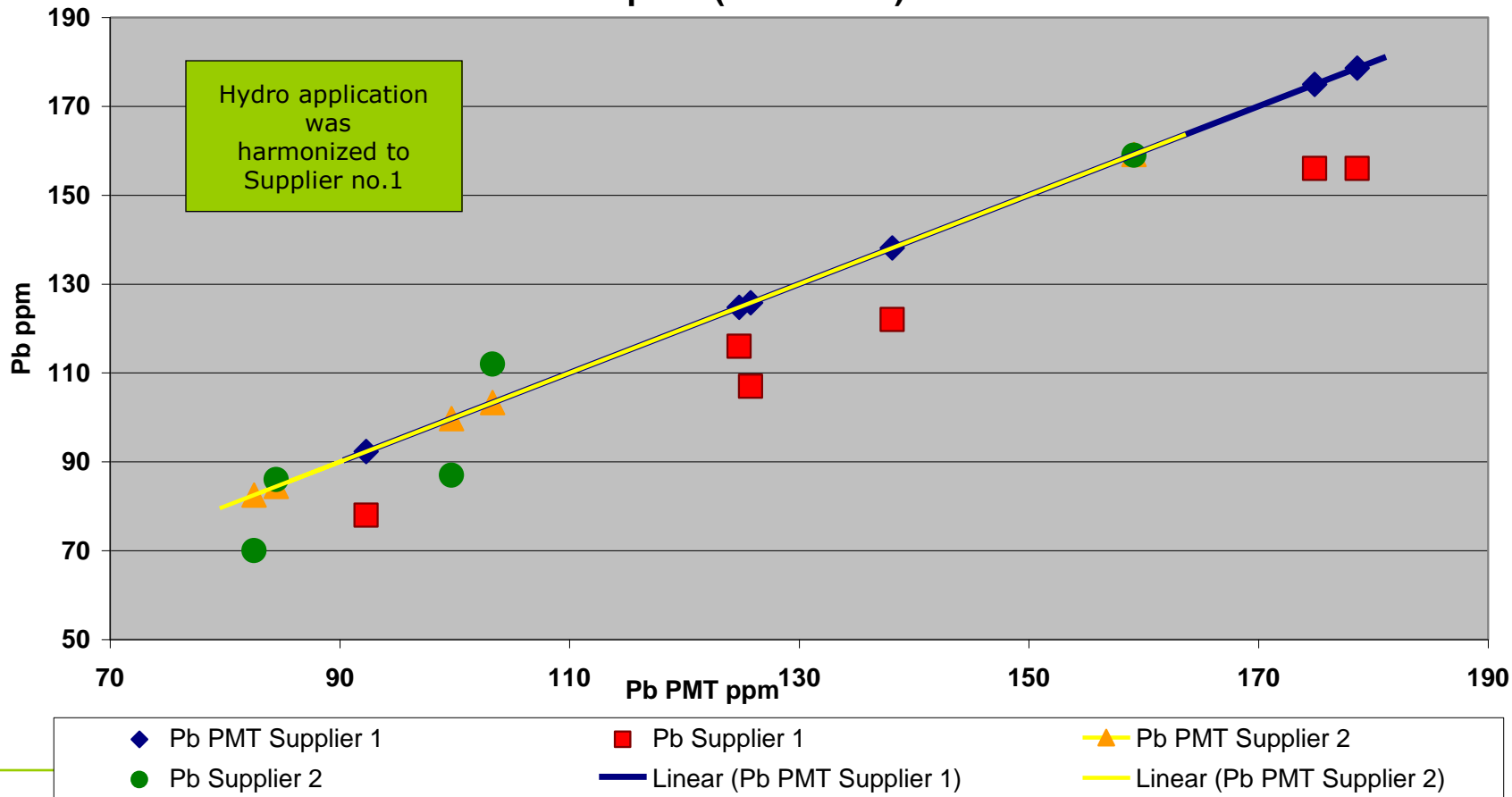




# FIRST RESULTS OF HYDRO MEASUREMENTS

## COMPARISON AGAINST SHIPMENT CERTIFIED VALUES FROM TWO SUPPLIERS

Lead - PMT results as the straight line compared with red Supplier 1 and blue Supplier 2 showing calibration differences when measuring the same samples (08.03.2010)



# ACTIONS TO ELIMINATE THE “TREND” DEVIATION

25 March 2010 Supplier 1 was asked to share with Hydro more details about the pitch application set-up:

- Sample preparation method
  - pressure, and time of pressing, eventual usage of  $H_3BO_3$  - Boric Acid
- Calibration model and selected standards used per element
  - if calibration with duplicate standards
  - if correction for matrix, carbon set as a balance compound
- Quantitative program
  - error (CSE) & measurement time per element

Hydro got only a few answers from Supplier 1 at this stage

- Photos how the sample is prepared
- Standards per element

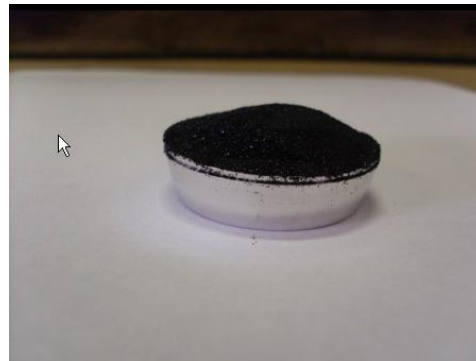
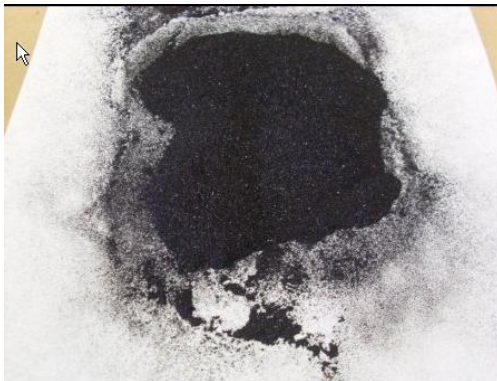
# SAMPLE PREPARATION

Hydro:

- pressing at 25.5 tonn (=250.07 kN), 5 sec
- Boric acid

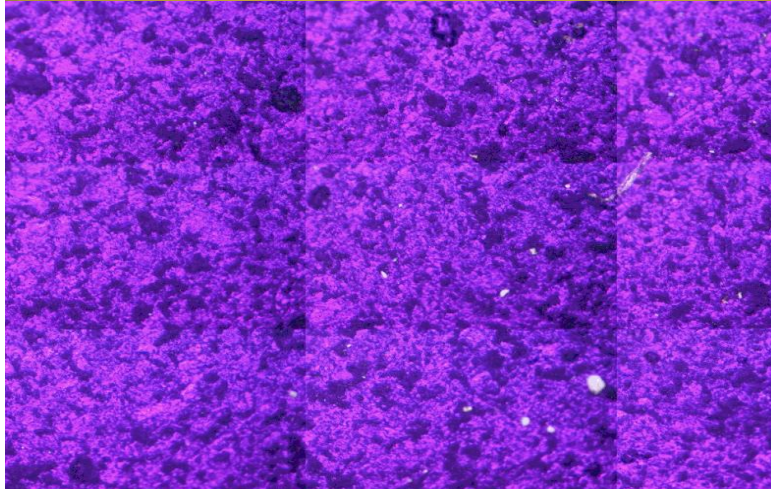
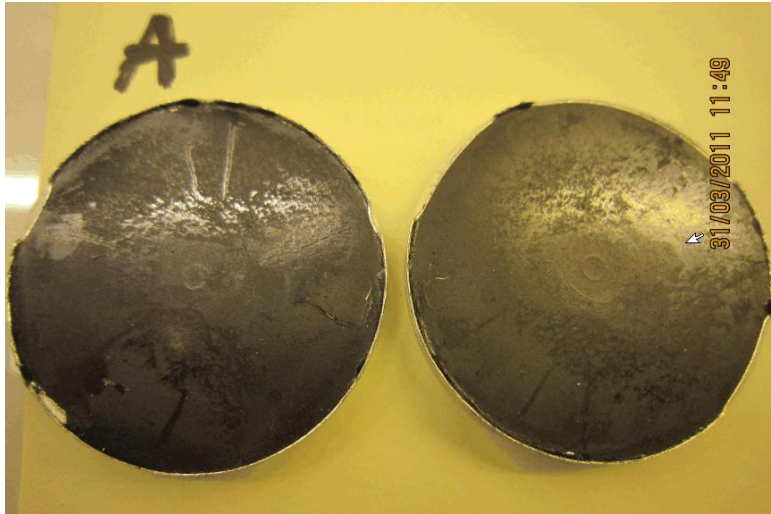
Supplier 1:

- pressing at 180 kN (=18.35 tonn), no time

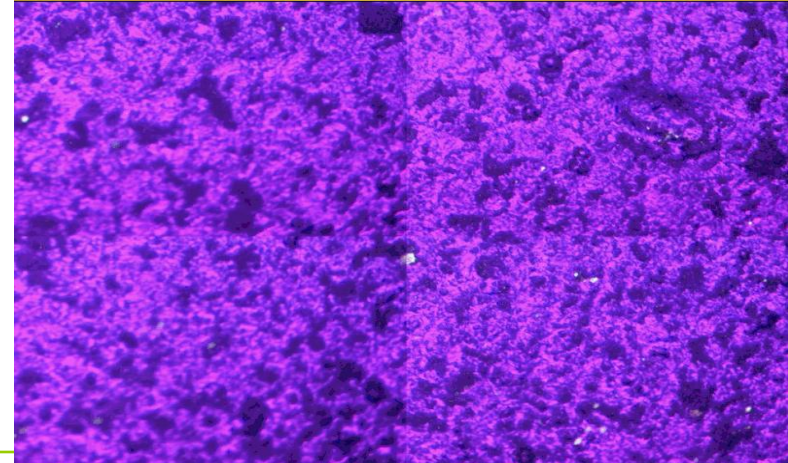
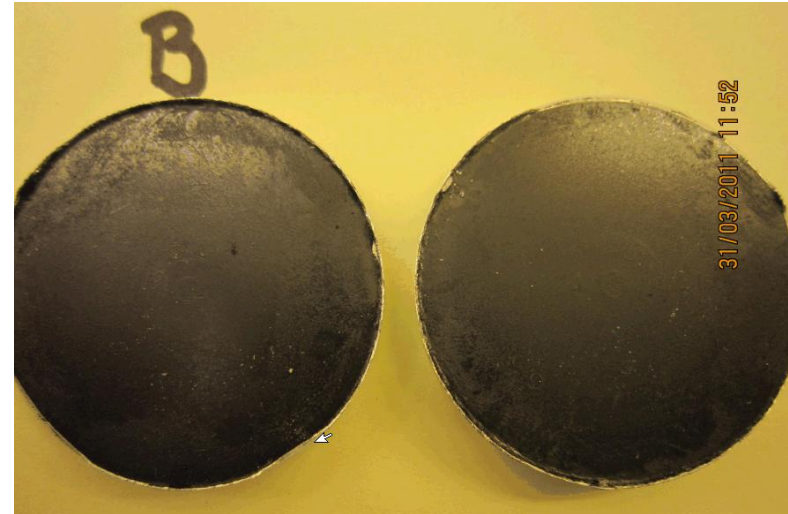


# TESTING FOR IMPROVED SAMPLE SURFACE

As Supplier 1 - Pressed only



Hydro - with boric acid at bottom





# ALSO RECEIVED CALIBRATION SET USEFUL FOR COMPARISON

19/11/2005 3:20:50

PANalytical

Page 1

## Calibration measurements for application - E-pek Cursus

Alcan set used in our laboratory

Standard name	Item	Na (ppm)	Al (ppm)	Si (ppm)	P (ppm)	S (%)	Cl (ppm)	Ca (ppm)	Ti (ppm)	V (ppm)
pitch-05	Incl/Excl									
	C(Chem)	20	367	(1540)	30	0,54	190	66	25	2
	Net rate	0,0337	1,6692	12,1587	1,3130	195,0810	3,2868	0,7229	0,4116	0,0571
pitch-04	Incl/Excl									
	C(Chem)	110	37	(750)	66	1,05	150	76	3	1
	Net rate	0,1548	0,2895	7,6257	2,5205	379,9617	2,5260	0,8351	0,0378	0,0046
pitch-03	Incl/Excl									
	C(Chem)	210	220	660	27	0,76	250	170	15	1
	Net rate	0,1957	1,1047	3,3794	0,9093	273,2307	4,2250	1,1147	0,2214	0,0477
pitch-06	Incl/Excl									
	C(Chem)	130	230	(820)	3	0,50	93	42	15	1
	Net rate	0,0868	1,0971	6,5884	0,0545	184,3975	1,7210	0,4940	0,2541	0,0294
pitch-07	Incl/Excl									
	C(Chem)	114	46	82	18	0,57	230	82	3,3	0,3
	Net rate	0,1783	0,2914	0,5197	0,6637	212,5260	3,9734	0,9578	0,0422	0,0087
UVd 70201	Incl/Excl		X	X	X	X	X	X	X	X
	C(Chem)	151								
	Net rate	0,1284	0,4333	0,6980	0,0898	190,7545	1,5107	0,4808	0,0944	0,0287
atek 5065	Incl/Excl	X								X
	C(Chem)	143	104	167	3	0,56	134	63	8	
	Net rate	0,2714	0,6530	1,1536	0,1841	192,4117	2,3929	0,7875	0,1264	0,0262

# INTERLABORATORY STUDY WITH SUPPLIER

After harmonization of Hydro XRF program to Supplier 1 there have been some differences between results measured in Hydro laboratory and reported values by Supplier 1. For most of the analysed elements the deviations have got obvious patterns.

More measurements were made to help evaluate Hydro XRF application and get more information to understand the deviations.

However, at this stage it became more obvious that differences in results are caused by additional standards used by Supplier 1. The primary reason for differences is two in-house calibration standards. This was revealed quite late in the harmonization work and practically shut down the effort.

# CALIBRATION SETS – COMPARISON

## Hydro uses fewer standards

19/11/2005 3:20:50

PANalytical

Page 1

### Calibration measurements for application - E-pek Cursus

Alcan set used in our laboratory

Standard name	Item	Na (ppm)	Al (ppm)	Si (ppm)	P (ppm)	S (%)	Cl (ppm)	Ca (ppm)	Ti (ppm)	V (ppm)
pitch-05	Incl/Excl									
	C(Chem)	20	367	(1540)	30	0,54	190	66	25	2
	Net rate	0,0337	1,6692	12,1587	1,3130	195,0810	3,2868	0,7229	0,4116	0,0571
pitch-04	Incl/Excl									
	C(Chem)	110	37	(750)	66	1,05	150	76	3	1
	Net rate	0,1548	0,2895	7,6257	2,5205	379,9617	2,5260	0,8351	0,0378	0,0046
pitch-03	Incl/Excl									
	C(Chem)	210	220	660	27	0,76	250	170	15	1
	Net rate	0,1957	1,1047	3,3794	0,9093	273,2307	4,2250	1,1147	0,2214	0,0477
pitch-06	Incl/Excl									
	C(Chem)	130	230	(820)	3	0,50	93	42	15	1
	Net rate	0,0868	1,0971	6,5884	0,0545	184,3975	1,7210	0,4940	0,2541	0,0294
pitch-07	Incl/Excl									
	C(Chem)	114	46	82	18	0,57	230	82	3,3	0,3
	Net rate	0,1783	0,2914	0,5197	0,6637	212,5260	3,9734	0,9578	0,0422	0,0087
UVd 70201	Incl/Excl		X	X	X	X	X	X	X	X
	C(Chem)	151								
	Net rate	0,1284	0,4333	0,6980	0,0898	190,7545	1,5107	0,4808	0,0944	0,0287
atek 5065	Incl/Excl	X								X
	C(Chem)	143	104	167	3	0,56	134	63	8	
	Net rate	0,2714	0,6530	1,1536	0,1841	192,4117	2,3929	0,7875	0,1264	0,0262

# CALIBRATION SETS – COMPARISON

## Supplier 1 uses in-house material . .

19/11/2005 3:20:50

PANalytical

Page 1

### Calibration measurements for application - E-pek Cursus

Alcan set used in our laboratory

Standard name	Item	Na (ppm)	Al (ppm)	Si (ppm)	P (ppm)	S (%)	Cl (ppm)	Ca (ppm)	Ti (ppm)	V (ppm)
pitch-05	Incl/Excl									
	C(Chem)	20	367	(1540)	30	0,54	190	66	25	2
	Net rate	0,0337	1,6692	12,1587	1,3130	195,0810	3,2868	0,7229	0,4116	0,0571
pitch-04	Incl/Excl									
	C(Chem)	110	37	(750)	66	1,05	150	76	3	1
	Net rate	0,1548	0,2895	7,6257	2,5205	379,9617	2,5260	0,8351	0,0378	0,0046
pitch-03	Incl/Excl									
	C(Chem)	210	220	660	27	0,76	250	170	15	1
	Net rate	0,1957	1,1047	3,3794	0,9093	273,2307	4,2250	1,1147	0,2214	0,0477
pitch-06	Incl/Excl									
	C(Chem)	130	230	(820)	3	0,50	93	42	15	1
	Net rate	0,0868	1,0971	6,5884	0,0545	184,3975	1,7210	0,4940	0,2541	0,0294
pitch-07	Incl/Excl									
	C(Chem)	114	46	82	18	0,57	230	82	3,3	0,3
	Net rate	0,1783	0,2914	0,5197	0,6637	212,5260	3,9734	0,9578	0,0422	0,0087
UVd 70201	Incl/Excl		X	X	X	X	X	X	X	X
	C(Chem)	151								
	Net rate	0,1284	0,4333	0,6980	0,0898	190,7545	1,5107	0,4808	0,0944	0,0287
atek 5065	Incl/Excl	X								X
	C(Chem)	143	104	167	3	0,56	134	63	8	
	Net rate	0,2714	0,6530	1,1536	0,1841	192,4117	2,3929	0,7875	0,1264	0,0262



# ROUND ROBIN - SELECTED MATERIAL FOR INTERLABORATORY MEASUREMENTS

Selected pitch sample materials (not milled) were sent to Supplier 1 for measurements late 2010:

Two 50 grams splits (1,2-original marking, 3 and 4 – changed to Hydro names)

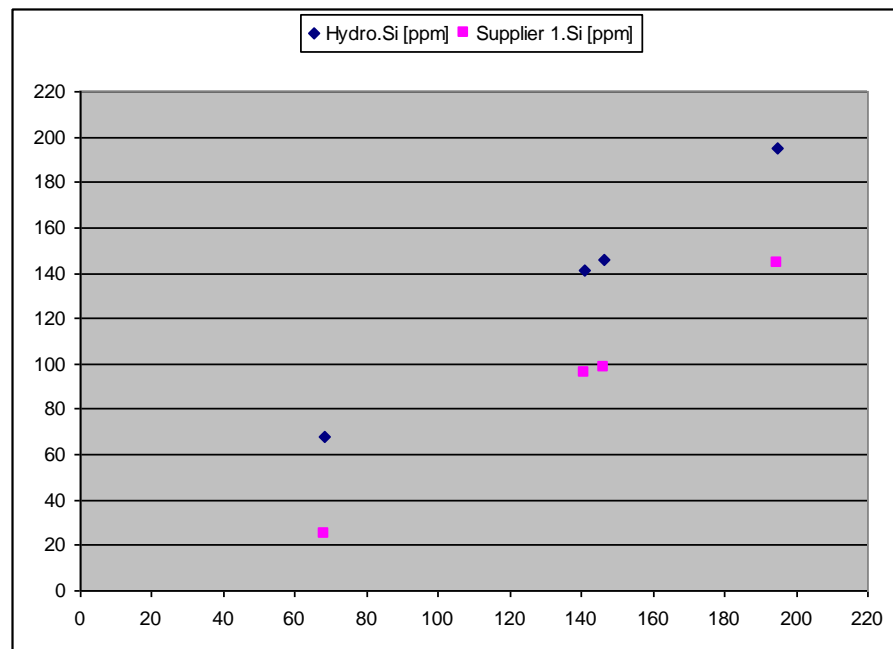
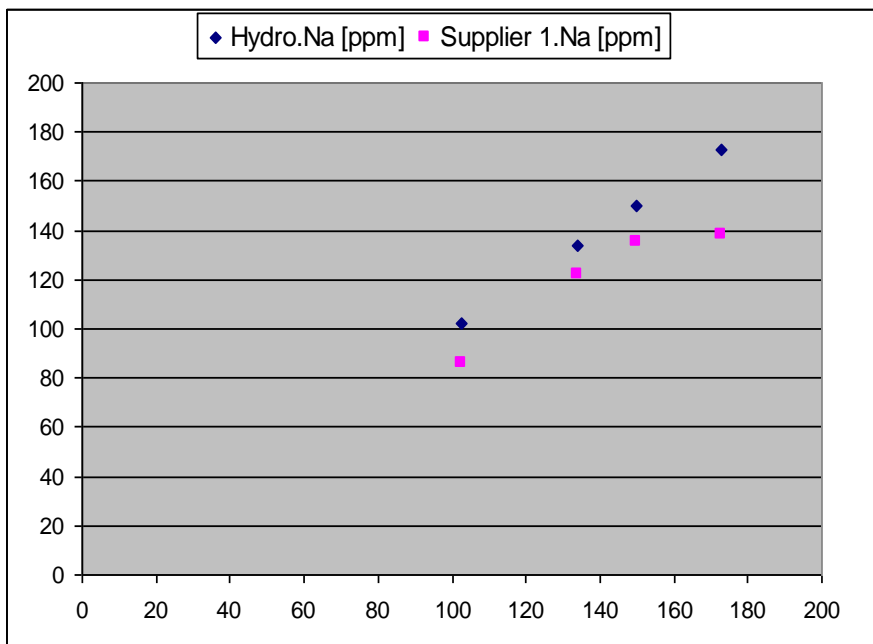
1. Vft Neuss 7/09
2. Impregneringspek Rutgers
3. Tarconord 01/00 (Hydro week 7/00)
4. Koppers UK (Hydro week 01/03)

Measure 3 parallels of each split (3x8 results)

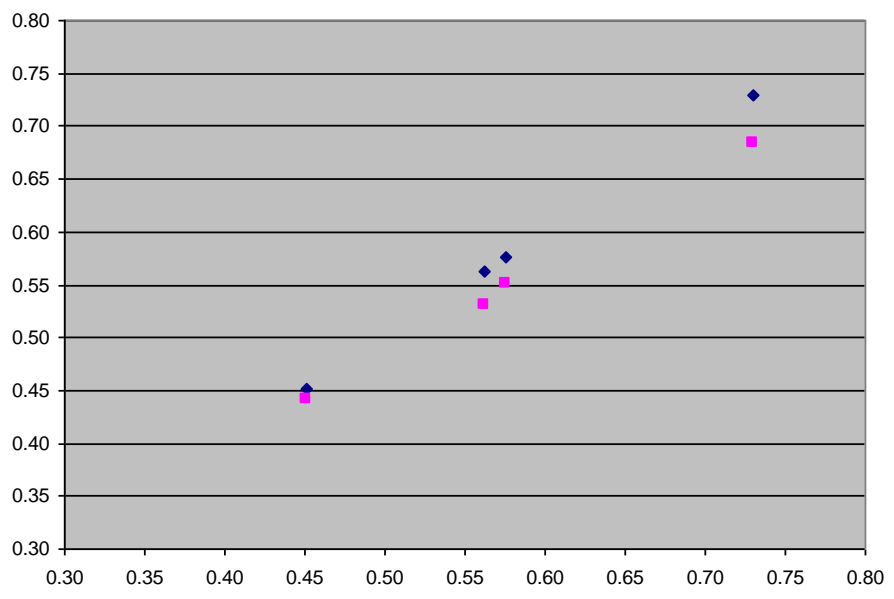
# ROUND ROBIN - AVERAGE RESULTS FOR THE SAMPLES

(FROM 2 SPLITS IN EACH 3 SAMPLE REPLICATES OF THE SAME MATERIAL)

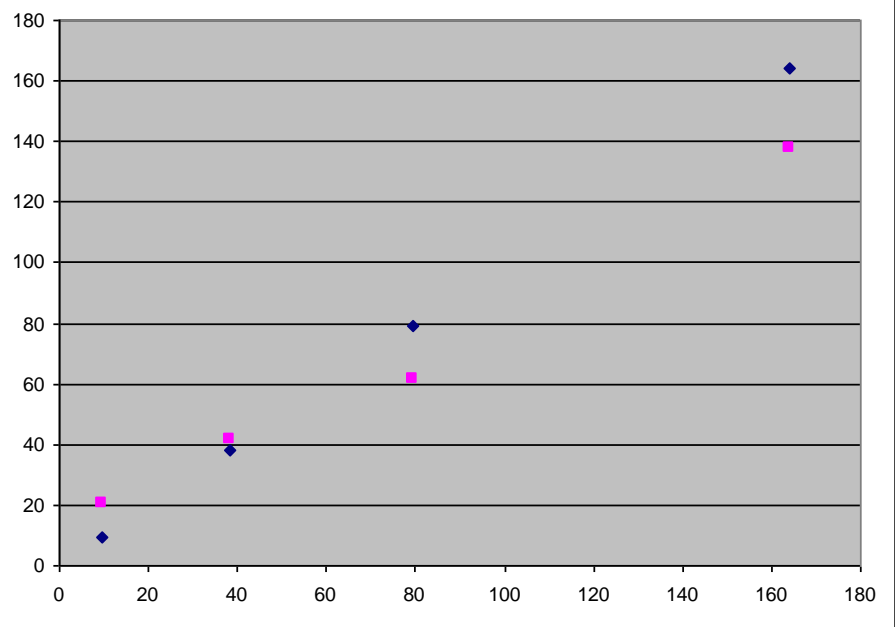
	Supplier 1 Hydro		Supplier 1 Hydro		Supplier 1 Hydro		Supplier 1 Hydro		Supplier 1 Hydro		Supplier 1 Hydro		Supplier 1 Hydro	
	Na [ppm]	Na [ppm]	Si [ppm]	Si [ppm]	S [%]	S [%]	Ca [ppm]	Ca [ppm]	Fe [ppm]	Fe [ppm]	Zn [ppm]	Zn [ppm]	Pb [ppm]	Pb [ppm]
	Supplier 1.Na [ppm]	Hydro.Na [ppm]	Supplier 1.Si [ppm]	Hydro.Si [ppm]	Supplier 1.S [%]	Hydro.S [%]	Supplier 1.Ca [ppm]	Hydro.Ca [ppm]	Supplier 1.Fe [ppm]	Hydro.Fe [ppm]	Supplier 1.Zn [ppm]	Hydro.Zn [ppm]	Supplier 1.Pb [ppm]	Hydro.Pb [ppm]
VIT-NEUSS 7/09	135	150	96	141	0.53	0.56	42	38	138	130	268	280	250	253
HYDRO WEEK 01/03 (Koppe	122	134	144	195	0.55	0.58	138	164	118	105	228	231	126	131
HYDRO WEEK 07/00 (Tarco	139	173	98	146	0.44	0.45	62	79	117	108	164	163	138	137
IMPREGNERINGSPEK RUT	86	102	25	68	0.68	0.73	20	10	62	53	203	211	123	136



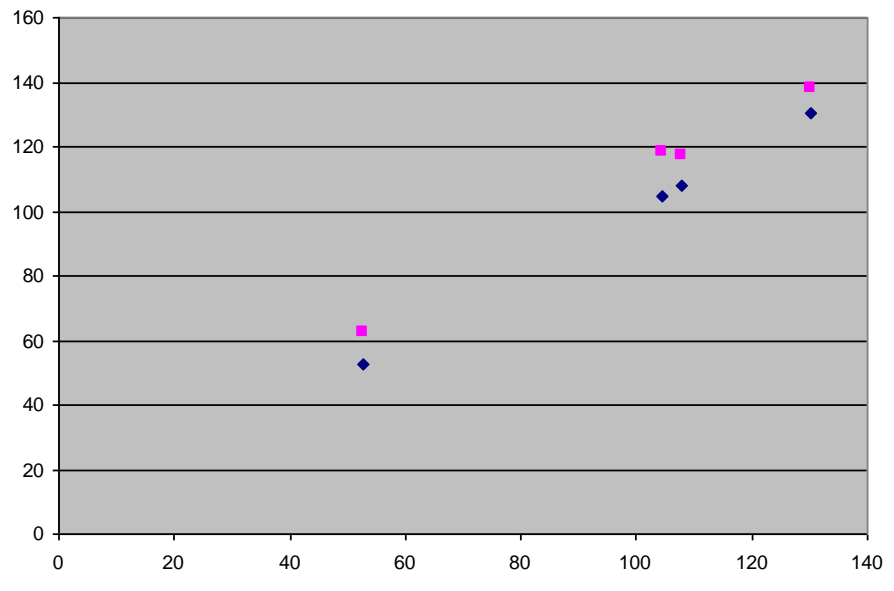
◆ Hydro.S [%] ■ Supplier 1.S [%]



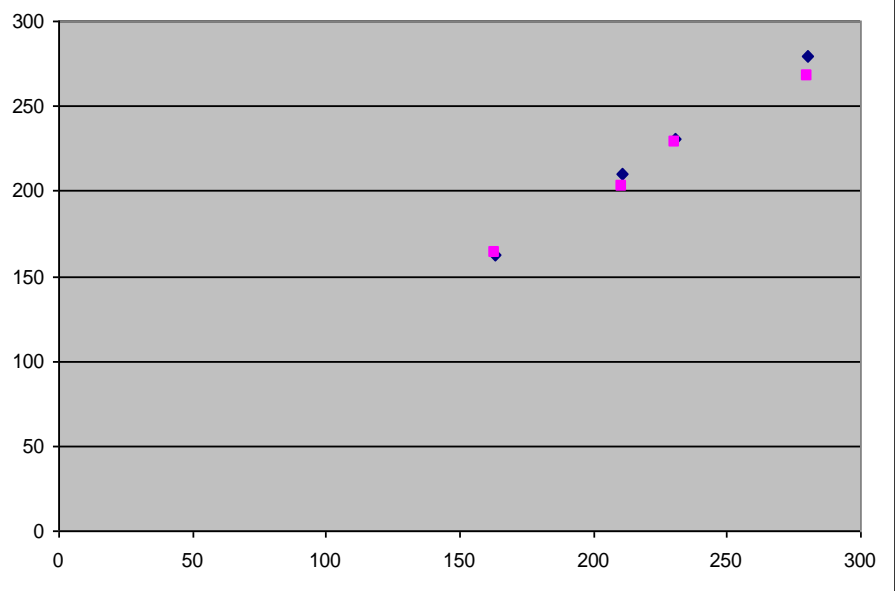
◆ Hydro.Ca [ppm] ■ Supplier 1.Ca [ppm]



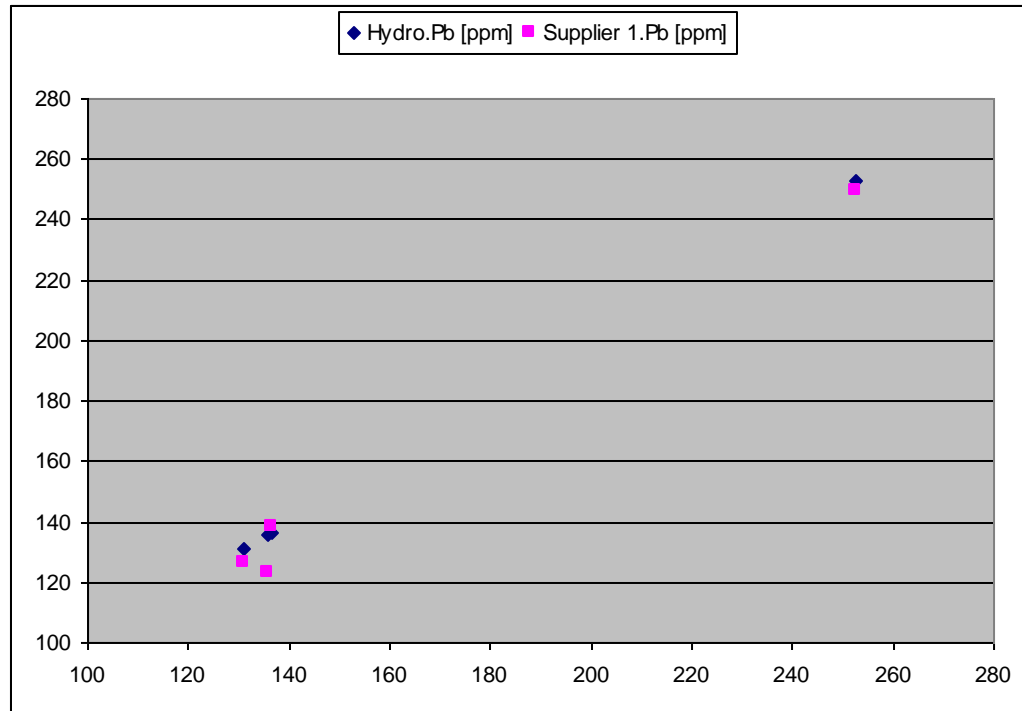
◆ Hydro.Fe [ppm] ■ Supplier 1.Fe [ppm]



◆ Hydro.Zn [ppm] ■ Supplier 1.Zn [ppm]



HYDRO



# SUMMING UP OUR EXPERIENCE

- It was not possible to harmonized fully the XRF application; the results will be deviating due to differences in the used standard sets - during the study we learnt that Supplier 1 uses two in-house standards
- Sample surface tends to be blurry after pressing –the effect of this on the final measurements' results is not known - the study showed that it is difficult to obtain good sample surface for pitch XRF measurements, however situation is improved with use of the boric acid
- The measuring time for pitch should not be long since the sample is heated during the measurement and this pitch tends to soften above 100°C
- Hydro has lowed the measuring time for the pitch application, by removing from application elements expected to be under 5 ppm, adjusting CSE% to 0,5 where possible. Nowadays, Hydro is measuring one sample in 6 minutes

[www.hydro.com](http://www.hydro.com)