

Proficiency testing for Phenol and Cyanide 2008 in water from a Coke plant

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Keywords:

Cyanide, phenol, coking plant, water, proficiency test, laboratory

Summary

A proficiency test on the determination of phenol and cyanide in water from a coking plant has been carried out. Twelve laboratories from ten European countries participated using their normal analytical methods.

The standard deviation for phenol levels of 700 ppm was about 40 ppm (6 % relative standard deviation) which seems acceptable. For free cyanide the standard deviation is about 30 % of the mean value on the level 2,4 ppm. The high standard deviation for free cyanide makes it difficult to compare results from different laboratories. Instability of the samples could have an influence.

For total cyanide the relative standard deviation is around 13 % which seems acceptable.

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Samples

The samples were two pairs of bottles of water from the Coke plant at SSAB Oxelösund sampled before biological treatment.

The first pair, for determination of phenol, was conserved with phosphoric acid and cupric sulfate. The second pair, for determination of cyanide, was conserved with sodium hydroxide. The samples were taken on two occasions in April 2008 and were stored at room temperature for some months to be stabilized. The concentrations of phenol were very stable while the concentrations of cyanide slowly decreased. It was asked for only one determination of each analytical parameter in each sample.

Analysis

The samples were supposed to be analyzed during any optional day between October 6 and 10, 2008. Every bottle had been filled with 100 ml sample as carefully as possible with pipette. The test samples should be diluted to suitable volume on the analysis occasion. Cyanide sample 2 had low concentration and could be analyzed undiluted.

Statistical evaluation

All concentration reported are put into tables and also plotted into graphs. An overall mean value and standard deviation were calculated for each analytical parameter and sample, including all samples and also after the removing of outliers. The broken lines in the plots show the standard deviation after removal of outliers and the straight line is the mean value also after removal of outliers.

The statistical tests applied are Grubbs 1 and Grubbs 2 (5 %) which are mean value tests. In Grubbs 1 (indicated with blue color) the individual mean value is compared to the overall mean value of the population. In Grubbs 2 (indicated with green color) two mean values are tested at the same time (the two highest values, the two lowest values or the highest and the lowest values). An outlier indicates that the accuracy is not good enough.

The Grubbs's test

$$G = \left| \frac{g_p - \bar{g}}{s} \right|$$

Grubb's test is used for a given set of data y_i ($i=1, 2, 3, \dots, P$) arranged in ascending order. The symbols in the equation refer to:

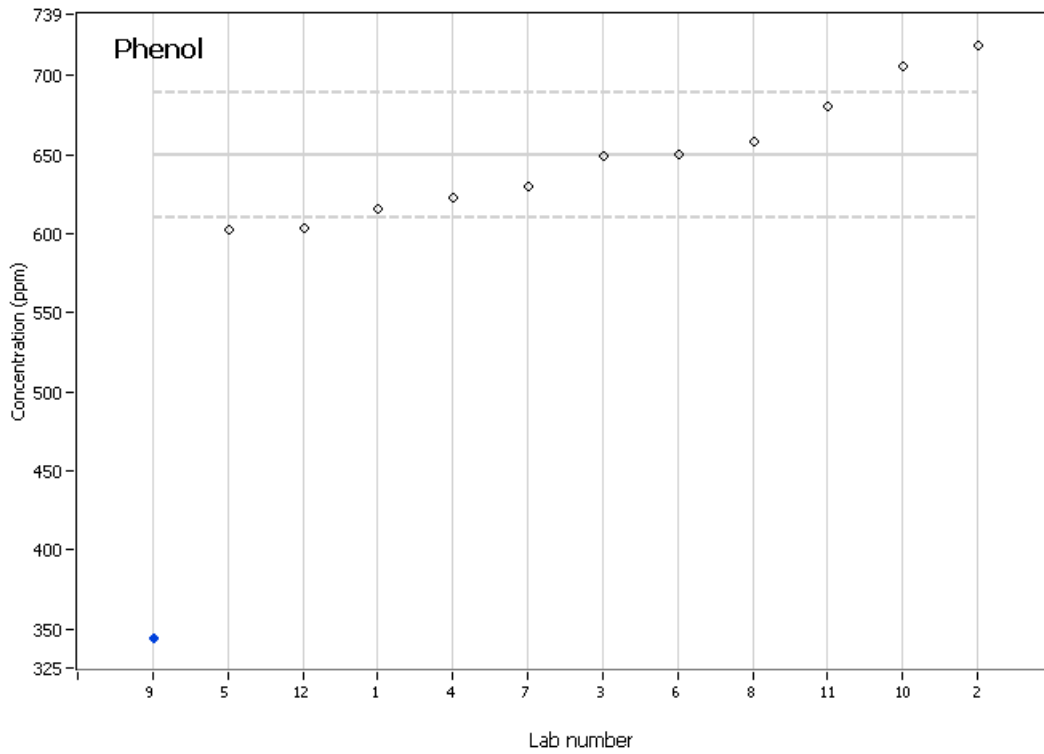
$g_p = \text{extreme value}$, $\bar{g} = \text{mean value}$, $s = \text{standard deviation}$

If $G >$ a critical value according to a table value, the result value tested is rejected at 95 % confidence level.

Only one determination of each sample and analytical parameter has been made by each laboratory and therefore no statistical tests of the variance such as Cochran's test are possible.

Results

Phenol Sample 1

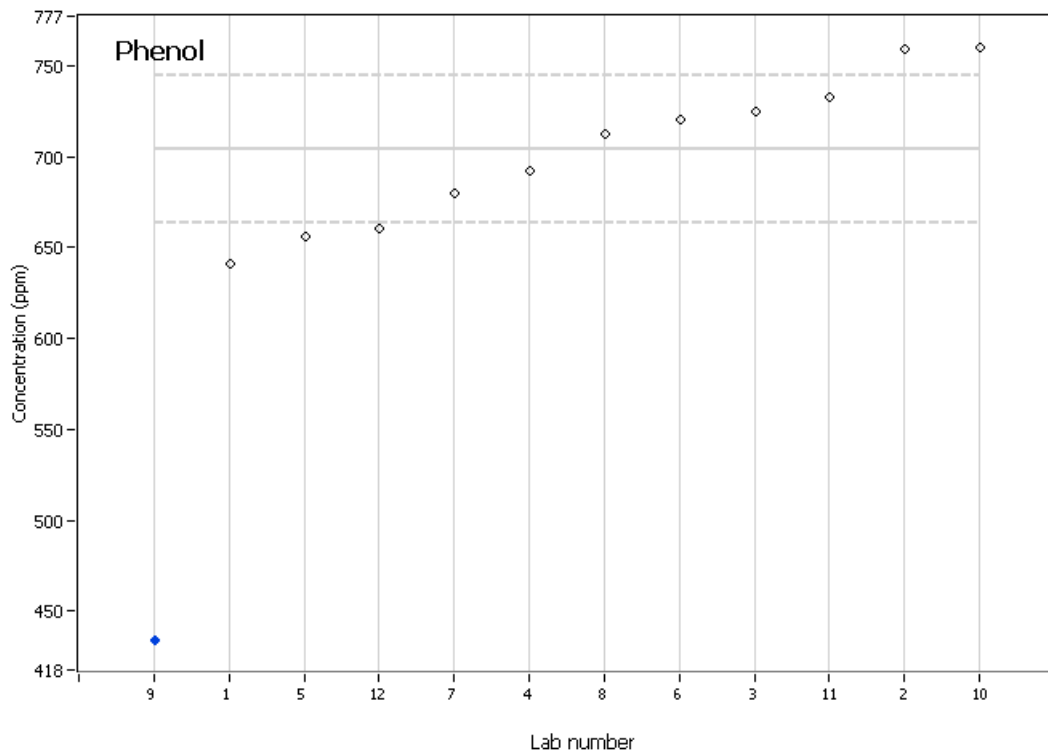


	All laboratories	Outliers removed
Labs	12	11
Mean	624	649
Stdev	95,9	39,6

Lab	Result (ppm)
9	344*
5	603
12	604
1	616
4	623
7	630
3	650
6	651
8	659
11	682
10	706
2	720

* Outlier marked with filled dot in chart

Phenol Sample 2

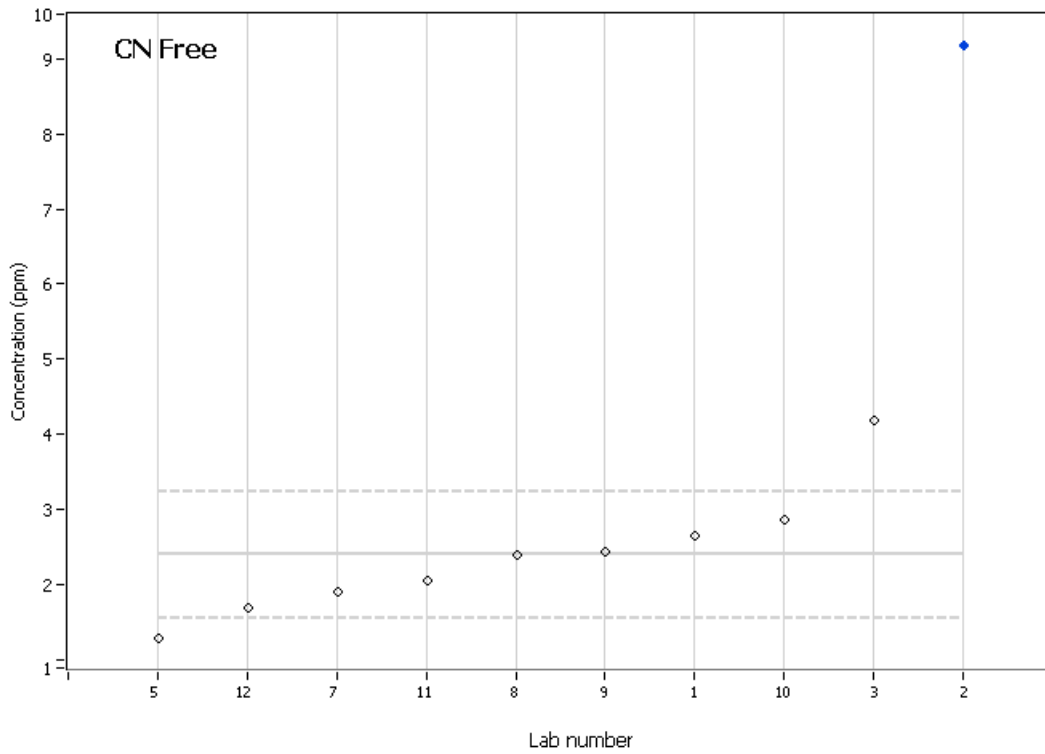


	All laboratories	Outliers removed
Labs	12	11
Mean	681	704
Stdev	87,1	40,8

Lab	Result (ppm)
9	434*
1	642
5	657
12	661
7	680
4	693
8	713
6	721
3	725
11	733
2	760
10	761

* Outlier marked with filled dot in chart

Free Cyanide Sample 1

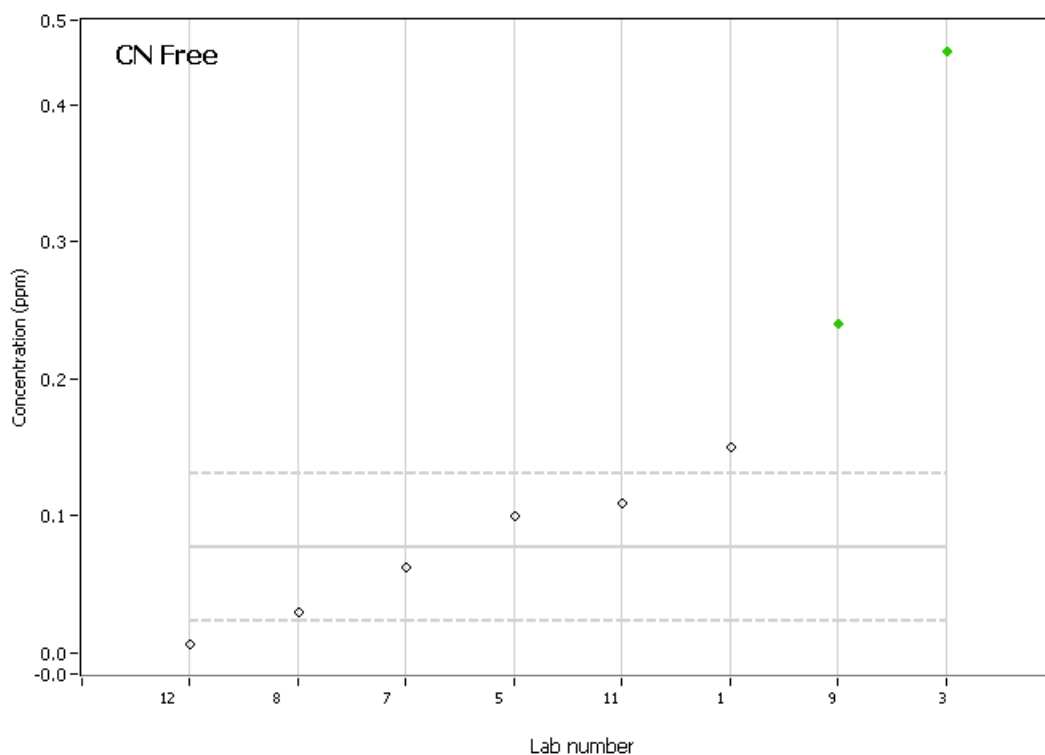


	All laboratories	Outliers removed
Labs	10	9
Mean	3,07	2,39
Stdev	2,29	0,84

Lab	Result (ppm)
5	1,28
12	1,70
7	1,90
11	2,06
8	2,41
9	2,44
1	2,66
10	2,88
3	4,20
2	9,20*

* Outlier marked with filled dot in chart

Free Cyanide Sample 2



Result

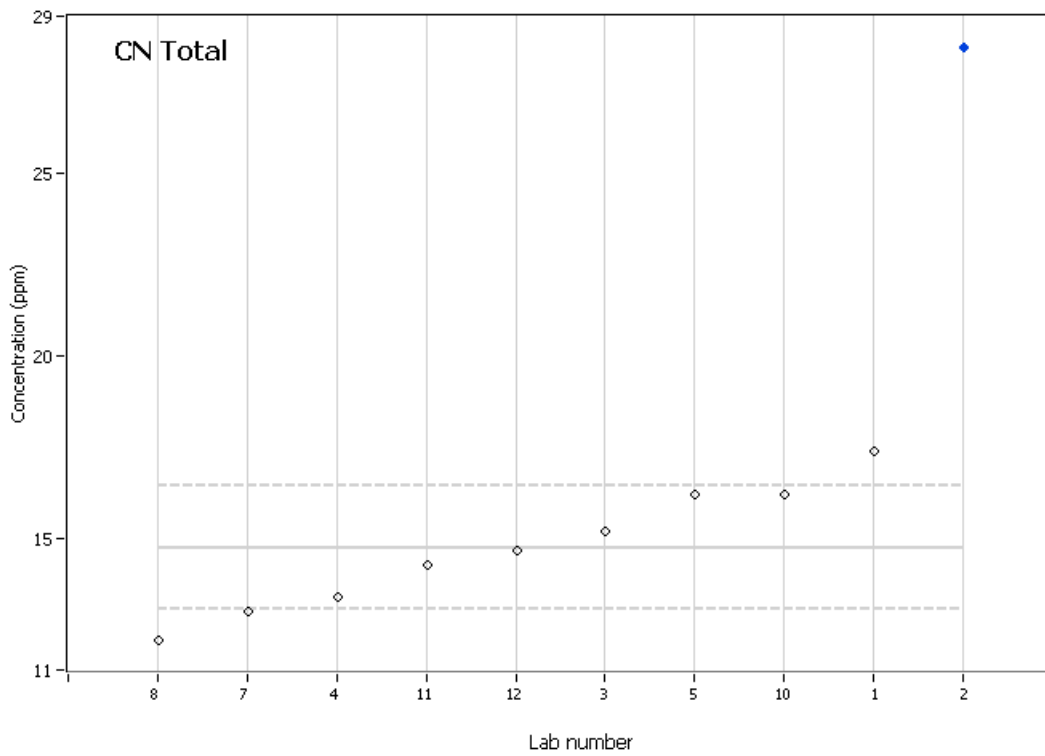
without the most extreme outliers.

	All laboratories	Outliers removed
Labs	10	6
Mean	0,914	0,076
Stdev	2,19	0,054

Lab	Result (ppm)
12	0,006
8	0,03
7	0,063
5	0,10
11	0,11
1	0,15
9	0,24*
3	0,44*
10	0,90*
2	7,10*

* Outlier marked with filled dot in chart

Total Cyanide Sample 1

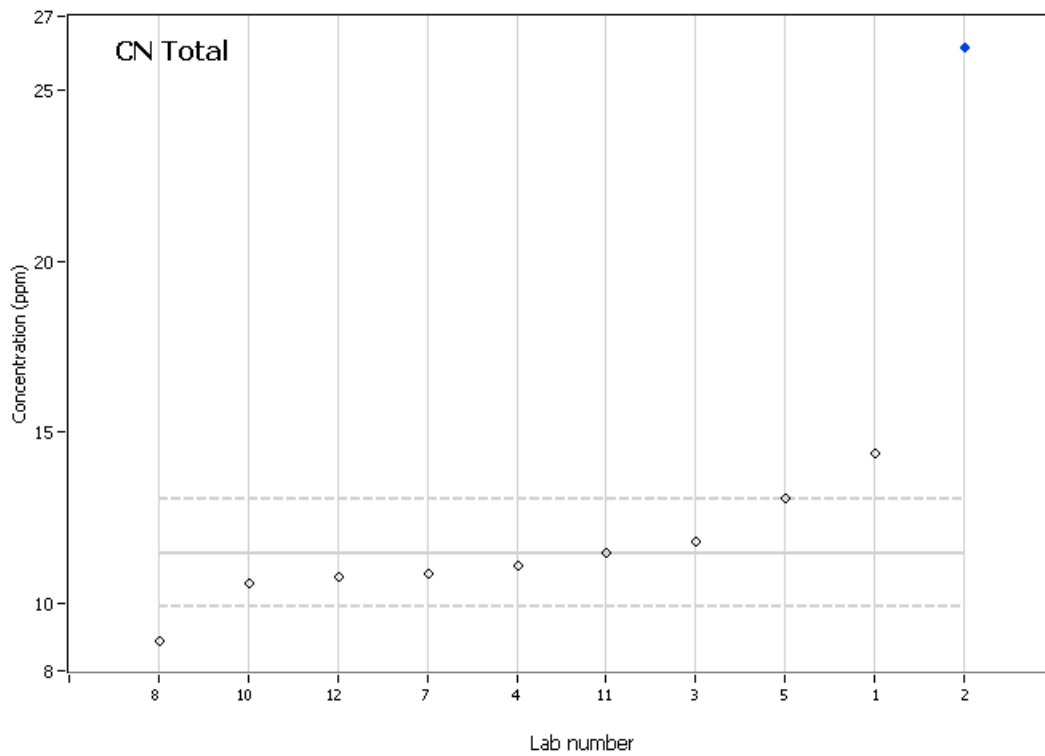


	All laboratories	Outliers removed
Labs	10	9
Mean	16,1	14,7
Stdev	4,64	1,70

Lab	Result (ppm)
8	12,2
7	13,0
4	13,4
11	14,3
12	14,7
3	15,2
5	16,2
10	16,2
1	17,4
2	28,5*

* Outlier marked with filled dot in chart

Total Cyanide Sample 2



	All laboratories	Outliers removed
Labs	10	9
Mean	12,9	11,4
Stdev	4,92	1,57

Lab	Result (ppm)
8	8,89
10	10,6
12	10,8
7	10,9
4	11,1
11	11,5
3	11,8
5	13,1
1	14,4
2	26,3*

* Outlier marked with filled dot in chart

Comments

Twelve laboratories took part in the Proficiency testing for Phenols but for Cyanide it was only ten participating laboratories. This does not really give a sufficient amount of data for statistical evaluation.

The standard deviation is approximately 40 ppm for a concentration of Phenols of about 700 ppm. The relative standard deviation of 6 % seems acceptable. For both samples one outlier (the same laboratory) is identified. This laboratory has diluted the samples 25 000 times and this is probably the reason.

For Free Cyanide Sample 1, one outlier is identified. After the removal of this outlier the standard deviation is still as high as one third of the mean value. For Sample 2 with a considerable lower concentration, the spread is even higher. After removal of four outliers, the standard deviation is two thirds of the mean. It seems difficult to compare results for Free Cyanide. Maybe the samples are not stable at such low concentrations or perhaps it is due to the many different methods used.

For both the samples for Total cyanide one outlier was found. The relative standard deviation (12 % and 14 %) seems acceptable.

Participants and used Method

Voestalpine Stahl GmbH Umwelt- und Betriebsanalytik, BG 03 voestalpine Stahl GmbH voestalpine-Str. 3 A-4020 Linz AUSTRIA	Dipl.-Ing. Andreas Schönauer Dr. Hubert Duchaczek	Phenol: Photometric method according to DIN 38409-16 (4-Aminoantipyrin).
U.S. Steel Kosice Labortest s.r.o Laboratorium Koksoune Vstupny Areal USS 04454 Kosice SLOVAKIA	Ing. Jozef Stano	Phenol: STN ISO 6439 Determination of phenol index. 4-aminoantipyrine spectrometric methods after distillation. Cyanide total: STN ISO 6703-1. Determination of cyanide. Determination of total cyanide, spectrometric method.
ISD Dunaferr Ltd. Material Testing and Calibration Laboratories H-2400 Dunaújváros Vasmu tér 1-3 Po. box 110 HUNGARY	Mária Simon Firényiné Ilona Sárai Szabó Szilvia Solymosi	Phenol: 4-Aminiantipyrine spectrometric method after distillation. Cyanide free: Barbituric acid/pyridine spectrometric method after purging and absorption I NaOH. Cyanide total: Barbituric acid/pyridine spectrometric method after purging and absorption I NaOH.
Corus M5 Technical Centre Corus Redcar Site Trunk Road Redcar Cleveland TS10 5 QW UNITED KINGDOM	Bill Asher	Phenol: Distillation followed by In-house method from: Methods for the Examination of Waters and Associated Materials. 'Phenols in Water and Effluents by GLC 4 aminoantipyrine or 3-methyl-2-benzo- thiazalinone hydrozone 1981'. Cyanide free: Aeration at pH 4.5 followed by colorometric procedure using p- phenylenediamine/pyridine reagent. In-house method based on "The Analysis of Raw Potable and Waste Waters" HMSO: Pages 226-230. Cyanide total: Distillation followed by titration with silver nitrate. In-house method based on "The Analysis of Raw Potable and Waste Waters" HMSO: Pages 226-230.

<p>Luxcontrol SA Service Laboratoire 1, Avenue des Terres Rouges L-4004 ESCH sur ALZETTE LUXEMBOURG</p>	<p>Dr Jérôme GEORGES</p>	<p>Phenol: Method Hach - 8047-4 aminoantipyrine method. Cyanide total: Kit Lange 315 – extraction with succinic acid.</p>
<p>Rautaruukki Oyj Laboratory Services Ruukki Metals P.O. Box 93 92101 RAAHE FINLAND</p>	<p>Mr. Keijo Eilola</p>	<p>Phenol: Photometric method, internal method. Cyanide free: Photometric method based on SFS 5734 standard method. Cyanide total: Photometric method based on SFS 5747 standard method.</p>
<p>ArcelorMittal Ostrava a.s. Hutní a chemické laboratore, Provozní laboratore Vratimovská 689 707 02 Ostrava – Kuncice CZECH REPUBLIC</p>	<p>Ing. Marek Zamazal</p>	<p>Phenol: CSN ISO 6439. Water quality. Determination of phenol index. 4- aminoantipyrine spectrometric method after distillation. Cyanide free: CSN ISO 6703-2. Water quality. Determination of cyanide. Part 2: determination of easily liberatable cyanide. Cyanide total: CSN ISO 6703-2. Water quality. Determination of cyanide. Part 1: determination of easily total cyanide.</p>
<p>ThyssenKrupp Steel Kaiser-Wilhelm-Strasse 100 WSK-A-CA (361) D-47166 Duisburg GERMANY</p>	<p>Mrs. Simone aus dem Spring</p>	<p>Phenol: DIN EN ISO 14402 (CFA). Cyanide free: DIN EN ISO 14403 (CFA). Cyanide total: DIN EN ISO 14403 (CFA).</p>
<p>Trinecké Zelezářny a.s. Laborator koksovny Prumyslová 1000 73970 Trinec CZECH REPUBLIC</p>	<p>Mgr. Jitka Petrová</p>	<p>Phenol: Determination of phenol with 4- nitroaniline spectrometric method after distillation. Cyanide free: Distillation: CSN ISO 6703-2. Concentration: Method by Hach for cyanide (pyridine-pyrazolone). Cyanide total: CSN ISO 6703-1, part 4.</p>
<p>SSAB Strip products Laboratoriet, pnr 105 971 88 LULEÅ SWEDEN</p>	<p>Lars Muotka</p>	<p>Phenol: SIS 02 81 28-1. Cyanide free: SS 02 81 77. Barbituric acid/pyridine spectrometric method after purging and absorption in NaOH.</p>

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Jan van der Hoek

Phenol: Dutch standard NEN 6670
(Photometric determination of the content of phenols volatile with water vapor.

Cyanide free: ISO 14403.

Cyanide total: Dutch standard NEN 6489
(Photometric determination of the content of total cyanide (anorganic), except CO-complex and isocyanathe, after distillation.

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Henrik Aldén

Phenol: 4-Aminiantipyrine spectrometric method after distillation.

Cyanide free: SS 02 81 77. Barbituric acid/pyridine spectrometric method after purging and absorption in NaOH.

Cyanide total: SS 02 81 76. Barbituric acid/pyridine spectrometric method after purging and absorption in NaOH.

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