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Proficiency testing for Thiocyanate in water from a Coke plant

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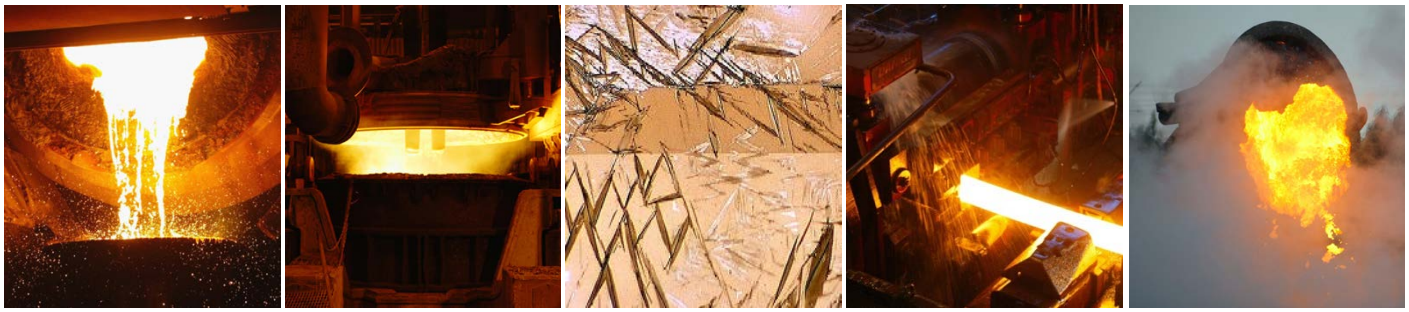


Foto: Stig-Göran Nilsson och Mats Hillert

Summary

A proficiency test on determination of thiocyanate in water from a coking plant has been carried out. Nine laboratories from six European countries participated using their normal analytical methods.

The standard deviation between laboratories for thiocyanate levels of 300 - 320 ppm was about 35 ppm (11-12 % relative standard deviation) which seems acceptable given that several different methods were used.

Keywords: Thiocyanate, coking plant, water, proficiency test, laboratory

Contents

SAMPLES

The two samples were water from the Coke plant at SSAB in Oxelösund, taken before biological treatment. No conservation was made, but before sending the samples were filtrated through a 0,45 µm Millipore filter. The samples were taken on two occasions in April 2013 and have been stored since then at room temperature to be stabilized.

ANALYSIS

The samples were supposed to be analyzed during any optional day between February 10 and 14, 2014. Every bottle had been carefully filled with 100 ml sample with a pipette.

All concentration reported are presented in tables and also plotted into graphs. An overall mean value and standard deviation were calculated after removing of outliers. The broken lines in the plots show the standard deviation and the straight line is the mean value.

STATISTICAL EVALUATION

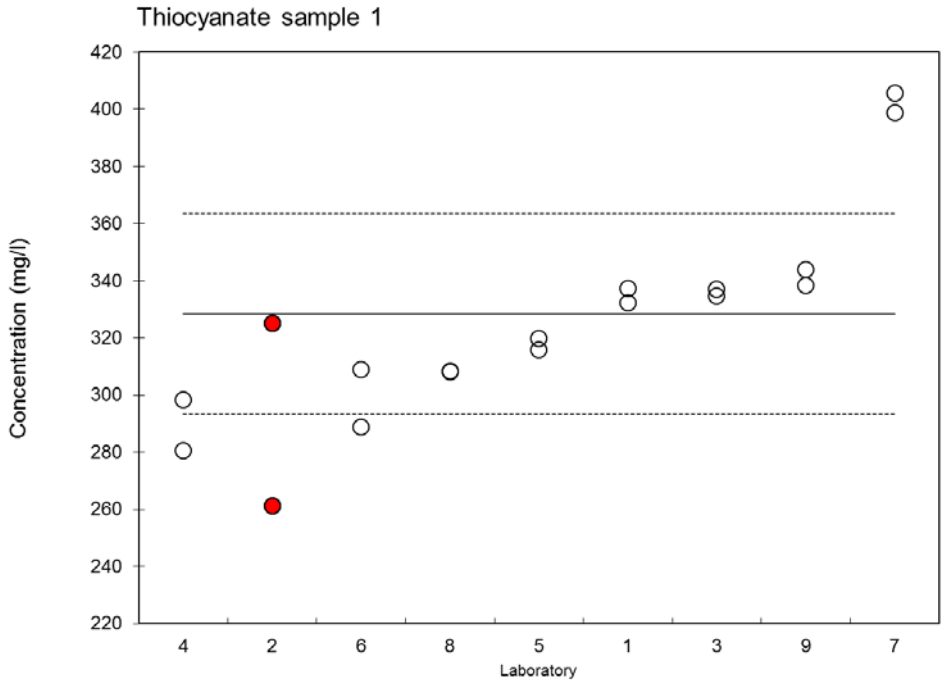
The evaluation of performance is based on statistical tests, Cochran´s test and the Grubbs´ single and Grubbs´ by pair tests. The assigned values have been determined by the evaluation software.

The Cochran´s test gives indications of discrepancies of a parameter in measurements between two determinations. Usually an outlying value will describe a poor precision, but in the special case, when all laboratories except one, have got the same results on both the days, a single laboratory can become a Cochran outlier. This can happen even if its results are very close to those of the other laboratories, and the results of the single laboratory differ marginally between the two days. This is not the case for sample 1 below.

The Grubb´s test is a mean value test, where every individual mean is compared to an overall mean of the population. An outlier indicates that the accuracy is not good enough.
If the results are scattered over a wide concentration range, there is an obvious risk that there will not be any outliers. This usually occurs when there are difficulties in the determination of an element, which can be the case when the concentration determined is low. But on the other hand if the number of participants is very few, less than in this study, there is a risk that everyone will be tagged as outliers.

RESULTS

Sample 1



In the graph colored values indicate that the testing machine is a statistical outlier; red – Cochran outlier, blue – Grubbs single outlier, green – Grubbs by pair outliers. Straight line indicate mean value and broken lines ± 1 σ.

Lab	Results (mg/l)	
	Test 1	Test 2
4	280,5	298,2
2	261,1 *	325,0 *
6	288,9	308,9
8	308,5	308,1
5	315,9	319,8
1	332,2	337,2
3	334,6	337,0
9	343,8	338,3
7	398,6	405,6

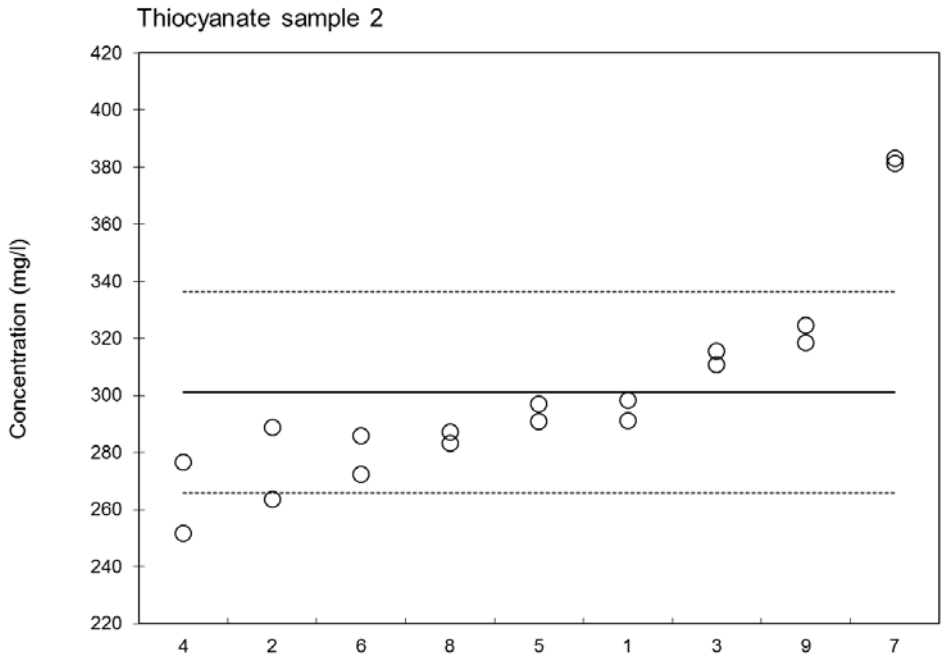
* Outlier removed from statistical calculation.

Statistical result	
No of labs	8
Mean	328,5
Sm	35,0
Sw	7,2
RSD%	10,7

Sm = Standard deviation between laboratories
Sw = Mean standard deviation for measurements within each laboratory

Several of the laboratories show a very good reproducibility. Laboratory number 2 however has measured a difference of 60 mg/l between the two samples. Laboratory number 7 has higher results then the other laboratories, but is not an outlier.

Sample 2



In the graph colored values indicate that the testing machine is a statistical outlier; red – Cochran outlier, blue – Grubbs single outlier, green – Grubbs by pair outliers. Straight line indicate mean value and broken lines ± 1 σ.

Lab	Results (mg/l)	
	Test 1	Test 2
4	251,8	276,5
2	288,7	263,6
6	272,3	285,8
8	287,2	283,1
5	290,9	297,1
1	291,2	298,4
3	315,5	310,7
9	324,5	318,5
7	381,3	383,0

No outlier in this test.

Statistical result	
No of labs	9
Mean	301,1
Sm	35,3
Sw	9,40
RSD%	11,7

Sm = Standard deviation between laboratories
Sw = Mean standard deviation for measurements within each laboratory

On sample 2 all laboratories have performed well. The measured difference between the two samples is in the same order for all laboratories, with little higher difference for laboratory number 2 and 4.

PARTICIPANTS AND USED METHODS

ISD DUNAFERR Co. Ltd. Directorate Material Testing and Calibration Laboratories Vasmü tér 1-3, H-2400 Dunaújváros, HUNGARY	Szilvia Solymosi	Precipitation with $ZnSO_4$, filtration, then detection by $FeCl_3$ spectrometric method
Tata Steel Strip Products UK Central Laboratories BOS Admin Block Margam Works, Port Talbot West Glamorgan, SOUTH WALES, SA13 2NG	Andrew R Jones Jason Francis	Colourmetric method
Tata Steel PO Box 1, Scunthorpe UK DN16 3BE	Helen Summerfield	Gallery analyzer (photometric using ferric nitrate/nitric acid)
Ruukki Metals Oy Rautaruukintie 155 92100 Raahe FINLAND	Satu Haapanen	Method ASTM D 4193-08 Thiocyanate reacting with ferric ions at a pH < 2 to form a colored complex which is determined colorimetrically at 460 nm
SSAB EMEA AB Laboratory R&D and Quality 971 88 LULEÅ SWEDEN	Lars Muotka	Inlab Ion Chromatographic method
SSAB EMEA AB Analysis & Metallography 613 80 OXELÖSUND SWEDEN	Henrik Aldén	Deutsche Einheitsverfahren zur Wasseruntersuchung, 17. Lieferung (1986) and SS 02 81 77-1.
Voestalpine Stahl Voestaplpine Str. 3 4020 LINZ AUSTRIA	Dr. Hubert Duchaczek	Phometric determination as Fe(III)-thiocyanate
AG der Dillinger Hüttenwerke Hauptlaboratorium Werkstraβe 1 D-66763 Dillingen/Saar GERMANY	Dr. Patrice Reeb	Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (DEU) D16
ThyssenKrupp Steel Ag 361 TIS-C-A Kaiser-Wilhelm Str. 100 471 66 DUISBURG GERMANY	Mrs. Simone aus dem Spring	DIN EN ISO 10304-1

DEN SVENSKA STÅLINDUSTRINS BRANSCHORGANISATION

Organisationen grundades 1747 och ägs sedan dess av de svenska stålföretagen. Jernkontoret företräder stålindustrin i frågor som berör handelspolitik, forskning och utbildning, standardisering, energi och miljö samt skatter och avgifter. Jernkontoret leder den gemensamma nordiska stålforskningen. Dessutom utarbetar Jernkontoret branschstatistik och bedriver bergshistorisk forskning.

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