Application Bulletin

Of interest to:	General analytical chemistry, water, waste water, environmental protection, metals, electroplating, mineral resources, cyanide, ISE, CN^-, process water, standard addition, potentiometry, steel, cast steel, ISE	P 1, 2, 10, 15

Determination of cyanide in process water of the steel industry

Summary

The production of steel involves many different materials and procedures. In order to achieve a smooth, reliable production process and obtain a good product quality, the materials and procedures have to be controlled very thoroughly. One important component in the steel production is process water that is used for cooling the blast furnace and for washing and cleaning of the top gases (blast-furnace gases). After top gas purification the scrubbing water contains dissolved cyanide and the water can only be returned to the public sewage if the cyanide concentration is below the legal limits.

The ProcessLab setup described here offers a measurement and monitoring solution and provides various options for reacting to any situation. With the aid of the input/output controller, the measured analytical values are easily transferred to the process control center in the form of 4…20 mA analog signals. On the basis of these values, all further process steps are initiated and controlled automatically in the process control center.

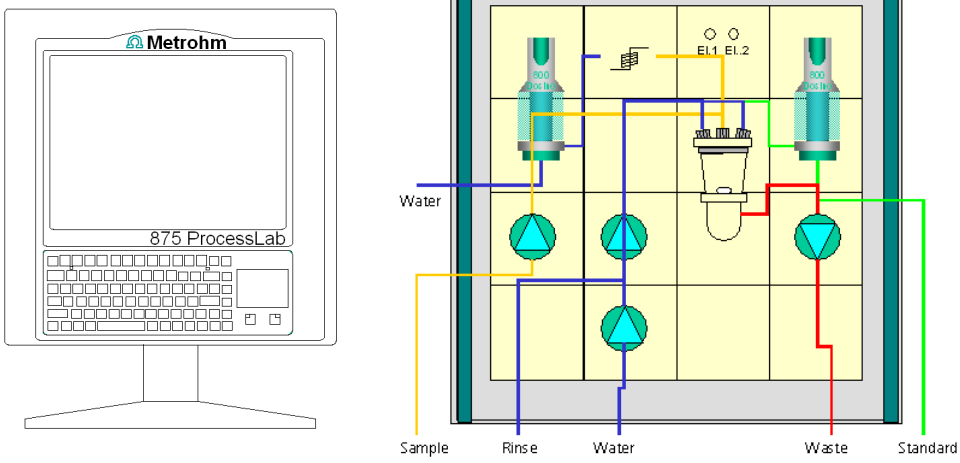
Features/general information

- Automated measurement of cyanide using the standard addition technique
- Autonomous action if the cyanide level exceeds a given limit
- Ready for analysis at any time (24 h)
- Less consumption of CN^--containing chemicals due to «Result on request»
- Analysis time approx. 5 minutes per sample
- Automated monitoring of reagent levels

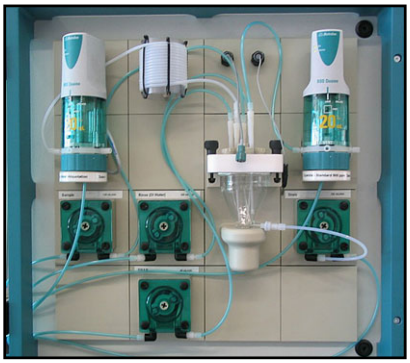
Parts used (only the most important parts are listed)s

- 1 x 2.875.0010; 875 ProcessLab Base Unit L, 1 Metrohm Dosing & Measuring Controller (incl. IPC, I/O controller and TFT/Keyboard terminal)
- 2 x 2.800.0010; 800 Dosino
- 2 x 6.3032.220; Buret 20 mL
- 2 x 6.7205.030; Peristaltic pump 320 mL/min
- 2 x 6.7205.020; Peristaltic pump 120 mL/min
- 1 x 6.7204.000; Vessel mounting with stirrer
- 1 x 6.7206.040; Sample loop 10 mL var. compl. for 875
- 1 x 6.7201.000; Measuring amplifier
- 1 x 6.0502.130; CN^- Ion-selective electrode
- 1 x 6.0750.100; ISE LL reference electrode
- 2 x 6.7202.100; Digital input 4 DI 24 V DC
- 2 x 6.7202.200; Digital output 4 DO 24 V DC
- 1 x 6.7202.400; Analog output 2 AO 4-20 mA

System overview



Wet part setup



Reagents

- TISAB* c(NaOH) = 0.1 mol/L
- CN^- standard 500 mg/L**
- Demineralized water

* **T**otal **I**onic **S**trength **A**djustment **B**uffer; ISE measurements need a strong ionic activity and a buffered or pH-controlled matrix

** To avoid dilution errors, the highest possible standard concentration should be used.

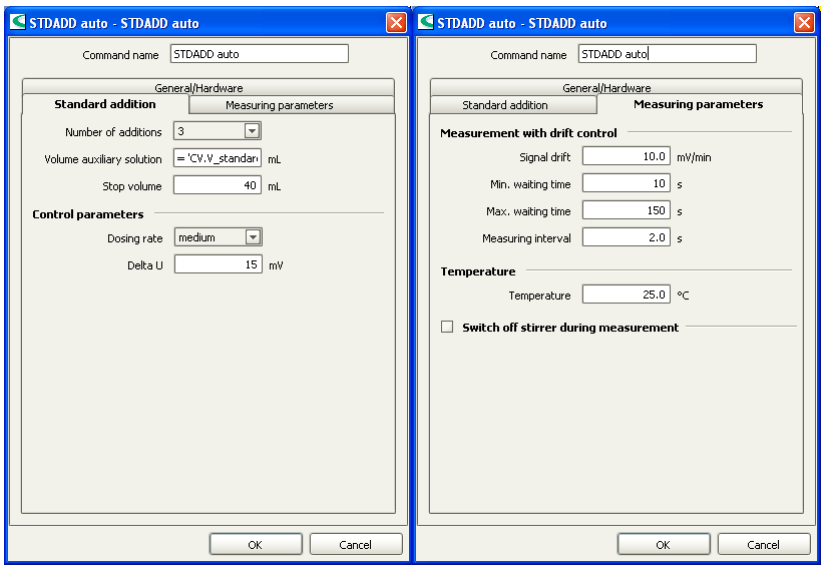
Calibration and storage of sensors

- Electrodes have to be checked regularly for correct function using a reference standard with known content
- When not used the CN- ISE is stored dry with the protection cap on
- There is no calibration necessary for this application

Analysis

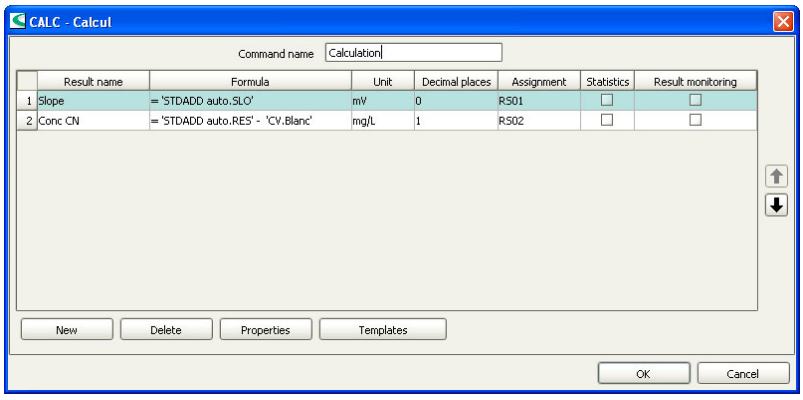
The determination of the cyanide content is based on the standard addition method using an ion-selective cyanide electrode (cyanide ISE). Prior to the first analysis the system is preconditioned using a method which flushes the tubing and the titration vessel. For the determination ProcessLab automatically transfers a defined amount of water sample into the titration vessel and then a Dosino takes an aliquot (10 mL) in a sample loop. The remaining sample is discharged and the titration vessel rinsed. Next 15 mL TISAB solution (NaOH, 0.1 mol/L) is transferred into the titration vessel as auxiliary reagent and then the sample is transferred from the loop back to the vessel. The cyanide content of the water sample is calculated by the standard addition method from the potential measurements performed after each addition of cyanide standard solution.

The measurements are carried out using the following parameter set:



Parameter set (may vary depending on the individual requirements)

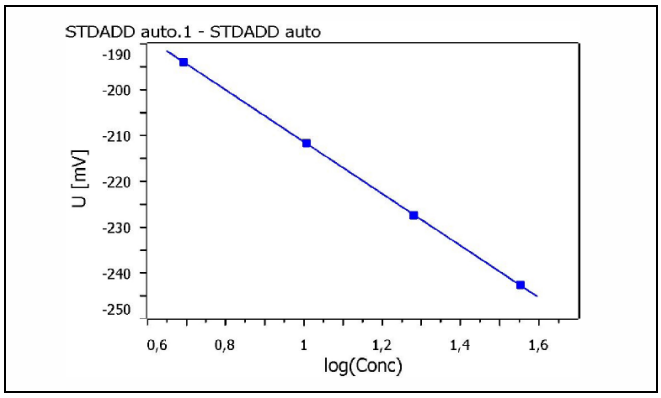
The amounts of cyanide contained in the treated process waters are normally so small that they are below the detection limit of the ion-selective cyanide electrode. To obtain a measuring solution whose cyanide content is in the usable linear region of the cyanide ISE, a known amount of cyanide standard solution is added to the original water sample (step 1). This means that at the start of the determination, the measuring solution contains cyanide ions of an unknown but very low concentration from the water sample as well as the exactly known amount of cyanide ions from the standard solution. After the determination, this known amount of cyanide ions added in step 1 has to be subtracted from the result obtained. The cyanide concentration of the measuring solution is determined by the standard addition method by adding further cyanide standard solutions (step 2).



Calculation example including the subtraction of the known amount of cyanide ions (CV.Blanc) added in step 1

Practical examples

An example of a standard addition curve is shown below together with the evaluation.



Plot of measuring results obtained with the standard additions

Slope ..... -56,6 mV
E (0) ..... -154,8 mV
F (-1) ..... 14,5 ppm
Variance 0,008

	dV [mL]	U [mV]	dU [mV]	t [s]
Sample		-194,0		97
Increment 1	0,312	-211,7	-17,7	165
Increment 2	0,552	-227,4	-15,7	253
Increment 3	1,077	-242,6	-15,2	416

Sample data

Origine Ech ..... blanc

Sample size ..... 10 mL

Results

slope ..... **-57 mV**

Conc CN ..... **14,5 mg/L**

Measured values and result of the standard addition method

In step 1, the cyanide content of the water sample is increased by 15.0 mg/L CN^- by the addition of standard solution. The determination of the content of this measuring solution by the standard addition method gave a result of 14.5 mg/L CN^-. This means that mathematically a value of -0.5 mg/L is obtained for the cyanide content of the water sample after subtracting the amount of cyanide ions added in step 1; the negative result is due to the measuring uncertainty.

Literature

Dr. Haider, Christian (2004) Monograph: «Electrodes in potentiometry» Metrohm No. 8.015.5013

Metrohm instructions for use: «Ion-selective electrodes (ISE)» No. 8.109.1476