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# Investigation on the interference of glyconitrile in cyanide determination according to ISO 14403

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# Abstract

Glyconitirle was identified as a positive interference during the cyanide determination following ISO 14403. Raising the pH during sample preparation leads to the decomposition of glyconitirle and to a false positive cyanide signal. The O/I Analytical CNSolution 3000 is a high throughput system with automatic sampling and easy handling, which severely suffers from the glyconitrile interference. A new method is set up und validated.

## Acknowledgment

I want to gratefully thank Dr. Helmar Wiltsche, who made it possible to realize this work. Thank you for your continuous interest and helpful advice.

I also have to thank my family for the unconditional support.

# 1. Introduction

Cyanide is a well-known **toxic compound** with severe effects on humans and the environment. A dose of **1mg per kg body weight** can already be lethal for humans, because the cyanide ion is directly inhibiting the cellular respiration (cytochrome oxidase).[1] It is frequently found in industrial as well as in municipal wastewaters, and therefore this compound is strictly regulated by public authorities. The limits for the drinking water content in the US and the EU are 0.2mg/L and 0.05mg/L, respectively.[2] Cyanide can occur in **various species**, which have different toxicities. This is primarily caused by the stability of the compounds that are formed from cyanide and the large spectrum of other substances. Two cyanide-containing fractions are distinguished in literature:

**WAD cyanide – Weak Acid Dissociable cyanide[2]**

This group of cyanides contains the most poisonous species. It consists of the **free cyanides**, which are hydrocyanic acid (HCN) and the cyanide ion ($CN^-$). Further, the **weak cyano-complexes** of zinc, copper, cadmium, mercury, nickel and silver belong to this class[3]. All this compounds have in common, that they can release cyanide at **pH 4**. Other frequently used terms with the same meaning are **available** and **easily released cyanide**.

**Total cyanide[2,4]**

Some cyanide containing compounds are rather stable and therefore have a lower toxicity. This especially applies to **organic cyanides** and **strong cyano-complexes** (of e.g. iron, cobalt, gold and platinum). The total cyanide is the sum of these und the WAD cyanides.

Because the fraction of the WAD cyanides has the highest impact on the environment, its determination is very important. Many decisions regarding the process management and wastewater treatment do directly rely on accurate analysis results. The aim of this work is to study interferences on methods used for the determination of WAD cyanides in order to ensure, that the analysis can be done exactly and without false detection of cyanides that are not part of the WAD fraction.

# 2. Methods

Due to the importance of WAD cyanides several regulative bodies provide procedures for the determination of this parameter. Two norms will be discussed in this chapter.

## 2.1. Description of ÖNORM M 6285[4]

**Aim/general**

This method contains procedures for the determination of **WAD-** and **total cyanide** from urban and industrial wastewaters. This work took a closer look on the analysis of free cyanide. It is performed by **acidic release** of HCN from the matrix, **absorption in alkaline solution** and **photometric quantification** by the pyridine/barbituric acid method. This method is regarded as the **reference technique** for the determination of WAD cyanide. This method is suitable for samples containing between 0.02mg/L and 0.25mg/L WAD cyanide.

**Apparatus and procedure**

If samples are **not analyzed immediately** after collection, 5mL sodium hydroxide (5M), 10mL phenolphthalein (0.03g phenolphthalein in 90mL ethanol and 10mL trichloromethane) and 5mL tin(II)chloride solution (50g $SnCl_2$*$2H_2O$ dissolved in 40mL 1M HCl; filled up with DI water to 100mL) have to be added per liter. The pH has to be adjusted to 8 with 1M NaOH solution, before 10 mL zinc/cadmium sulfate solution (100g $ZnSO_4$*$7H_2O$, 100g $3CdSO_4$*$8H_2O$ in 1000mL DI water) are added. Samples should be kept in a cool and dark place.

For the **release** and **absorption** of hydrocyanic acid, 10mL zinc/cadmium sulfate (see above), 10mL EDTA (100g ethylenediaminetetraacetic acid dissolved in 940mL DI water) and 50 mL buffer solution (80g potassium hydrogen phthalate dissolved in 920mL DI water), 0.3g zinc dust (>98% of particels <62µm) and 100mL of fresh or stabilized wastewater have to added to a round bottom flask. After adjusting the pH to 3.9±0.1 with 1M HCl or 1M NaOH, the apparatus has to be closed immediately. (This part was done differently in this work, because it is not practicable in every day routine analysis of multiple samples. Following the common practice in the industry, sample and reagents are mixed in a beaker. Also, the pH adjustment is done before the

transfer to the release and absorption apparatus.) The absorption vessel has to be filled with 10 mL of 1M NaOH solution before the air throughput is set to 30 to 60 L/h. After four hours, the extraction is complete.

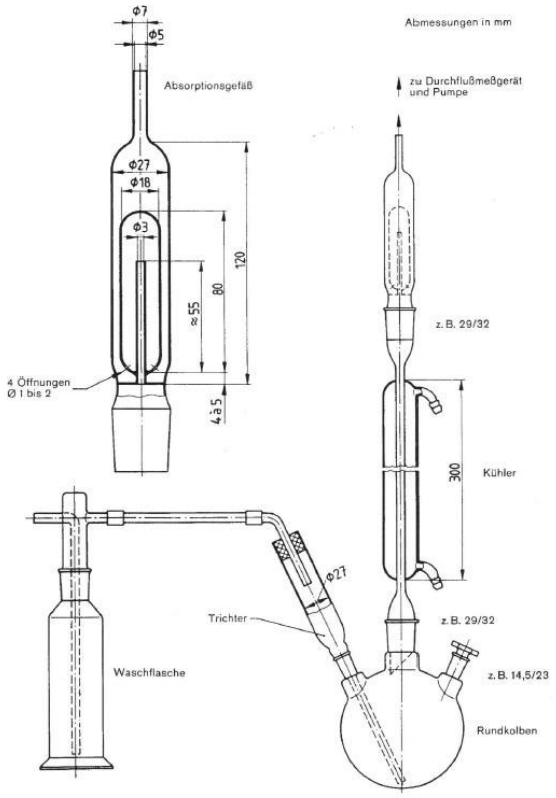



*Figure 1: Apparatus for the release and absorption of WAD cyanide[4]*

In the last step, the amount of absorbed cyanide is determined **photometrically** by the **pyridine/barbituric acid method**. Therefore the 10mL absorption solution has to be transferred to a 25mL volumetric flask, which is then made up to volume. 10mL of this solution is pipetted to another 25mL volumetric flask. Then 2mL buffer (pH 5,4; 5g NaOH; 11.8g succinic acid filled up to 100mL with DI water), 4mL HCl (1M) and 1mL chloramine-T solution (N-chloro 4-methylbenzenesulfonamide sodium trihydrate filled up to 50mL with DI water) are added. The flask is then closed and left for five minutes. 3mL of the pyridine/barbituric acid reagent (3g barbituric acid, 15mL pyridine, 3mL HCl 1.12 g/mL will up to 50mL with DI water) have to be added to start the colorimetric reaction. The measurement should be done after 20±5 minutes in 10mm cuvettes at 580nm.

**Analytical performance**

According to ÖNORM M 6258, the coefficient of variation found in a round robin test was **28%** for stabilized samples. During this work, **poor reproducibility** over the whole concentration range could be observed too. One reason may be the complex procedure, which provides many possibilities for the loss of analyte. As described later, especially the pH adjustment to low values can cause significant problems. In the literature, some of these problems were also described for similar methods.[5]

**Advantages and disadvantages**

This method can be done with **ordinary laboratory equipment** at relative **low cost**. However, Operators need to be trained before carrying out this procedure for the first time to minimize errors.

A significant disadvantage is the **long duration** of the **analysis** of at least 5 hours. This results in a very long response time, which is not desirable in wastewater management. The workload can also **not exceed 10 samples** per shift and operator, because all measurements have to start at the same time and need an individual apparatus.

## 2.2. Description of EN ISO 14403[6] (OIA-1677[3]) and OI Analytical CNSolution 3000

**Aim/general**

The CNSolution 3000 (OI Analytical, United States) is a commercial instrument performing analysis according to the **USEPA method OIA-1677**. This method is consistent to EN ISO 14403, which regulates the characteristics of flow injection analysis with gas diffusion and amperometric detection for the determination of WAD cyanide.

It is a high throughput system with automatic sampling and easy handling. It shows **sufficient reproducibility** (see section 18.3 of OIA-1677[3]) and has a **wide operational range** (0.005 to 0.2 mg/L).

**EN ISO 14403[6]**

EN ISO 14403 regulates the determination of total and free cyanide using continuous flow analysis (CFA). A wide variety of samples is possible with a typical limit of detection of 3µg/L in an operational range of 10µg/L up to 100µg/L. Known interferences are oxidants (e.g. chlorine), sulfides, aldehydes and thiocyanate.

For the determination of total cyanide, a UV lamp is necessary to degrade complex bound cyanide. All following steps are the same for both total and free cyanides and are described below.

Part of this standard is also the regulation of CFA using continuous distillation.

**CNSolution 3000 and OIA-1677[3]**

This method does not need any complex preparation steps. The pH of samples has to be raised to 11.0±0.1 with 1M sodium hydroxide solution and solid components of the samples have to be removed by filtration. To ensure a stable instrument detector baseline, it is necessary to switch on the pump at least 30 minutes before the measurement starts.

Figure 2 shows the flow diagram of the OI Analytical CNSolution 3000. It is a modular system with four main components located in one housing. In addition, an OI Analytical 120-position autosampler is used. The PC based software “Winflow 4.0” is used to control the instrument and for the interpretation of the recorded data.

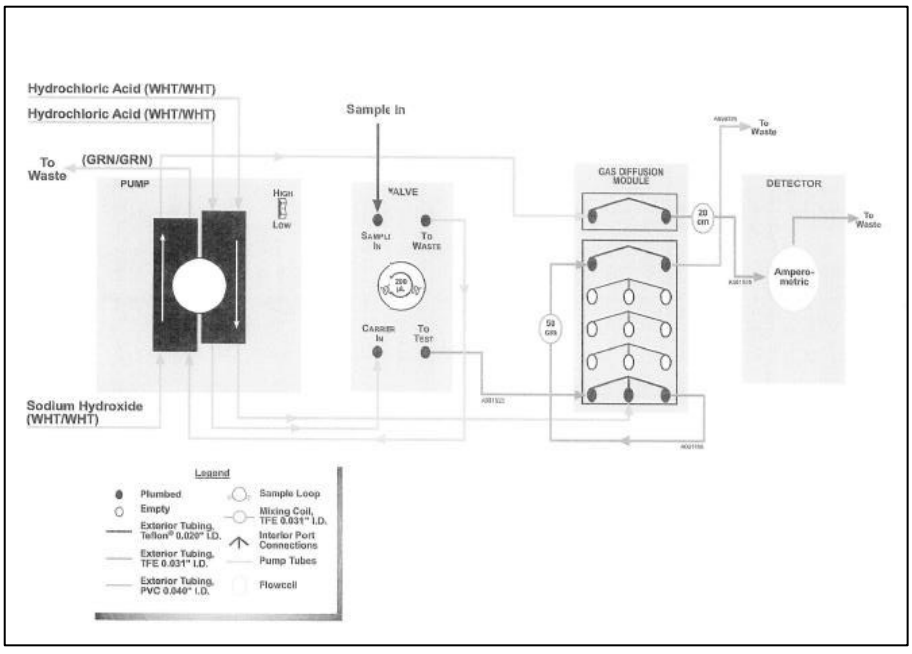



*Figure 2: flow diagram of the CNSolution 3000 device for the measurement of WAD cyanide[3]*

The **peristaltic pump** (Figure 3) has four channels. One transports 0.1M sodiumhydroxide solution, two contain 0.1M hydrochloric acid and the last one is connected to the “to waste” exit of the **six-port-valve** (Figure 4). This part is the second module in Figure 2 and does the sample switching. It has two inlets, one for the incoming stream from the autosampler and the other for the 0.1M HCl carrier stream. Two of the ports are connected to a 100µL sample loop and the last two ports are used as an exit to the waste container and the further analysis system.

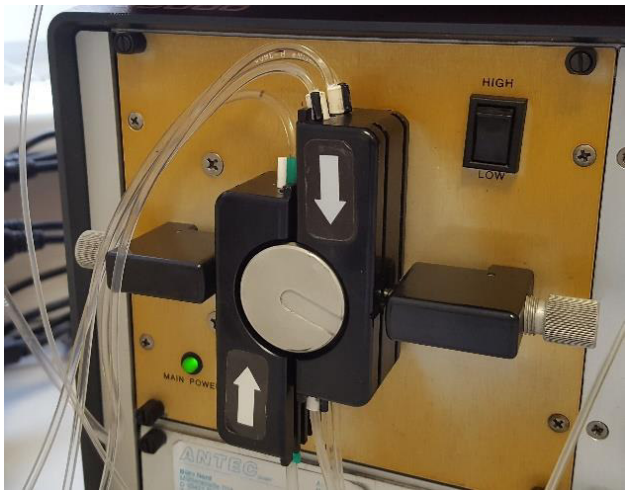


*Figure 3: Peristaltic pump*


The **six-port-valve** consists of two plates. One contains six ports that are connected in pairs through cannels located on the other plate. This results in two operational states, which can be selected by twisting of the plats against each other. During “loading”, the sample coming from the autosampler is flushed through the sample loop to the waste container. If the valve is switched to “inject”, the carrier stream will transport the sample from the sample loop into the “to test” outlet.

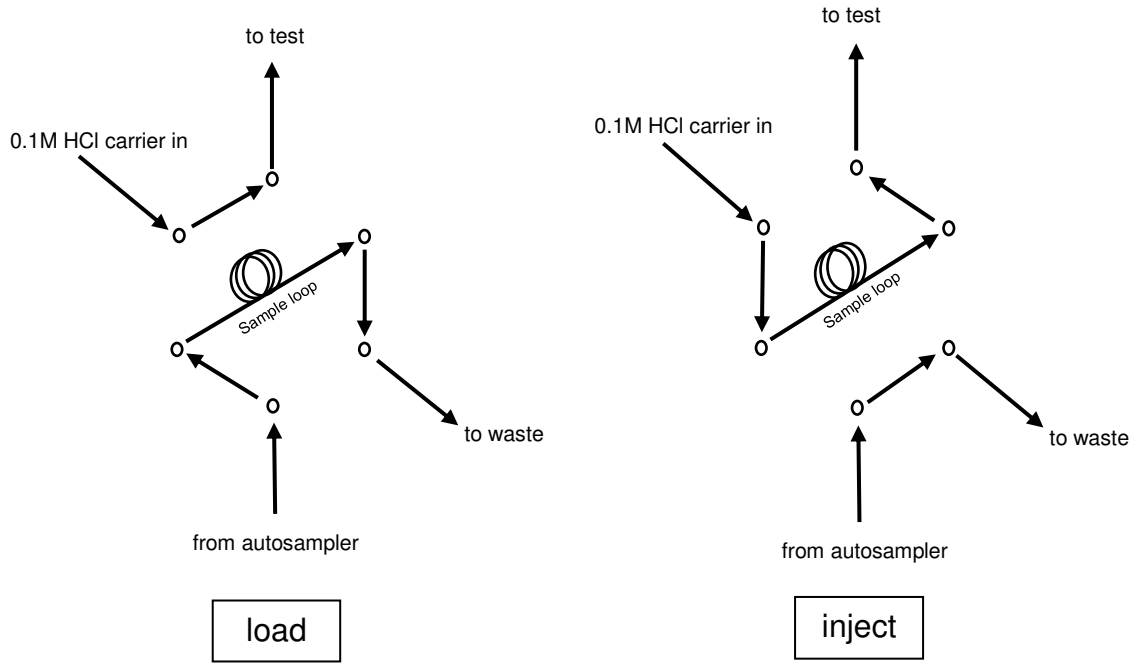



*Figure 5: Operation states of a six-way-valve*

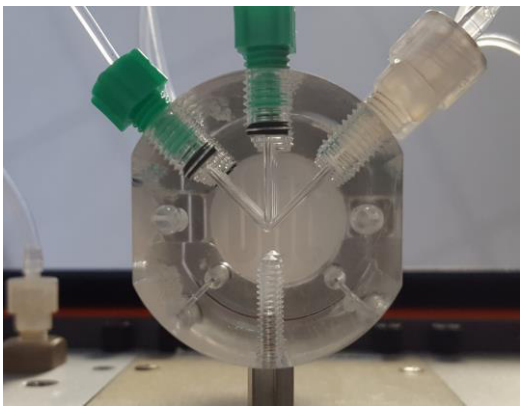


*Figure 6: Mixing chamber*

100µL sample are now transported by the continuous flow system to the **mixing chamber** (Figure 6) where it is acidified by the second 0.1M HCl stream. Investigations during this work showed, that the flow rate of the sample and the HCl are similar before mixing and that the resulting pH is close to 1 for samples up to pH 12.

The formed hydrocyanic acid is now transported to the **gas diffusion chamber** (Figure 7), where it is permeating through a hydrophobic polypropylen membrane into the 0.1M NaOH stream. In the alkaline medium, the cyanide ion is formed again.

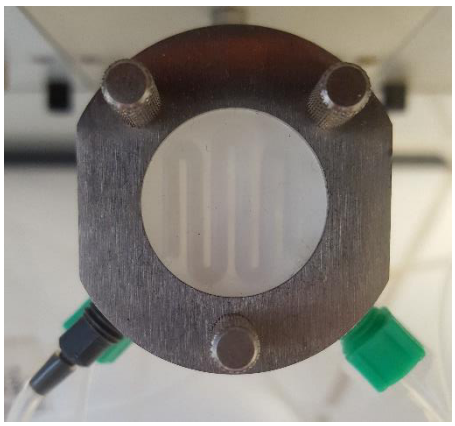


*Figure 7: Gas diffusion chamber, top down perspective*

The amperometrical detection takes place in the **detector module** (Figure 8). It is a three-electrode assembly consisting of a silver working electrode, a

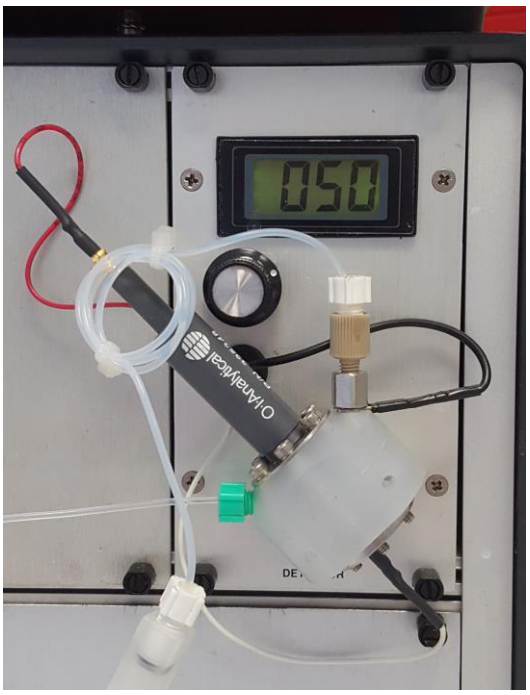



*Figure 8: Detector module*

silver/silver chloride reference electrode and a flow through stainless steel counter electrode. The applied potential is 0.050V.

The peak current is used for the calculation of the concentration, which is done automatically by the software “Winflow 4.0” using a two-point calibration.

In Figure 9 all of these parts/modules can be seen together. The above described mixing and the diffusion chamber are both located on the same module (third from the left). Additional pictures con be found in the appendix (section

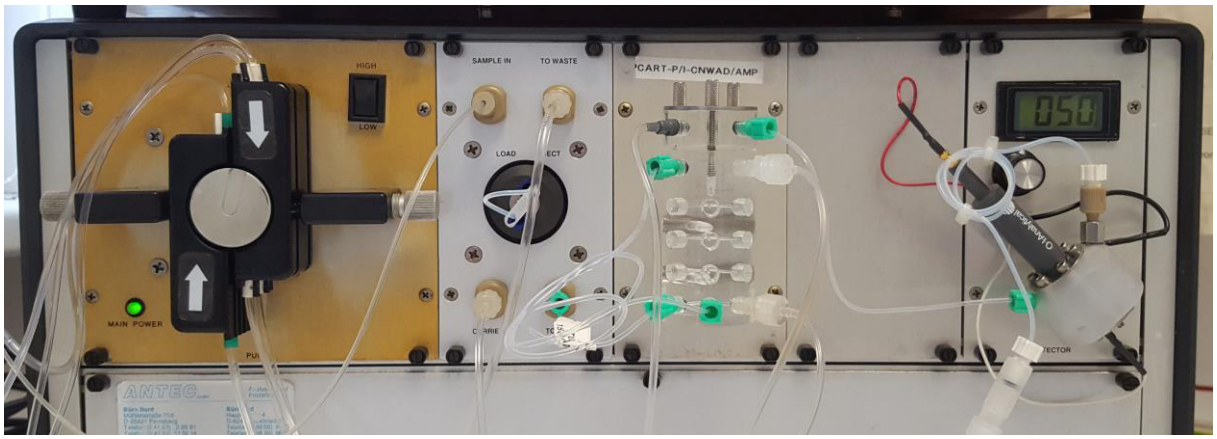



*Figure 9: Complete setup of the OI Analytical CNSolution 3000*

**Analytical performance**

Nine laboratories participated in a validation study to show the reliability of this method[3]. Various typical matrices were tested, but only the results for DI water with 0,01M NaOH (pH 12) should be mentioned here.

*Table 1: Results of an interlaboratory validation study showing the reliability of OIA-1677*

| Sample | $CN^-$ Concentration [mg/L] | Average Recovery [%] | Rel. Standard Deviation [%] |
|---|---|---|---|
| **DI water 0,01M; NaOH (pH 12)** | 0.1 | 108 | 4.0 |
| **DI water 0,01M; NaOH (pH 12)** | 0.2 | 101 | 8.0 |
| **DI water 0,01M; NaOH (pH 12)** | 10 | 103 | 2.0 |

During this work, the CNSolution 3000 showed lower standard deviations in most cases (for examples see appendix section 11.2.). In the comparison of different methods, a **relative standard deviation of 2%** was seen as a representative value for the calibration at 0.2mg/l $CN^-$.

**Advantages and disadvantages**

A very clear advantage of this method is the **very short analysis duration**. The calibration of the instrument takes approximately 12min and the triple determination of one sample can be done in about 6min. The total time necessary for a set of five samples is less than 45min. Along with the necessary baseline stabilization before the measurement and the sample preparation, the total time between the unexpected arrival of a sample at the lab and the complete results is less than one and a half hour. In comparison to the ÖNORM M 6258[4], the CNSolution 3000 has a **more complex setup**, which may fail at some point. In that case, troubleshooting should not be any problem, because of the easily accessible components.

**Additional Information**

During this work, the pH was not always set to 11 during the sample preparation. If the standard method was changed, it was always noted in the experiment description.

## 2.3. Comparison

Additionally to the already mentioned aspects, the **analytical performance** and the **measurement duration** are clear advantages of the CNSolution 3000 following OIA-1677 over the ÖNORM M 6258. In everyday use, it is a very practical system, which is capable of handling a **large variety of wastewater samples** and has a **wider operating range**.

Nevertheless, every laboratory using this system should also be capable of performing analysis according to the ÖNORM method. It is an easy and reasonable way **to confirm results** and **bridge device malfunctions**.

# 3. Problem description

During daily routine analysis of waste water samples, the CNSolution 3000 following OIA-1677 showed **systematically higher** results than the reference method ÖNORM M 6258[4]. The measured values were nearly **twice as high** and this behavior was observed over a long period. Device malfunction or an analytical error could be excluded by careful investigation of each step. It was also noticed, that **increasing the pH value** during sample preparation **raised the difference in the obtained values** between the two methods.

Because of this issue, the legal emission limit of 0.1mg/L WAD cyanide can be easily exceeded while the actual concentration in wastewater is much lower. Therefore, the accurate quantification of the WAD cyanide concentration is crucial, because it is directly linked to decisions regarding process management and wastewater treatment.

# 4. First investigations with known interferences

A set of initial experiments was performed to gain insights into the factors that might affect the differences between the two norm methods for determining WAD cyanide. Some of the experiments were already conducted during the setup of the OIA-1677[3] method, but they were redone in this work to ensure reproducible and consistent results.

The following list is not in a chronological order. They were done at different times and do not refer to each other.

## 4.1. Dissociation of Non-WAD cyanide complexes

The aim of this experiment was to quantify the amount of cyanide released from strong cyanide complexes of metals such as iron or cobalt.

Both cyanide complexes of **iron** were investigated during this work. They could not be synthesized in situ and therefore have to be dissolved from solid state (p.a. grade). Investigations were done with and without the presence of a known amount of free cyanide. The amount of added **hexacyanoferrate (II)** and **(III)** is given in mg/L of CN bound in the complex. This concentration would only be encountered, if a total cyanide analysis would have been performed. The investigated concentration range was rather wide, because the effect of these complexes is only noticeable at high levels. Following tables contain the measurement results for potassium hexacyanoferrat (II) and (III) from triple determinations.

*Table 2: Interference study with potassium hexacyanoferrate (II);*
*Values for 100mg/L were eliminated because of high RSD; n=3; SD not shown for clarity;*

| mg/L $CN^-$ from $K_4[Fe(CN)_6]$ | Signal [pA] | c($CN^-$) [mg/L] | RSD [%] | Recovery [%] |
|---|---|---|---|---|
| **0.5** | 1504 | 0.005 | 2.8 | 1 |
| **1** | 3061 | 0.009 | 2.1 | 0.9 |
| **2** | 5797 | 0.018 | 2.1 | 0.9 |
| **25** | 60825 | 0.188 | 1.4 | 0.8 |
| ~~**100**~~ | ~~32594~~ | ~~0.101~~ | ~~4.9~~ | ~~0.1~~ |

The results listed in Table 2 show, that the effect of strongly-bound cyanide on the determination of WAD cyanide is negliable. Less than 1% of cyanide added as strongly-bound cyanide was detected by the used method. Therefore, potassium hexacyanoferrate (II) cannot cause positive interference. The result of the 100 mg/L sample was not taken into account, because the very high concentration may distorts the measured value.

*Table 3: Interference study with potassium hexacyanoferrate (II) in the presence of free cyanide; n=3; SD not shown for clarity;*

| mg/L $CN^-$ from $K_4[Fe(CN)_6]$ + 0.1 mg/l $CN^-$ | Signal [pA] | c($CN^-$) [mg/L] | RSD [%] |
|---|---|---|---|
| **0.5** | 28377 | 0.088 | 0.5 |
| **1** | 20898 | 0.065 | 0.9 |
| **2** | 34250 | 0.106 | 2.2 |
| **25** | 81826 | 0.253 | 2.2 |

In the presence of free cyanide, it was also noticeable that only high concentrations of hexacyanoferrate (II) resulted in significantly higher cyanide values. However, at low hexacyanoferrate (II) concentrations unexpectedly low spike recoveries of only 65 % were encountered. The reason for this is unknown and further experiments would be needed to clarify this point.

*Table 4: Interference study with potassium hexacyanoferrate (III) ; n=3; SD not shown for clarity;*

| mg/L $CN^-$ from $K_3[Fe(CN)_6]$ | Signal [pA] | c($CN^-$) [mg/L] | RSD [%] | Recovery [%] |
|---|---|---|---|---|
| **0,5** | 974 | 0.003 | 3.6 | 0.6 |
| **1** | 1949 | 0.006 | 3.5 | 0.6 |
| **2** | 3476 | 0.010 | 0.8 | 0.5 |
| **25** | 28453 | 0.086 | 2.5 | 0.3 |
| **40** | 16748 | 0.052 | n.a. | 0.1 |
| **60** | 23626 | 0.073 | n.a. | 0.1 |
| **80** | 32040 | 0.099 | n.a. | 0.1 |
| **100** | 38792 | 0.117 | 4 | 0.1 |

*Table 5: Interference study with potassium hexacyanoferrate (III) in the presence of free cyanide; n=3; SD not shown for clarity;*

| mg/L $CN^-$ from $K_3[Fe(CN)_6]$ + 0.1 mg/L $CN^-$ | Signal [pA] | c($CN^-$) [mg/L] | RSD [%] |
|---|---|---|---|
| **0,5** | 35027 | 0.106 | 0.2 |
| **1** | 34891 | 0.105 | 0.6 |
| **2** | 37544 | 0.113 | 0.8 |
| **25** | 68136 | 0.205 | 4.3 |

Potassium hexacyanoferrate (III) did not cause any interferences at concentrations typically encountered in waste water samples. The cyanide recoveries always stayed below **1%**.

**Cobalt** forms another strong cyano-complex, which was investigated. For this test, solutions of cobalt and cyanide are mixed one hour before the analysis. The used amount of Cobalt is measured in molar equivalents in regard to the initial concentration of cyanide (0.2 mg/L).

*Table 6: Interference study with cobalt*

| Equivalents of $Co^{2+}$ | Signal [pA] | c($CN^-$) [mg/L] | Recovery [%] |
|---|---|---|---|
| **+0.5 eq.** | 8.190 | 0.024 | 12 |
| **+1 eq.** | 5.553 | 0.016 | 8 |
| **+2 eq.** | 4.701 | 0.014 | 7 |
| **+2 eq.** | 5.772 | 0.017 | 8.5 |

The result of this experiment was not clear. Either the cyano-complex was not formed completely or a portion of the cobalt complex is decomposed and the released cyande could be detected. Either way, the recovery rates were around 10%.

**Conclusion:**

Hexacyanoferrates were found to cause a positive interference on the WAD cyanides at very high concentrations. However, typical samples do not contain 100 to 1000 times more total than WAD cyanide. Therefore, it is **very unlikely** that these complexes caused the difference between ÖNORM 6285 and OIA-1677. This also holds true for cyanocomplexes of cobalt.

## 4.2. Thiocyanate and Cyanate

The potential cyanide release of **thiocyanate** and **cyanate** was also investigated. Even though it was considered unlikely, that these compounds caused the observed differences between the two norm methods.

Synthetic standards are produced by adding solid KSCN and KCNO to DI water. The concentrations were calculated in mg/L $CN^-$, which theoretically could be released.

The following tables show the results of this experiment:

*Table 7: Interference study: Thiocyanate; n=3; SD not shown for clarity;*

| mg/L $CN^-$ from KSCN | Signal [pA] | c(CN) [mg/L] |
|---|---|---|
| **0.5** | 65 | <LOD |
| **1** | 266 | <LOD |
| **2** | 365 | <LOD |
| **25** | 500 | <LOD |
| **100** | 818 | 0.003 |

*Table 8: Interference study: Cyanate; n=3;*

| mg/L CN- from KCNO | Signal [pA] | c(CN) [mg/L] |
|---|---|---|
| **0.5** | -129 | <LOD |
| **1** | -55 | <LOD |
| **2** | 104 | <LOD |
| **25** | 188 | <LOD |
| **100** | 187 | <LOD |

**Conclusion:**

Thiocyanate and isocyanate **did not interfere** with the determination of cyanide using the CNSolution 3000.

## 4.3. Flocculation agent[7]

Some wastewater treatment procedures contain the application of **flocculation agents** such as **VTA EA 83**. It is an anionic polyacrylamide compound, which is used to accelerate the solid – liquid separation during sedimentation and flotation. It was also suspected to influence the cyanide determination by either releasing cyanide ion or interfering with the electrochemical detector (similar to sulphide, see section 4.5)

Two sets of standards were measured during this experiment. In the first set of experiments the amount of flocculation agent remained constant, while the cyanide concentration was varied. In the second set, the cyanide concentration remained constant, while the flocculation agent was varied.

The following tables show the results in detail.

*Table 9: Interference study flocculation agent (floc.a.), cyanide concentration variation; n=3; SD not shown for clarity;*

| Target c($CN^-$) [mg/L] | c(floc. a.) [mg/L] | Signal [pA] | Measured c(CN) [mg/L] | Difference [%] |
|---|---|---|---|---|
| **0.01** | 1.5 | 4323 | 0.012 | 23 |
| **0.02** | 1.5 | 8021 | 0.023 | 14 |
| **0.05** | 1.5 | 17683 | 0.050 | 1 |
| **0.10** | 1.5 | 33416 | 0.095 | -5 |
| **0.15** | 1.5 | 49458 | 0.141 | -6 |
| **0.20** | 1.5 | 65800 | 0.188 | -6 |
| **2.00** | 1.5 | 646058 | 1.843 | -8 |

*Table 10: Interference study flocculation agent, constant cyanide concentration; n=3; SD not shown for clarity;*

| Target c($CN^-$) [mg/L] | c(floc. a.) [mg/L] | Signal [pA] | Measured c(CN) [mg/L] | Difference [%] |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| **0.2** | 0.5 | 68242 | 0.188 | -6 |
| **0.2** | 1 | 67541 | 0.186 | -7 |
| **0.2** | 1.5 | 66275 | 0.183 | -9 |
| **0.2** | 2 | 67358 | 0.185 | -7 |
| **0.2** | 5 | 67247 | 0.185 | -7 |

**Conclusion**: The presence of flocculation agent **did not increase** the measured cyanide concentration. However, spike recoveries in the range of 91 – 94% indicate a potential influence of the flocculation agent on the electrochemical cyanide determination. These low results might also be caused by the production procedure of the samples and the instrument inaccuracy.

## 4.4. Acetonitrile

**Acetonitrile** was also investigated during this work, because it is a potential component of wastewater, too.

It was tested in multiple concentrations at pH 8.3 and 11 with the CNSolution 3000. One sample was also analyzed according to the ÖNORM M 6258 at a release pH of 3.2 and 3.9.

The Acetonitrile concentration in the following table refers to the maximum releasable amount of cyanide. For example, 0.01 mg/L cyanide can be released from a standard containing 0.014 mg/L acetonitrile.

*Table 11: Interference study acetonitrile; n=3*

| Acetonitrile | CNSoultion 3000 | | ÖNORM M 6258 | |
|---|---|---|---|---|
| [in mg/L contained $CN^-$] | ~ pH 8.3 [mg/L $CN^-$] | pH 11 [mg/L $CN^-$] | ~ pH 3.2 [mg/L $CN^-$] | pH 3.9 [mg/L $CN^-$] |
| **0.01** | <LOD | <LOD | | |
| **0.02** | <LOD | <LOD | | |
| **0.05** | <LOD | <LOD | | |
| **0.1** | <LOD | <LOD | | |
| **0.15** | <LOD | <LOD | <LOD | <LOD |
| **0.2** | <LOD | <LOD | | |

**Conclusion:**

In the investigated concentration range, **no effect of acetonitrile on the determination of WAD cyanide** was observed.

## 4.5. Sulfide

According to OIA-1677[3] and literature on comparable techniques[5], sulfide is the **most frequently mentioned positive interference**. Like cyanide, it is able to pass a hydrophobic membrane from the acidic to the alkaline side ($H_2S$ is hydrophobic) and it leads to a similar signal at the detector as cyanide.

Following OIA-1677, water samples containing sulfide should be treated with lead carbonate to form insoluble lead sulfide. In this form, sulfur does not cause any more problems if the precipitated PbS and the excess of $PbCO_3$ is filtered off immediately (see below).

According to experienced lab staff, this method works well in most cases. Sometimes however, the positive interference could not be eliminated. This phenomenon should be investigated via the following experiment.

**Lead carbonate treatment of wastewater samples**

Cyanide in wastewater samples was quantified with the CNSolution 3000 at pH values from 10.5 to 12.5 with and without the addition of $PbCO_3$. Additionally, the results were compared to values from the ÖNORM method and the separately performed routine

method (also done with CNSolution 3000). Additionally the sulfide concentration was determined spectrophotometrically.
The aim of this experiment was to investigate if the removal of sulfide has any influence on the pH dependence of the measured signal.

**Procedure:**
Five beakers were filled with approximately 80ml of the same sample. After the pH value was adjusted to 10.0, 10.5, 11.0, 11.5 and 12.0 with 1M NaOH, the first measurement with the CNSolution 3000 was conducted. To remove sulfide from the samples, a small amount (one spatula tip; ~0.1g) of $PbCO_3$ was added to the samples. This addition needs to be done immediately before the measurement, because thiocyanate might be formed from the precipitated lead sulfide and cyanide. During this experiment, the stirring time was about 1 minute.

**Evaluation:**
For two weeks, samples from three different origins were analyzed daily in four different ways (CNSolution 3000, CNSolution 3000 daily routine analysis, “Skalar” continuous measurement device, ÖNORM M 6285). A large set of data was generated, but only limited knowledge could be extracted from it. Some measurements were discarded, because of failure during the analysis or statistical issues (e.g. high coefficient of variation). The remaining results had no uniform behavior. Some of them showed the same issues as observed during the routine analysis (see section 4.6). However, others represented the complete opposite.

**Conclusion:**
This investigation indicates a strong matrix dependent behavior of the $PbCO_3$ treatment that was not always able to eliminate the positive interference from sulfides or other matrix constituents. It was further considered likely, that **another component** in the matrix, also interfered with the cyanide determination leading to higher signals.
The influence of sulfide on the cyanide measurement needed in any case a more detailed investigation.

## 4.6. pH dependence of the positive interference

During earlier investigations on the positive interference of the sample matrix on the cyanide signal, a pH dependence of the measured signal was observed. The concentration increased with the pH value, which was adjusted during sample preparation. This was especially strange, because the sample is acidified with 0.1M HCl immediately after injection to the system. Therefore, the difference in pH in the diffusion camber can be expected to be very low. There was no plausible explanation how any of the known positive interferences (e.g. sulfide) can cause this behavior.

The following diagram shows an example for this pH dependence, done with spiked, real wastewater samples. It was measured during the sulfur investigations (see 4.5). The results are normalized to pH 11 to show the deviation from the measurement following ISO 14403.

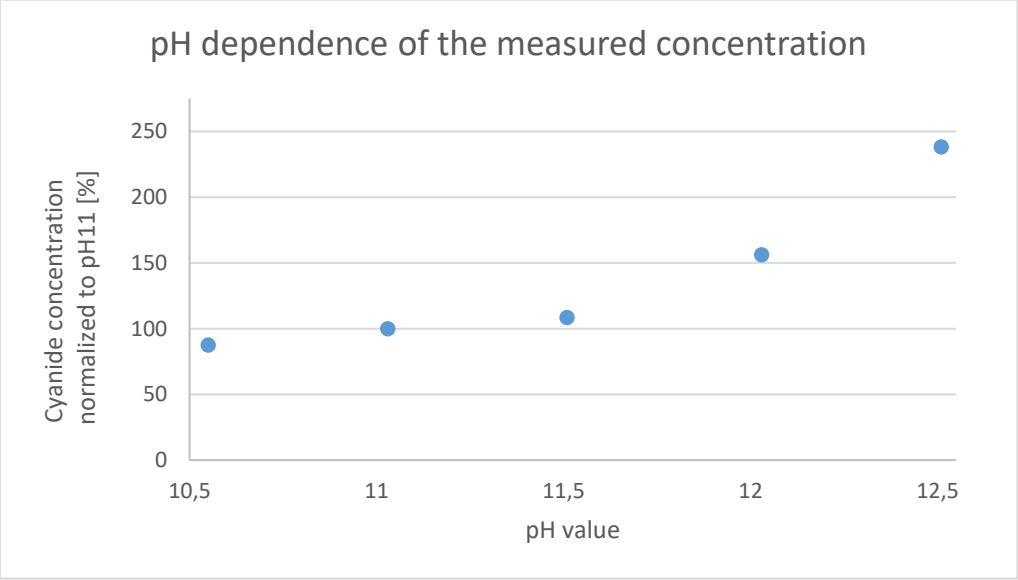



*Figure 10: pH dependence of the measured signal (CNSolution 3000); RSD in all cases smaller than 2%*

# 5. The Cyanohydrin-hypothesis

## 5.1. Introduction

Because some possible interferences had been eliminated (see chapter 4), a more general literature study was started. In the course of this, the **Degussa-treatment**[8] helped developing a new theory. It is a method developed to eliminate cyanide from washing waters of waste gas scrubbers.
The Degussa treatment is a staged procedure: At first, dust and other coarse particles are removed from the waste gas by cyclones and electro filters. Then, fine cleaning is done with gas scrubbers. The resulting wastewater contains cyanide or metal-cyanide-complexes, which are treated with formaldehyde at pH of about 7 (slightly acidic to alkaline). The reaction product is **glyconitrile $HOCH_2CN$**. In the next stage, it is hydrolyzed using $H_2O_2$ to obtain glycolic acid, which is easily **biodegradable**. Thereby, cyanide is removed from the wastewater.

**Formaldehyde** is a product of incomplete combustion, it could therefore also be present in gas scrubbing wastewaters. If the wastewater reaches **slightly alkaline** pH values, the **formation of glyconitrile** can be expected to take place to a certain extend as well. The concentration of cyanide is therefore lowered and glyconitrile potentially behaves different during the analysis according to ÖNROM 6285[4] and EN ISO 14403[6].

## 5.2. Literature research

This chapter presents the current status of **formaldehyde-interference** in the cyanide determination in literature. At first, a closer look is taken at ÖNORM M 6285, OIA 1677 and EN ISO 14403. Then a paper, which is focused especially on glyconitrile, is analyzed. In the last section, additional knowledge on the mechanism of glyconitrile formation is gathered and evaluated.
The consequences of all this information will be combined into the **Cyanohydrin-Hypothesis**, which is explained in section 5.3.

**Glyconitrile** (Figure 11[9]) is a compound formed by nucleophilic addition of formaldehyde and cyanide with the formula $HOCH_2CN$. It belongs to the substance class of **Cyanohydrines** (Figure 12[10]), which are obtained by the reaction of any aldehyde or ketone with cyanide. The functional region of the molecule consists of a **hydroxyl**- and a **cyano**-group, which are located on the same carbon atom.

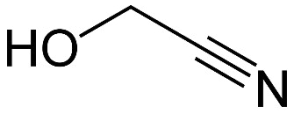



*Figure 11: Structure of Glyconitrile (cyanohydrin of formaldehyde[9]*

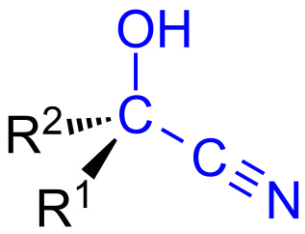



*Figure 12: Functional group of Cyanohydrins[10]*

### 5.2.1. A closer look at ÖNOR M 6285[4], EN ISO 14403[6] and OIA-1677[3]

After cyanohydrins and in particular glyconitrile had become the target of investigations, the methods ÖNOR M 6285, EN ISO 14403 and OIA-1677 were carefully reviewed.

**ÖNROM 6285**

In section 1 “Aim and area of application”, it is mentioned, that the presence of aldehydes and in particular formaldehyde can cause lowered measurement values.
In the course of the definition of different cyanides, (see 2. “Definitions”), it is indicated, that cyanohydrins are only partly determined as total cyanide and that nitriles in general are not part of the easily released cyanides.
However, it is also stated, that the behavior of cyanohydrin during the chemical fusion for the determination of total cyanide is not well understood.

**OIA-1677**

Aldehydes are listed as interferences (see section 8.5). The addition of ethylendiamine is suggested as a treatment method, but it is not described how this affects the measurement results. Further research on the mechanism is necessary.

**EN ISO 14403**

This method states, that organic cyanides should not be determined as free cyanide by this method.

**Conclusion:**

It is likely that aldehydes lower the cyanide concentration due to the formation of cyanohydrin. This compound seems to be instable at certain conditions (determination of total cyanide) and is measured as cyanide in this case.

### 5.2.2. Main literature

During an extensive literature search, only one paper covering matrix-induced interferences in the determination of cyanide had been found.[11] Unfortunately, the full text is in Japanese. Only the abstract and the labels of the figures are written in English. Nevertheless, it was very enlightening, because it linked the observed deviation between ÖNORM M 6285[4] and OIA 1677[3] with the presence of formaldehyde.

In this investigation, total cyanide is determined according to JIS K 0102[12], which is quite similar to the ÖNORM M 6285: Hydrogen cyanide is also released from the matrix and absorbed by a sodium hydroxide solution. The quantification is done spectrophotometrically with 4-pyridinecarboxylic acid-pyrazolone.

The authors believe that formaldehyde and cyanide contained in the samples react to form cyanohydrin. This results in lowered recoveries of total cyanide and a method is presented to avoid this. At first, the pH is raised to 12, which leads to **decomposition** of cyanohydrin back to cyanide and formaldehyde. To ensure no new cyanohydrin is formed during the analysis (at low pH during CN release), formaldehyde is eliminated with tetrahydroborat.

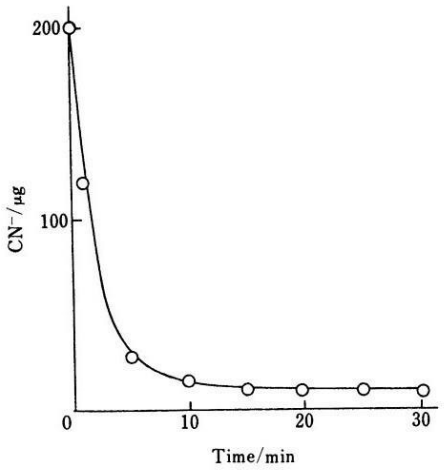



*Figure 13: Time dependent formation of cyanohydrin at pH 7 (200µg CN-; 300µg HCHO)[11]*

The first figure in this paper depicts the **time dependence** of the cyanohydrin formation. The reaction is done at pH 7 with a slight molar excess of formaldehyde. This shows that the reaction needs at least **10 minutes** to reach equilibrium. This is rather quick but it is only reached a conversion factor of about **95 percent**.

Figure 14 shows the **equilibrium concentration** of the decomposition reaction at different pH values. It starts at 95% cyanohydrin at pH 7, which represents exactly the conditions of Figure 13. At pH 13, approximately 25% cyanohydrin remain in the sample. At pH11 (measurement pH of the CNSolution 3000) about half of the cyanide is released.

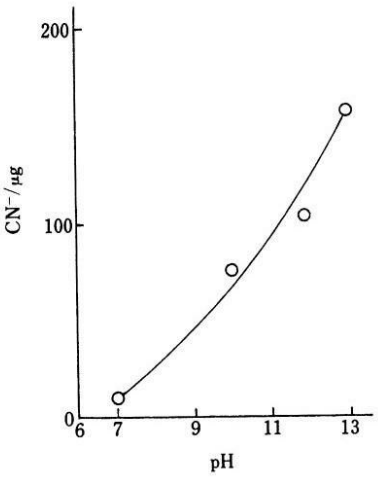



*Figure 14: pH dependence of cyanohydrin (CN-:200 µg; HCNO: 300µg[11]*

Figure 15 gives insight into the **pH-dependency** of the elimination reaction of formaldehyde with tetrahydroborane. At a pH of 12 and after a reaction time of 30 minutes, nearly all the cyanohydrin has been decomposed.

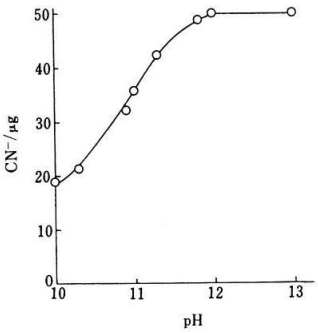



*Figure 15: Effect of pH on the elimination of formaledhyde (CN-:50µg; HCHO: 500µg; NaBH4: 0.3g;)[11]*

These three figures provide important information on the chemical behavior of the cyanide/formaldehyde/glyconitrile-system and are useful during the development of the **Cyanohydrin-Hypothesis** as explained later.

### 5.2.3. General Literature on Cyanohydrin

During the literature search, several publications treating the **formation reaction** of cyanohydrin were found. Most of them describe reactions for chemical synthesis, but their findings can be expected to also apply to wastewater matrices. The proposed mechanism is the **base catalyzed nucleophilic addition.**[13,14,15] Polar solvents like water are especially beneficial, because the carbonyl group of the cyanohydrin is activated by interactions with OH.[13] The equilibrium is not completely on the side of the products. The reaction is **reversible** and strongly **dependent on the pH.**[13,14] Although the reaction is base catalyzed, **hydrogen ions stabilize** the formed alkoxide.[13,16] Therefore a two-step mechanism is proposed: **1. Base catalysis 2. Acidic stabilization.**[13]

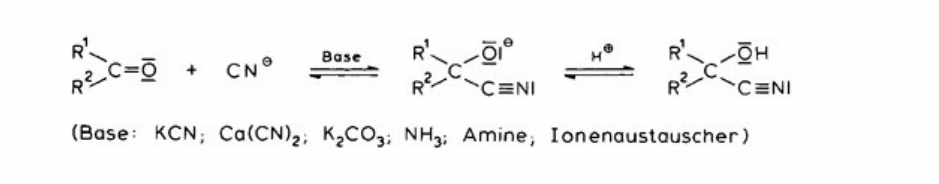



*Figure 16: Reaction mechanism cyanohydrin formation [13]*

The most stable products are formed by aldehydes, but the reaction will also take place with ketones.[5,13,14,16,17]

Only one publication deals with **cyanohydrin as an interference** in the analysis of cyanide using the CNSolution 3000.[17] Because in this case total cyanide is determined, cyanohydrins are seen as a negative interference. Ethylenediamin-treatment is the only suggested countermeasure, but it is claimed that this will only prevent additional formation of cyanohydrin. The recovery of cyanide from cyanohydrin is not possible.

Another issue observed during the cause of this master thesis is the rising cyanide concentration during storage. If samples are stabilized by raising the pH to 12 with sodium hydroxide, it seems reasonable to assume – based on the mechanism just discussed - that additional cyanide is formed.

## 5.3. Cyanohydrin-Hypothesis

In this section, all previously gained knowledge about cyanohydrins and in particular glyconitrile is merged into the **Cyanohydrin-Hypothesis**.

Cyanide and formaldehyde are both products of incomplete combustion and therefore both can be present in wastewaters side by side. These two species form cyanohydrin at a pH of 7 to 8 in an equilibrium reaction. The product can then be stabilized in a neutral or slightly acidic environment.

During the ÖNORM M 6258 analysis, the pH value is never raised above the original level of the sample. At a pH of 3.9 free cyanides are released to the gas phase, but glyconitrile remains in solution. In contrast, the sample preparation for the determination of available cyanides using the CNSolution 3000 includes adjusting the pH to 11 before the measurement. This leads to a shift of the reaction equilibrium to the side of cyanide and formaldehyde. As it is depicted in Figure 17, at pH values above the pKs of hydrocyanic acid the alcoholate of glyconitrile (pKs 16) is formed. This compound is less stable and therefore the reverse reaction is preferred.

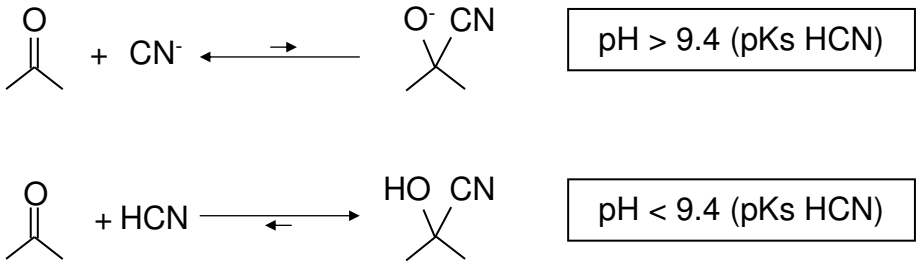



*Figure 17: Formation reaction equilibrium of glyconitrile*

At this point, it is important to note, that glyconitrile is not an interference in the classic sense. It is not a completely different substance like for example sulfide, which unintentionally leads to a signal at the detector. The decomposition of cyanohydrins causes a real increase of the cyanide concentration. However, cyanohydrin is per definition not part of the easily liberable cyanide fraction, because it cannot be released at a pH of 4[2]. Further, it is only partly determined as total cyanide during ÖNORM M 6258 analysis.

Because of this, it is reasonable to consider cyanohydrins as interferences during the determination of WAD cyanides. Approaches to eliminate their influence on the measurement are therefore seen as legitimate.

# 6. Investigations on the Cyanohydrin-Hypothesis

To prove and extend the knowledge on the properties of cyanohydrin, a series of experiments with synthetic standards was performed. Glyconitrile in the form of a ~55% solution in water with ~0.5% phosphoric acid as stabilizer was used, purchased from Sigma Aldrich (~577g/L; product #: 374768[18]; lot #: BCBF4937V; CAS-number 107-16-4). This solution was originally intended to be used in synthesis applications, therefore its concentration was not exactly known. This had to be accepted, because it was not possible to find a p.a. grade source for this compound. Further, a concentration measurement could not be performed, due to the lack of an appropriate analytical technique. The calculation of the dilution steps are based on 55-masspercentage glyconitrile. Lacking the knowledge of the exact concentration of glyconitrile is certainly unsatisfactory however, all experiments using this stock solutions will provide a general trend that is only biased with a constant factor.

## 6.1. pH-dependence of the formation reaction and the reverse reaction

It is known from the literature, that cyanohydrin is only stable in neutral to acidic solutions, which was also confirmed by the fact that the stock solutions were stabilized with acid. Examined important factor is certainly how alkaline pH values influences the equilibrium between glyconitrile and cyanide.

**Procedure**

Six standards with a concentration of ~0.44 mg/L glyconitrile were produced by a three-step dilution from the 55-masspercentage stock solution. In the case of complete degradation of glyconitrile, this would have resulted in a cyanide concentration of 0.2

mg/L. Before the measurement, the pH values of the standards were adjusted to 7, 8, 9, 10, 11 and 12 using sodium hydroxide. Then they were measured with the CNSolution 3000 as quickly as possible (<2min). The calibration was done at pH 12, following the standard measurement procedure.

**Results and Interpretation**

Glyconitrile showed the behavior expected from the literature. Up to the pKs of hydrocyanic acid (9.4), the measured cyanide concentration remained at a rather low level. At higher pH, the degradation of glyconitrile increased rapidly and reached 80% at pH 11.

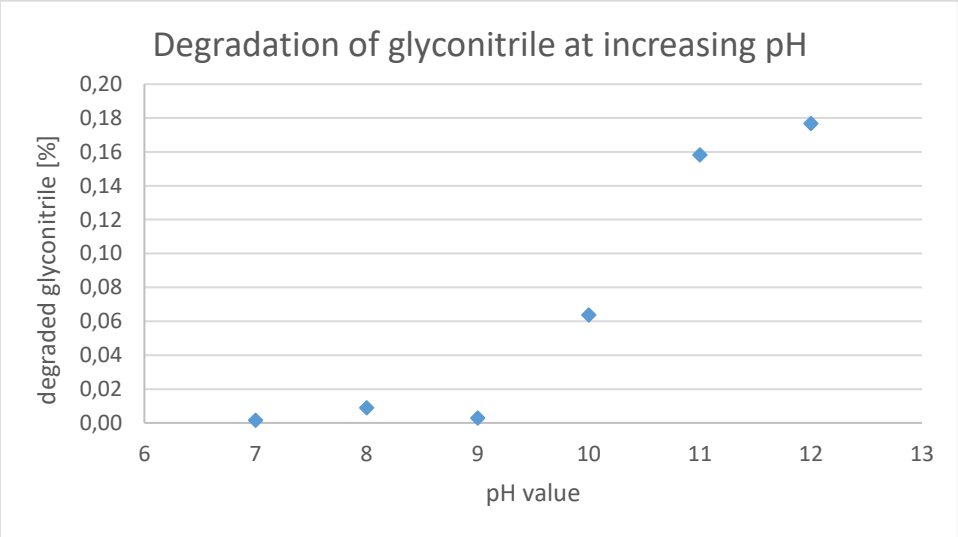



*Figure 18: Degradation of glyconitrile at increasing pH; SD smaller than dot*

At this point should be mentioned, that it was extensively investigated how the sample pH influences the measurement results of the CNSolution 3000 (see section 7.2). From these experiments it was concluded, that the pH adjustment during the sample preparation itself has no effect on the signal at the detector. That means that samples, which contain the same amount of cyanide, will always produce the same measurement result. This is at least valid in the range of pH 6 to pH 13. Effects that lead to corruption of the measured concentration will also be explained later.

## 6.2. Reaction time

The reaction time is also a very important factor for the glyconitrile degradation. From the literature is known[11], that the equilibrium of the formation reaction of gyconitrile is reached in about 10 minutes. This is also more or less the time between the adjustment of the pH during sample preparation and the actual analysis. However, it is unknown, what happens after this short period of time.

**Procedure**

Standards with a glyconitrile concentration of ~0.44 mg/L were repeatedly measured at pH 7, 11 and 12 over a duration of at least one hour.

**Results and Interpretation**

For these three pH values, no change in the amount of released cyanide could be observed (measurement results pH 7: 0.003mg/L CN; pH 11: 0.189±0.005; pH 12: 0.183±0.001; RSD <1%). As expected, the equilibrium had been reached before the start of the measurement. This is particularly important, because in case of a multi-sample-measurement, the residence time on the autosampler and therefore the time for the formation of cyanide differs significantly.

## 6.3. Comparison ÖNORM M 6258 – CNSolution 3000

The aim of this experiment was to compare the ÖNROM method to the one used with the CNSolution 3000 (at pH 7 and 11). The standards were produced using waste water, which contained only traces of cyanide by itself. This was done to include matrix effects in the experiment.
To proof the stability of glyconitrile during the ÖNORM M 6258 analysis, the stripped sample was further analyzed with the CNSolution 3000 at pH 11.

**Procedure**

The complete experiment was done with two identical standards with 0.1 mg/L cyanide and 0.22 mg/L glyconitrile (equals additional 0.1 mg/L cyanide at 100% decomposition; the maximal cyanide concentration assuming 100 % decomposition was consequently 0.2mg/L). As sample matrix, a typical exhaust gas scrubber wastewater was used instead of DI water.

CNSolution 3000: After the production, these standards had a pH close to 7. Hence, no adjusting was necessary for the measurement at pH 7. For pH 11, samples were adjusted with 1M sodium hydroxide solution.

ÖNORM M 6258: Another aliquote of the samples was immediately treated following the standard ÖNORM M 6285[4] procedure.

Furthermore, the residue of the ÖNORM analysis (content of the flask) was analyzed at pH 11 with the CNSolution 3000. To overcome the buffer capacity of the ÖNORM M 6258 reagents, 5M sodium hydroxide solution was necessary though the fine-adjustment of the pH was done with 1M NaOH.

**Results and Interpretation**

The following table contains the measurement results, which were corrected by the cyanide concentration of the matrix.

Higher cyanide levels were detected at pH 11 than at pH 7. This result is in accordance with the Cyanohydrin hypothesis. At higher pH, about half of glyconitrile was decomposed and detected as cyanide.

*Table 12: Comparison CNS3000 - ÖNROM M 6258 - Experimental results; n=3; SD not shown for clarity;*

| Method | Sample 1 corr. [mg/L CN] | Sample 2 corr. [mg/L CN] |
|---|---|---|
| **CNS 3000 pH 7** | 0.10 | 0.10 |
| **CNS 3000 pH 11** | 0.15 | 0.15 |
| **ÖNORM pH 3.9** | 0.07 | 0.08 |
| ***ÖNORM residue CNS 3000 pH 11*** | 0.07 | 0.07 |

The ÖNORM M 6258 analysis showed values below 0.1 mg/L, which could be explained by the complex procedure. The loss of some of cyanide in the cause of this

procedure can always happen and clearly contributes to the high variation coefficient of this method. For this experiment, it was important to prove, that glyconitrile is not released from the sample. When the residue of the cyanide release was analyzed with the CNSolution 3000, 0.7 mg/L cyanide could be found. This means that nearly all of the bound cyanide remained as such, because it is known from earlier experiments that only 80% of the glyconitrile will degrade at pH 11.

## 6.4. Conclusion

From the presented experiments using synthetic glyconitrile standards, the previously proposed cyanohydrin-hypothesis could be **confirmed** and additional insight on the properties of this substance was gained.

It was observed, that the pKs of hydrocyanic acid is clearly reflected in the equilibrium between glyconitrile and free cyanide. Because of this, measurements at pH 11 will not only quantify WAD cyanide but also some of the cyanide bound in glyconitrile.

The equilibrium of the decomposition reaction of glyconitrile was reached before the measurement started, and did also not change in a reasonable amount of time. This will be particularly important for the development of an appropriate storage method.

It was also possible to show, that glyconitrile **is not decomposed at a pH of 3.9** (ÖNORM M 6258). It remains in solution during the release of cyanide. Nevertheless, if it is further analyzed using the CNSolution 3000 it could be detected as cyanide.

The following figure shows a graphical representation of the **relationship between released cyanide and the pH value**.

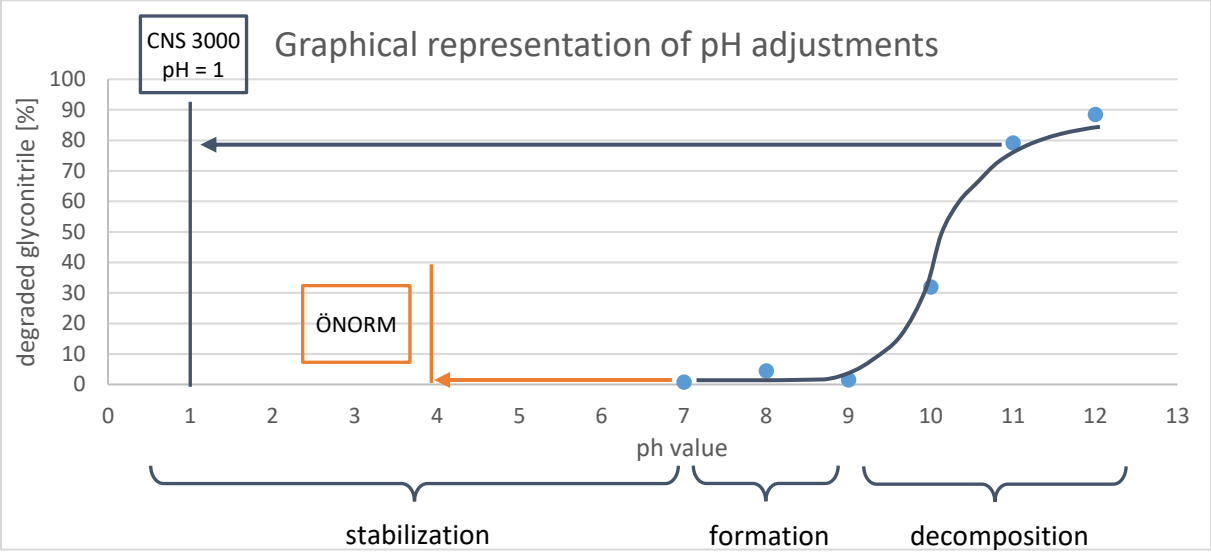



*Figure 19: Graphical representation of pH adjustments during analysis with ÖNORM M 6258 and CNS3000; SD smaller than dot*

Samples arriving in the laboratory for analysis generally had a pH of approximately **7**. The orange arrow indicates the pH adjustment to 3.9 (vertical orange arrow), which is done during the **ÖNORM M 6258** analysis. In this case, no cyanide is released from glyconitrile, because the sample pH never had been in the decomposition region.

If the measurement is done according to **OIA-1677**, the pH is raised to 11 during the sample preparation. This is represented by the blue curve, which is defined by the measurement points found by the experiment "pH-dependence of formation and reverse reaction" (section 6.1). In the CNSolution 3000 itself, the pH is lowered rapidly to one (vertical blue arrow). There is not enough time for the reformation of glyconitrile, because at low pH values, no base catalysis is possible. At the detector, the released cyanide is then measured **in addition** to the cyanide originally contained in the sample. The same principle can also be applied when samples are stabilized for storage. If the pH is raised above 9, glyconitrile will become problematic for any kind of cyanide determination.

## 7. Elimination of the glyconitrile-interference

It had been proven, that glyconitrile leads to **severe interference**, if the pH of the sample exceeds 9 at any time during cyanide analysis. Because this is the case during analysis following OIA-1677[3], a new sample pretreatment had to be developed.

### 7.1. Chemical treatment: ethylene diamine

As already stated (section 5.2), the treatment with ethylene diamine is a suggested method for aldehyde containing samples [3 5]. However, the underlying mechanism is not explained in literature.

According to the literature, the treatment with ethylene diamine can only prevent further formation of cyanohydrin[17]. The regeneration of cyanide is not possible. This information was considered important, as it was thought, that cyanohydrins could somehow be eliminated by this treatment.

However, a closer look on the reaction mechanism revealed that this is not the case. The following figure shows the first steps of the Strecker-Synthesis[19], which works with primary and secondary amines as well.

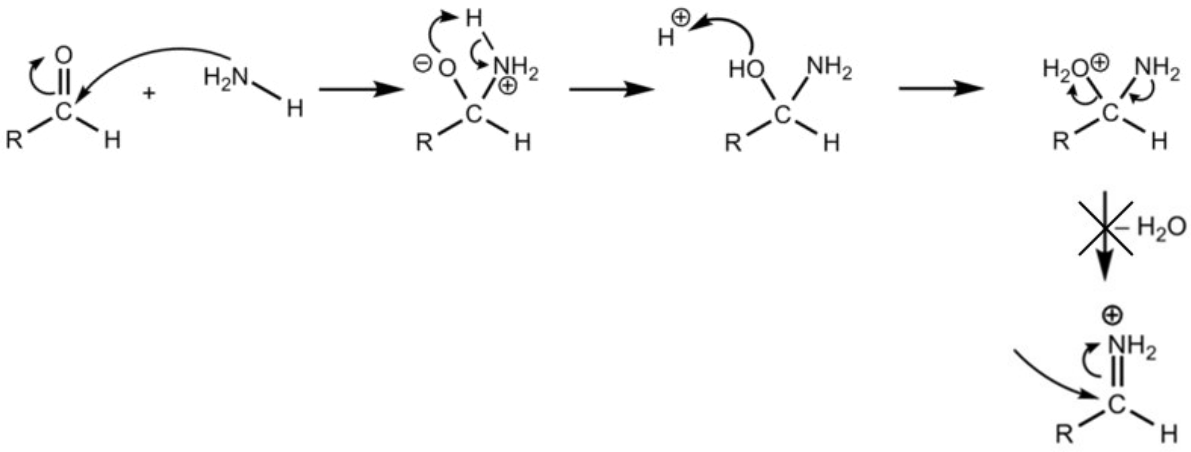



*Figure 20: Reaction mechanism ethylendiamine treatment (derived from Strecker synthesis); modified version [20]*

It is evident, that the amine binds to the carbon of the aldehyde group to form a compound that has an amino and a hydroxyl group in geminal position. This is the final stage, if the reaction is performed in an aqueous medium. The elimination of water is not thermodynamically reasonable in this case, though in non-aqueous media it will take place.

**Conclusion**

The ethylene diamine treatment can only **remove free formaldehyde** from samples. The contained amount of cyanohydrins is not altered and therefore no improvement of the issues investigated in this work were expected.

## 7.2. Change of measurement pH value

Another promising approach was to avoid raising the pH to 11 before the measurement with the CNSolution 3000. Thereby the decomposition of glyconitrile to cyanide and formaldehyde could be circumvented in a very simple way, though it had to be investigated, if the sample pH itself has any influence on the measurement result.

### 7.2.1. Description according to the cyanohydrin theory

If the pH of the samples is **not increased to 11** before the measurement, **no decomposition** of cyanohydrin will occur. In this case, a measurement with the CNSolution 3000 should be in better agreement with the ÖNORM M 6258. The green arrow in the following figure represents this new approach.

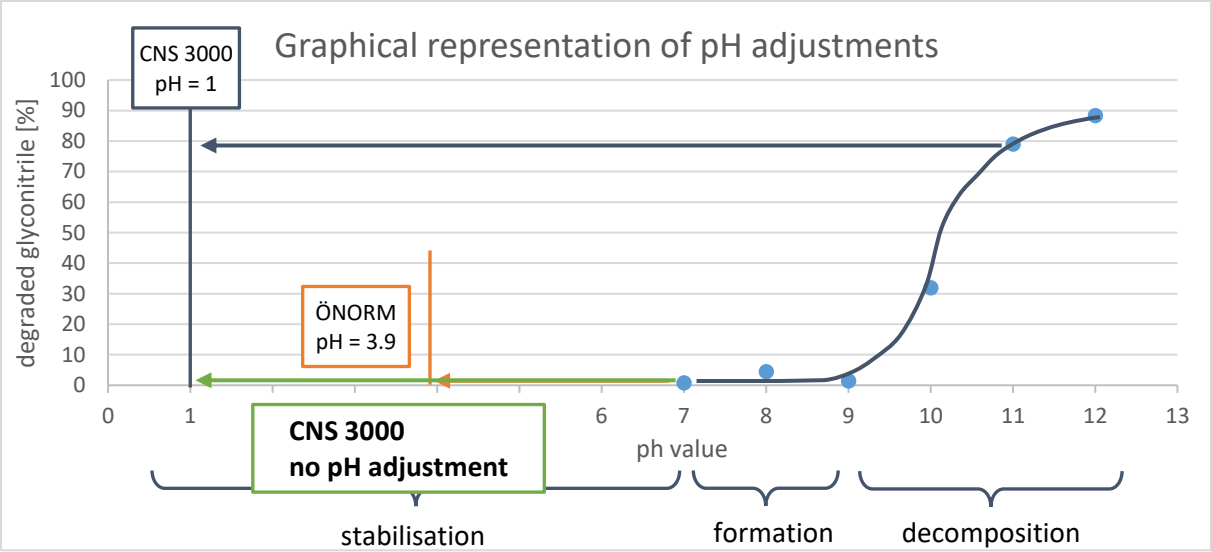



*Figure 21: Graphical represetation of the direct measurement with the CNS 3000; Updated version of Figure 19; SD smaller than dot*

It can be seen, that the pH is **never raised** above the initial sample pH, which represents the same way in which samples are treated during an ÖNROM analysis. Thereby the cyanide level remains constant and in theory, glyconitrile should not cause elevated cyanide data.

### 7.2.2. Equality of measurements at pH 7 and pH 11

At first, it had to be investigated, if the change of the sample pH has any effect on the measurement with the CNSolution 3000. This is particularly important, because investigations, which were done before this work, indicated some kind of pH dependence of potassium cyanide standards if they are adjusted to a lower pH than 12.

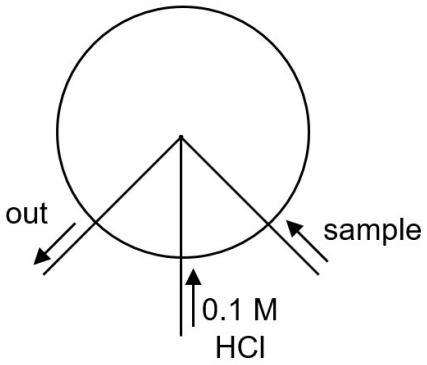



*Figure 22: Mixing chamber CNS 3000*

### Theoretical investigation: pH value in the diffusion chamber

Because the setup was explained in detail in section 2.2, only the mixing chamber, which is positioned between the sample loop and the diffusion camber, will be depicted schematically here (Figure 22).
To determine the pH of the outgoing stream, the flow rates and the pH of the entering streams had to be considered. The sample still had a pH of 11 at this position and the pH of a solution containing 0.1M hydrochloric acid was one. The flow rates were unknown, and therefore had to be measured experimentally.

### Flow rate measurement

The tubes for HCl and sample were disconnected from the mixing cell and the amount of liquid emitted in 60 seconds was collected in a tared beaker. In the case of the out-stream, the collection is done at the entrance to the diffusion cell. The following table contains the results for all three streams.

*Table 13: Flow rates of the mixing chamber streams*

| stream | Flow rate [g/min] |
|---|---|
| **HCl** | 0.92±0.04 |
| **sample** | 0.86±0.03 |

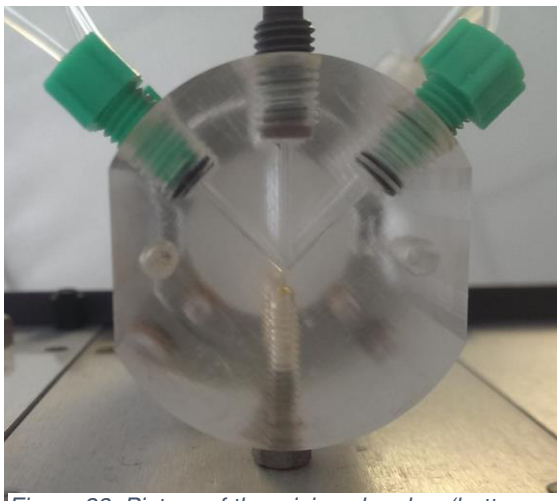


*Figure 23: Picture of the mixing chamber (bottom up view)*

The flow rate of the inlets were nearly the same. The HCl stream might has a little bit lower throughput because it has to pass the sampling unit on its way between the pump and the mixing cell. Due to backpressure in the mixing cell the outgoing stream had a lower flow rate than the incoming ones, if they were not connected to the mixing cell. Due to this tailback, it was concluded that the data on the flowrates only had **qualitative** character. Because it was known that, the

channels of the mixing chamber (Figure 23) have the same diameter, the mixing ratio of the incoming stream should rather be **1+1**.

### Calculation of the pH in the gas diffusion chamber

The samples are acidified, because only hydrocyanic acid, the protonated form of cyanide, can pass the hydrophobic membrane in the gas diffusion chamber. The following table contains the calculated pH values present in this component for samples with different pH. The results are based on a 1+1 mixing of 0.1 M HCl solution and the different samples.

*Table 14: pH in the diffusion chamber for different samples*

| Sample type (pH) | Calculated pH in the diffusion chamber |
|---|---|
| **Calibration standard (pH 12)** | 1.04 |
| **Regular sample (pH 11)** | 1.0043 |
| **Stabilized sample (pH 8)** | 1.0000043 |
| **Untreated sample (pH 7)** | 1 |

### Conclusion

Because this is a **theoretical comparison**, the significance of the results was not considered. From a theoretical point of view, **no pH dependence** should be expected pH range from 7 to 12. The pH at the gas diffusion membrane is in any case **below the pKs of hydrocyanic acid** (9.4). The origin of this issue is the focus of subsequent investigations.

### 7.2.3. Measurement of standards with pH values lower than 11

To prove equality of the measurement at pH 7 and pH 11 it was necessary to produce standards from potassium cyanide and potassium tetracyanozincate. It was observed that synthetic standards show some kind of pH dependency, if their pH is adjusted to lower values. A series of experiments was done to demonstrate, that the instrument did not cause this issues. Contrary to first assumptions, it was suspected that the so-called **CN-loss** (short for cyanide-loss) was caused by the pH adjustment with very small amounts of acid itself.

1. **CN-loss pH 7 – pH 9.4 – pH 11**

To show that low spike recoveries were not caused by the instrument or the method used, a standard adjusted to pH 7 was measured at pH 7 (sample 1) and at pH 11 (sample 2). Further, another part of the same standard was measured at its production pH of 9.3 (sample 3) and afterwards also at pH 11 (sample 4).
This will allow a clear distinction between the two possible scenarios potentially responsible for cyanide loss:

1. A pH dependence of processes within the **instrument** could cause the reduced measurement signal. In this case, there would be different measurement results for sample 1 and 2 and also for 3 and 4. However, sample 2 and 4 should show the same result.
2. The reduced measurement signal might also be induced by the **pH adjustment** itself. This process involves the actual loss of cyanide during the preparation of the sample. This can be expected to lead to the same result for the measurements of the samples 1 and 2 and for the samples 3 and 4. But more important, the cyanide concentration of the samples 3 and 4 will be close to the ideal value, whereas the first two samples will have a lower cyanide content.

**Procedure:**

An unstabilized 0.2mg/L Cyanide standard (sample 3) was produced from solid potassium cyanide. As a reference, one part was immediately adjusted to pH 11 (sample 4). Another 200 mL of the standard were transferred to a beaker and treated with a few drops of very diluted HCl to lower its pH to 7. Afterwards it is divided into two beakers, which were covered and left at the lab bench until just before the beginning of the measurement (sample 1 and 2). At the same time as the autosampler takes up sample 1, the content of the one beaker was brought to pH11 (sample 2).
To make this procedure more convenient, the samples were positioned on the autosampler in the following order: 4 -> 1 -> 2 -> 3. The complete experiment was repeated twice.

**Results and Interpretation**

*Table 15: Results CN-loss pH 7 – pH 9.4 – pH 11; max. standard deviations = 0.002mg/L; n=3; SD not shown for clarity;*

| Sample/experiment | 1 [mg/L] (recovery) | 2 [mg/L] (recovery) |
|---|---|---|
| **Sample 1 (pH 7)** | 0.180 (89.9%) | 0.175 (87.5%) |
| **Sample 2 (pH 11)** | 0.186 (93.1%) | 0.169 (84.5%) |
| **Sample 3 (pH 9.3)** | 0.204 (102%) | 0.208 (104%) |
| **Sample 4 (pH 11)** | 0.200 (100%) | 0.208 (104%) |

Sample 3 and 4 always showed the desired value of 0.20mg/L. For sample 1 and 2 the cyanide recovery were lower (80-90%), but no significant difference could be seen between the measurement at pH 7 and 11. This leads to the assumption, that the previously described **case two** could be applied here.
This implied that the measurement procedure itself is **not pH dependent, but the sample preparation causes the observed losses**. The amount of cyanide, which is contained in the sample, will always be determined correctly in the range between pH 7 and 12. But if the pH is adjusted by addition of acid, the cyanide recovery is lowered by approximately 10 to 15%.

## 2. CN-loss

As already demonstrated, the pH adjustment had significant influences on the cyanide recovery in synthetic solutions. A series of experiments was conducted to further investigate the extent of the CN-loss. In this section, the most significant results are presented.

### pH dependence

**Procedure:** A series of cyanide standards containing 0.2 mg/L CN (pH 9.2) was set to **pH 7**, **8** and **9** using strongly diluted hydrochloric acid. Immediately (t<5sec) after this initial pH adjustment, the pH of these standards was readjusted to 11.
Because of the low buffer capacity of the unstabilized standards only one drop of 1M NaOH had to be added to obtain a **pH of 10**. To ensure consistent test conditions, this standard was given the same residence time (t<5sec) as the first three samples. After this, the pH was adjusted to 11 as well.
The pH of the last standard was only raised to **pH 11**, without any other treatment. This procedure was selected to simulate the loss of cyanide when unstabilized standards are adjusted to different pH values. It was also attempted, that all standards had the same residence time (t<5sec) at a certain pH value.

**Results and Interpretation**: Lowered cyanide recovery was found for samples, which were adjusted to a lower pH. In contrast to this, the sample, which was only treated with NaOH, showed a recovery rate of nearly 100%. The following figure shows all results.

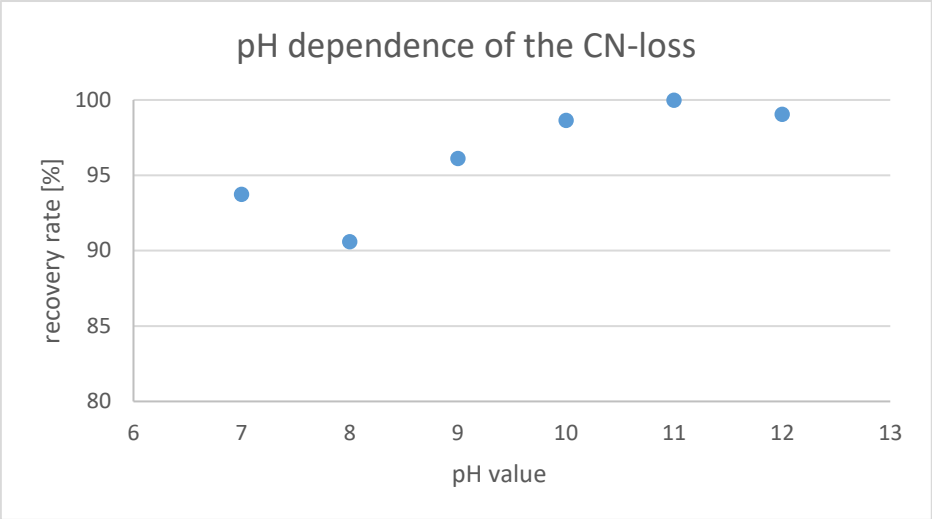



*Figure 24: CN-loss during the adjustment to different pH values;; n=3; SD smaller than dot*

**Time dependence**

**Procedure:** 500mL unstabilized 0.2mg/L CN standard (pH 9.3) were produced (see above). Each of seven 100 mL beakers was filled with approximately 70mL of this standard and the pH was lowered to 7 with strongly diluted HCl. The individual samples were left uncovered at the lab bench for 0, 1, 2, 5, 7, 10 and 15 minutes. Afterwards the pH of all samples was raised to 11, which prevented further release of cyanide form the solution. A reference sample was produced by setting the pH to 11 immediately after production.

**Results and Interpretation:** The reference sample showed exactly the expected value of 0.2mg/L cyanide. Systematic errors form the production of the standard (e.g. minute dilution of the sample by pH adjustment) could therefore be excluded.
It is apparent, that the pH adjustment itself was responsible for a $CN^-$loss of approximately 8%. More cyanide was not lost until 10 minutes passed by. The data are shown in the following figure.

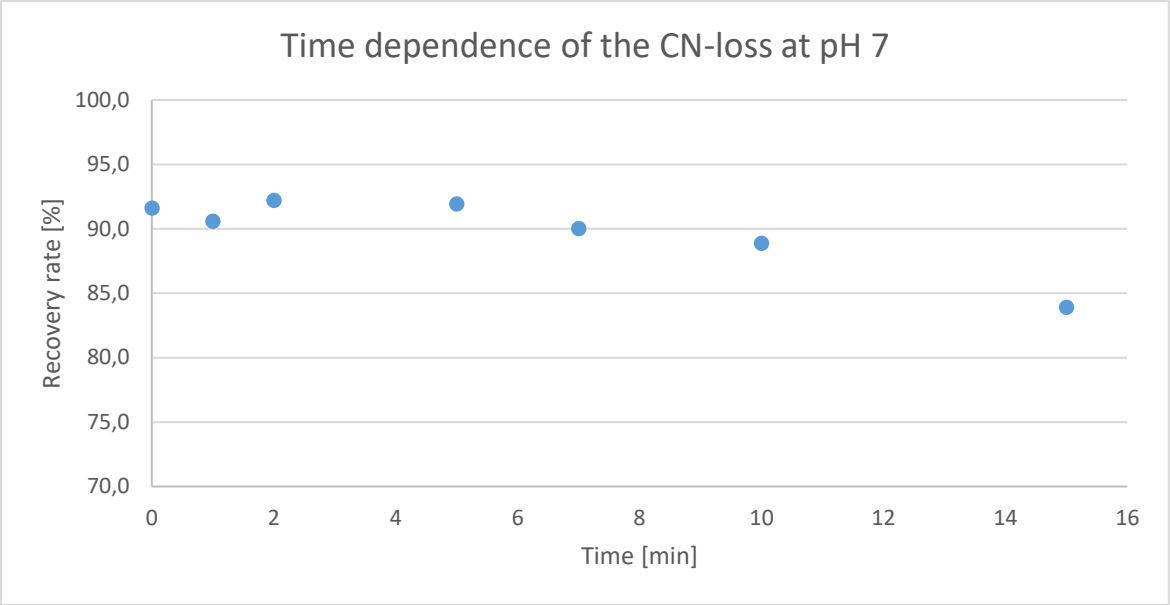



*Figure 25: Time dependence of the CN-loss at pH 7; n=3; SD smaller than dot*

## 3. Consequences for ÖNORM M 6258[4]

After evaluation of these experiments, it became clear, that the CN-loss may also be an issue during the analysis following ÖNORM M 6258. During the sample preparation, the pH value is lowered to 3.9 in uncovered beakers. The transfer to the release apparatus does not happen until all samples are prepared, as discussed in the introduction.

This sample preparation step deviates from the original procedure described by ÖNORM M 6258, that recommends to perform the whole sample preparation in the three-necked flask of the release apparatus while the gas flow though the absorption solution is already established.

Although the modified version of ÖNORM M 6258 had been validated in the past, additional investigations are needed.

### 7.2.4. Validation experiments

In this section, it will be shown that it is legitimate to change the measurement pH of OIA-1677 from **11 to 7**. This will be done by a series of comparative experiments that are evaluated statistically.

#### 1. Comparison of calibration curves at pH 7, pH 11 and pH 12

To show, that the CNSolution 3000 is usable at pH 7 as well as at pH 11, calibration curves were recorded at both of these pH values. The investigated concentration range was between 0.02 and 0.2 mg/L cyanide.

**Procedure:**
The standards were diluted from an unstabilized KCN stock solution and acidified to pH 7 with 3 to 4 drops of highly diluted hydrochloric acid. Until the measurement starts, the samples were stored in the same closed graduated flasks, which were used for their production. The transfer to the autosampler happened not until moments before the measurement starts. At the same time, the unused residual of the sample was stabilized with 2 drops of 1M NaOH solution. After all pH 7 standards had been analyzed, the residuals were adjusted to pH 11 and afterwards measured themselves (CN-loss compensation).

**Evaluation:**
Before each set of measurements a calibration is necessary, because the electrical signal (pA) can drift within several hours. Because of this raw signals cannot be compared directly. At first, they had to be converted to concentrations.
The goal of this experiment was to show that the deviation between the measurements at pH 7 and pH 11 was lower than the measurement uncertainty (twice of the standard deviation of the calibration). Therefore, the highest value of this sample series was used. The software-based automatic elimination of outliners was not taken into account. Additionally, the calibrations were evaluated using the software “Validata”.

**Results:**

**Measurement uncertainty:** The calibration of the measurement "0922_03" (see appendix) had a standard deviation of 2%. Therefore, the two-sigma boundary for this method was **4%**, which was seen as a very reasonable value. As it was mentioned before, this was far better than the ÖNORM M 6258[4] method. The relative standard deviation of all results for this method in a ring trail was 28%. Although ring trails have a rather high RSD compared to single measurements (different operators, instruments, days, etc.), it is clear that by using the CNS3000 a higher method precision can be attained.

The following table contains the results for the measurements at pH 7 and pH 11. In both cases. The calibration was done at pH 12.

*Table 16: Results of the comparison of calibration curves at pH 7 and pH 11; ; n=3; SD not shown for clarity;*

| Standard | pH 7 [mg/L CN] | pH 11 [mg/L CN] | pH 11 – pH 7 [mg/L CN] | Delta [%] |
|---|---|---|---|---|
| **1** | 0.017 | 0.017 | 0.000 | -0.22 |
| **2** | 0.043 | 0.044 | 0.001 | 2.96 |
| **3** | 0.092 | 0.089 | -0.003 | -**3.37** |
| **4** | 0.138 | 0.135 | -0.003 | -2.11 |
| **5** | 0.184 | 0.183 | -0.001 | -0.78 |

**Validata** (Excel macro for method validation)**:** It is known that the measurement can be done correctly at pH 11. For this reason, pH 7 standards were also measured at pH 11. By doing so, the "true" concentration of the standards could be determined. It was lower than the concentration, which would have been achieved only by dilution of the stock solution, because of the pH adjustment. During the "Validata" analysis, the concentration values determined at pH 11 were combined with the peak hights (in pA) from the measurement at pH 7.

To allow a comparison, a calibration curve at pH 12 was also recorded.

**pH 7:** Between 0.02 mg/L and 0.2 mg/L, **variance inhomogeneity** could be observed. Consequently, the operating range was reduced to 0.05 to 0.2 mg/L.

**pH 12: Variance inhomogeneity** could also be observed when standards with pH 12 were measured. Again, the elimination of the calibration point with the lowest concentration could solve this problem.

Linearity and the operating range **are secured** for pH 7 and 11.

The complete validate reports can be seen in the appendix section 11.3.

A **F-test** was performed to compare the method standard deviation. Therefore the concentration determined at pH 11 was used for both series (pH 7 and pH 11). The calculated test value (PG=1,52) was smaller than the tabulated one (PG=4,11; confidence 90%). The recovery function further showed that **no proportional or constant systematic deviation**. This indicated that both measurements are equal.

## 2. $PbCO_3$ treatment

In order to remove sulfide (severe positive interference) from samples, a treatment with $PbCO_3$ is recommended by OIA-1677[3]. It had to be investigated if this method works at a pH of **7** in a concentration range between 0.02 and 0.2 mg/L. Further, it was investigated how a **variation of the amount** (0.1g-2g) of $PbCO_3$ influences the measurement.

### 2.1. 0.02 – 0.2 mg/L Cyanide + 0.2 g $PbCO_3$/100mL

100 mL Cyanide standards with a concentration of 0.02 – 0.2 mg/L were treated with 0.2 g $PbCO_3$. The method OIA-1677 recommended to add $PbCO_3$ **immediately after the sample collection**. A pH value of 7 should therefore be no problem. It had to be proven that no problems occur during the measurement of $PbCO_3$ containing samples.

**Procedure:**

The standards were produced from unstabilized potassium cyanide stock solutions. For the acidification to pH 7, highly diluted hydrochloric acid was used. The standards were left covered on the lab bench until one minute before the analysis. Then they were transferred to $PbCO_3$ containing beakers. Turbidity could be observed. For the transfer to the auto sampler, syringe filters (Rotilabo 25mm, 0.45µm pore size, CME membrane, PVC housing) were necessary.
The residuals of the samples were stabilized with two drops of a 1M sodium hydroxide solution and covered with "Parafilm". The exact adjustment to and the measurement at pH 11 was done after the measurement at pH 7.

**Results:**
The following table contains the results of the measurements at pH 7 and pH 11.

*Table 17: Results 0.02 – 0.2 mg/L Cyanide + 0.2 g $PbCO_3$/100mL; mean values, rounded; n=3; SD not shown for clarity;*

| Standard | pH 7 [mg/L CN] | pH 11 [mg/L CN] | Delta [%] |
|---|---|---|---|
| **1** | 0.018 | 0.018 | -**2.0** |
| **2** | 0.045 | 0.045 | -0.8 |
| **3** | 0.093 | 0.093 | -0.4 |
| **4** | 0.139 | 0.137 | -1.6 |
| **5** | 0.184 | 0.188 | 1.8 |

The deviation between pH 7 and pH 11 was in all cases small than the precision of the method of 4%. This indicated that regardless of the pH value is 7 or 11 the method works **equally well** in the presence of $PbCO_3$.

The evaluation of calibration data using "Validata" showed **variance inhomogeneity** again. The highest concentration level was eliminated. Additionally, the linearity test was not passed. This can be explained by a slight deviation of the calibration points 0.15mg/L and 0.20 mg/L from the calibration curve. The analysis of residuals, which was plotted by validata can be seen in Figure 26. For the complete validata report, see appendix section 0.

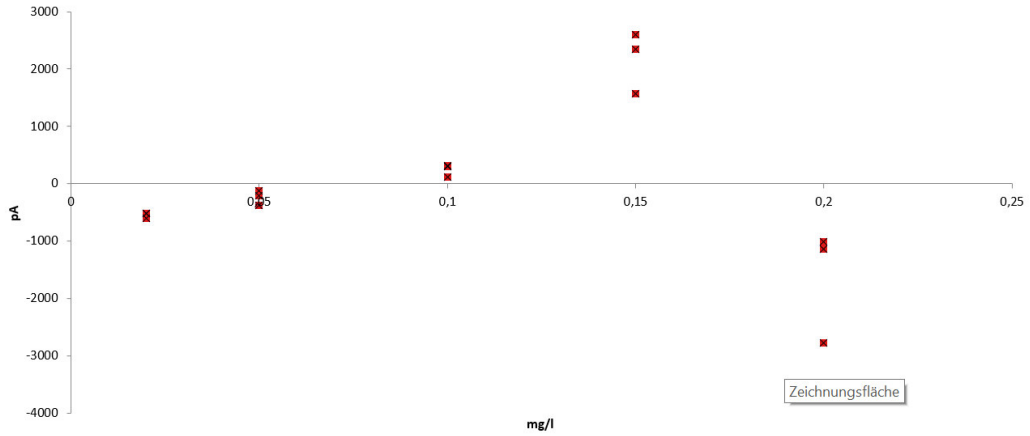



*Figure 26: Analysis of residuals of 0.02 – 0.2 mg/L Cyanide + 0.2 g PbCO3/100mL from validata*

The pH 7 and the pH 11 methods were also compared using the F-test, which showed that these two techniques are **equal** for a confidence of 90%. The analysis of the recovery function showed, that **no constant** or **proportional systematical deviation** is expected (confidence 95%)

## 2.2. $PbCO_3$ – excess and shortage

In routine analysis, the amount of $PbCO_3$ was not weight exactly before the application. It was recommended to use one "**spatula tip"**. To examine the effect of variations in $PbCO_3$ addition, different amounts of $PbCO_3$ were tested.

**Procedure:**

The standards were produced from an unstabilized KCN stock solution, which was adjusted to pH 7 with highly diluted hydrochloric acid. The samples were stored in volumetric flasks until one minute before the analysis. Then the standards were transferred to beakers, which contained different amounts of $PbCO_3$. To avoid contaminations of the instrument, syringe filters (Rotilabo 25mm, 0.45µm pore size, CME membrane, PVC housing) were used during autosampler loading. Again, the remains of the samples were stabilized with two drops of sodium hydroxide solution. The exact adjustment was done after the first determination was finished.

**Results:**

The following table contains the results of the samples, which were treated with different amounts of $PbCO_3$ and determined at pH 7 and pH 11.

*Table 18: Results of the $PbCO_3$ variation; data for 0.2g $PbCO_3$ from previous experiment 2.1.; n=3; SD not shown for clarity;*

| PbCO3 [g] | pH 7 [mg/L CN] | pH 11 [mg/L CN] | delta [%] |
|---|---|---|---|
| **0.1** | 0.151 | 0.149 | -0.9 |
| **0.2** | 0.184 | 0.188 | **1.8** |
| **0.5** | 0.165 | 0.166 | 0.8 |
| **1** | 0.185 | 0.183 | -0.9 |
| **2** | 0.188 | 0.186 | -1.2 |

No **significant difference** could be observed between the measurements at pH 11 and pH 12. The maximum deviation is **1.8%**.

A shortage or excess of $PbCO_3$ should therefore **not cause any problems** if no sulfide is present. Nevertheless, the reasonable amount of **0.2g**, which is approximately one spatula tip, is recommended.

*Figure 27: 0.2g of PbCO3*

### 3. Cyanohydrin – Dilution into the operation range

During routine operation, situations of **high cyanide concentrations** can occur. Usually the deviation between ÖNORM M 6258 and OIA-1677 is particularly high in this case. To make samples analyzable, they have to be **diluted** into the operation range (0.02-0.2 mg/L). This experiment should show that this is applicable for samples, which contain cyanide as well as glyconitrile.

**Procedure:**

The standards were produced from unstabilized cyanide stock solutions. At first, the volumetric flasks were filled halfway with DI water. Then the necessary amount of cyanide and glyconitrile stock solution (~577g/L; Sigma Aldrich 374768[21]; lot#: BCBF4937V; CAS-number 107-16-4) was added. After that, the flasks were filled up to the mark. The molar ratio between these two compounds is 1:1 at all concentrations. Table 19 shows the concentrations of glyconitrile and cyanide present in the standards.

*Table 19: Cyanide and glyconitrile concentration of standard 1-5*

| # Standard | c(CN) [mg/L] | c(Cyh.) [mg/L] | Dilution |
|---|---|---|---|
| **1** | 0.10 | 0.21925 | - |
| **2** | 1 | 2.1925 | 1+9 |
| **3** | 10 | 21.925 | 1+99 |
| **4** | 20 | 43.85 | 1+199 |

The dilution into the operation range was done according to the factors which were given in the previous table. The pH of the samples 1 and 4 were 8.24 and 9.84, respectively. The adjustment to pH 7 was done with highly diluted hydrochloric acid. The samples were stored in volumetric flasks until the analysis started. Again, the samples were stabilized with two drops of 1M NaOH solution and adjusted to pH 11.2 after the first measurement was finished.

**NOTE:** It has to be considered, that the CN-loss **cannot be determined** during this experiment. For any other measurement in this section, at first a measurement was done at pH 7. Then the same samples were also determined at pH 11 to obtain comparable results. However, if glyconitrile is also present in the system, the cyanide concentration will rise with increasing pH value.
From previously experiments (section 7.2.3), it was assumed that the CN-loss was also in the range of 10-15%. In any case, the cyanide concentrations **should never rise** above the initial level.

**Results:**

*Table 20: Results Validation experiment 3 - Dilution into the operation range; n=3; SD not shown for clarity;*

| Standard [mg/L $CN^-$] | Measured conc. pH 7 [mg/L] | Deviation from ideal value [mg/L] | Measured conc. pH 11 [mg/L] | Deviation ph 11- pH 7 [mg/l] |
|---|---|---|---|---|
| **0,1** | 0,093 | 0,007 (7%) | 0,174 | 0,081 |
| **1** | 0,100 | 0,000 (0%) | 0,179 | 0,079 |
| **10** | 0,097 | 0,003 (3%) | 0,178 | 0,081 |
| **20** | 0,096 | 0,004 (4%) | 0,176 | 0,081 |

All of the measured standards showed results **close to the ideal value**. It seems that glyconitrile-cyanide-systems have a lower CN-loss, because at pH 7 nearly all of the cyanide can be recovered.
It can also be seen that at pH 11 the same amount of glycinitrile is degraded in all samples. The amount is also in the range of the previous experiments.

## 4. Conclusion of the Validation experiments

In experiment one, it was shown that the measurements of the same samples at pH 7 and pH 11 lead to **similar results**. Deviations between them are within the uncertainty

of the method and are nearly an order of magnitude **lower** than at the ÖNORM M 6258[4].
It was also shown that samples treated with $PbCO_3$ could be measured at pH 7. The amount of $PbCO_3$ should be approximately 0.2g, but there are no negative effects encountered up to 2g.
No problems will also arise from samples with a cyanide content up to **20mg/L** as dilution works **perfectly fine** to obtain samples within the calibration range of the method.

### 7.2.5. Storage of samples before and during the measurement

Below its pKs value (9.4), the majority of cyanide is obviously present as **hydrogen cyanide**. This **volatile** compound is able to evaporate from the liquid phase and is consequently lost. Because the newly developed method involves the measurement at pH 7, it is considerably likely that lower results will be found. The following experiments were done to estimate the magnitude of this effect.

#### 1. CN-loss during the measurement

As described before, cyanide is lost to the gas phase from uncovered samples at pH 7. In this experiment, it was examined how the cyanide concentration of a real sample changes, if it was left uncovered for 1.5 hours on the autosampler.
The only sample treatment was filtering. Three test tubes were filled and measured five to six times each. The time dependent CN-loss of a real sample is described by 16 mean values plotted in Figure 28.

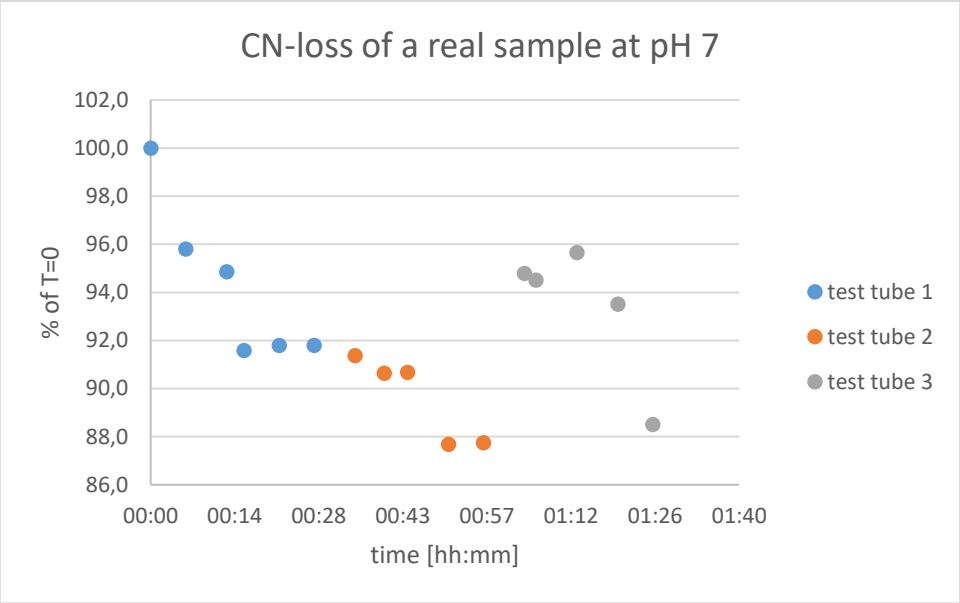



*Figure 28: CN-loss of a real sample on the autosampler; three test tubes containing with the same standard*

From Figure 28 it can be deduced that in general the cyanide concentration continuously decreased during the first hour. With the cyanide loss in test tube 3 however doesn't follow this general trend, though the reason for this remains unclear. However, the generalized statement appears valid, that the cyanide loss in samples of pH 7 involves several factors besides time. The nature of these additional factors remains unclear and further investigations will be needed to fully understand the cyanide loss at pH 7.

## 2. Sample storage at pH 6.5

As already discussed sample storage at high pH values should be avoided, because of the decomposition of glyconitrile. However, it is known that cyanide is lost to the gas phase at medium to low pH values. This experiment should clarify if storage in **bubble free sealed flasks** in a r**efrigerator** is a viable solution to this problem.

*Figure 29: Bubblefree cooled storage using Erlenmeyer flasks and polymere plugs*

In routine analysis, samples with a pH value of approximately 6.5 had been observed in some cases. Therefore, samples with this pH were plausible to be investigated during this work.

**Procedure**: Four samples were produced from an unstabilized potassium cyanide stock solution. The pH adjustment was done with highly diluted hydrochloric acid. Each sample was transferred to a 300ml ground joint Erlenmeyer flask, which was filled until it overflows. Bubble free sealing was achieved by application of a polymer plug, while the flasks were slightly tilted. At the same time, a reference sample was taken from each standard to determine the cyanide concentration before storage.
Sample 1 and 2 remained bubble free sealed in the refrigerator for 24 hours. After the first determination, they remained another day sealed in the fridge but this time with a little air bubble on top. Sample 3 and 4 were analyzed after a storage time of 48 hours. All measurements were done after adjusting the pH to 11 prior analysis.

**Results:**

*Table 21: Sample storage pH 6.5; measured concentrations; n=3; SD not shown for clarity;*

| sample | c day 0 [mg/L] | c day 1 [mg/L] | c day 2 [mg/L] |
|---|---|---|---|
| **1** | 0.180 | 0.184 | 0.188 |
| **2** | 0.188 | 0.191 | 0.192 |
| **3** | 0.181 | - | 0.192 |
| **4** | 0.187 | - | 0.194 |

*Table 22: Sample storage pH 6.5; concentration drop in mg/L and %*

| sample | Drop after 24h [mg/L] | Drop after 48h [mg/L] | Drop after 24h [%] | Drop after 48h [%] |
|---|---|---|---|---|
| **1** | -0.005 | -0.009 | -2.6 | -4.8 |
| **2** | -0.003 | -0.004 | -1.5 | -2.0 |
| **3** | - | -0.011 | - | -6.2 |
| **4** | - | -0.007 | - | -3.8 |

All samples showed a slightly increased cyanide concentration though this can be explained by the **uncertainty** of the measurement. In any case, **no cyanide loss** was

observed. Therefore, this method seems to be a **reasonable alternative** to sample storage at high pH values.

Furthermore, a stabilization with zinc ions should be investigated in the future. The formation of a weak cyano-complex could improve the stability of free cyanide. This technique is already used by Merck[22] at their cyanide stock solutions.

# 8. Formaldehyde analytics

Unfortunately, it was not possible to examine real wastewater samples during this work, because of the **insufficient content** of glyconitrile. The reason was the unavailability of samples with elevated formaldehyde concentrations. Formaldehyde is present in the investigated wastewater samples only during atypical process conditions in the gas scrubber. However, a method to determine the **formaldehyde** concentration is presented. As discussed before (see section 5.3), this aldehyde can be released from samples containing glyconitrile and is therefore seen as an indicator for this interference.

**Method description: Formaldehyde-2,4-DNPH HPLC-DAD**

A convenient way to determine formaldehyde is **derivatization** and quantification using **HPLC-DAD**. In the first step 2,4-dinitrophenylhydrazine is added to the sample. After the derivative has formed, it is extracted using SPE cartridges.

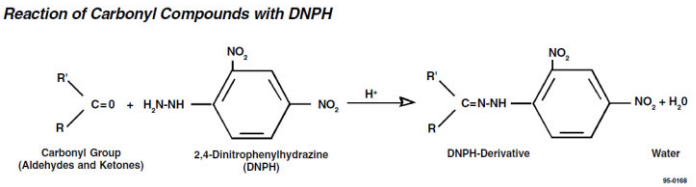



*Figure 30: Reaction Equation Aldehyde Derivatization[23]*

The elution is done with acetonitrile. The high performance liquid chromatography with diode array detection uses a RP 18 column (5µm, 4.6 x 150mm) and is operated isocratically (solvent MeOH:$H_2O$ 70:30; flow rate 1mL/min). 360nm is the recommended detection wavelength. The measurable concentration range starts at **1mg/L** is linear at least up to 25mg/L.

This analysis should be performable relatively easy, if suitable instrumentation is available. Otherwise, contract laboratories, like the **Institute of Analytical Chemistry and Food Chemistry** at the **TU Graz**, are able to do this determination.

# 9. Conclusion

The aim of this work was to identify a **positive interference**, which caused a deviation between the cyanide measurement results of OIA-1677[3] and ÖNORM M 6285[4]. Further, an appropriate technique to avoid this should be developed.

In the course of this work, both methods were extensively investigated and characterized (see section 2). The most common interferences were investigated, but none of them could be identified as the source of the observed issues (see section 4).

**Glyconitrile** was suspected to release cyanide at high pH values. It was observed that the **pH** has a strong impact on the glyconitrile-cyanide-equilibrium. Three regions could be identified. The formation happens at pH 7 to 8, the decomposition above pH 9 and below pH 7 glyconitrile is stable. This is the reason why the cyanide determination following the ÖNROM is not affected by this interference. During its procedure, the pH is never raised above 8 and therefore no glyconitrile decomposes resulting in not additional release of cyanide. (see section 6) Much to the contrary, following OIA-1677 a pH change of the sample to pH 11 is requested by this norm.
However, the **pH adjustment** to higher values during the sample preparation should be avoided as otherwise the gyconitrile-decomposition takes place.
A new method based on OIA-1677 was developed wherein the pH remains at 7 and validation experiments showed that this new method is **statistically coherent** with the old one and can be **used as a replacement** (see section 7).

It was also investigated how the **sample storage** should be done in the future. A new bubble-free and cooled storage method was characterized and showed promising results (see section 7.2.5). Further investigations and longtime studies on this topic and especially on the stabilization using ionic zinc are highly recommended.

Another issue, which came to mind during the investigations, is the potential loss of cyanide to the gas phase during the adjustment of the sample pH value. If the pH is lowered to 7, the cyanide concentration decreases in the range of 10%. Although a

significant impact is not suspected, additional research is recommended, to examine the influences of this effect on the procedure of ÖNORM M 5862.

In section 10 the new **Recommended Procedure** is presented. If glyconitrile is present in samples, its application is highly recommended. It is based on the existing method (OIA-1677) and harmonizes it to the ÖNROM M 6285.

# 10. Measurement instructions for the pH 7 method

As the last step of this work, a new **Recommended Procedure** for the sample preparation and conservation was developed. It is based on the existing methods OIA-1677[3] and ISO-14403[6] and takes into account the newly gained knowledge about cyanohydrin interference.

**Sample Preparation and Conservation**

300mL of samples, which are not analyzed immediately, have to be transferred into a 300mL Erlenmeyer flask (with ground joint) and sealed bubble free with a polymer plug. The flask has to be kept in a refrigerator.

50mL of samples, which are analyzed immediately, should be transferred to a 100mL beaker. It should be covered air tight with Parafilm. If the presence of sulfides is suspected, a spatula tip (~0.2g) of $PbCO_3$ should be added to the samples shortly before the measurement starts. After short stirring the sample is drawn up into a syringe and transferred to an autosampler test tube through a syringe filter (Rotilabo 25mm, 0.45µm pore size, CME membrane, PVC housing). The first 3mL have to be discarded.

The handling of the instrument itself is the same as described in the CNSolution 3000 operators manual.

# 11. Appendix

## 11.1. Additional pictures of CNSoltuion 3000

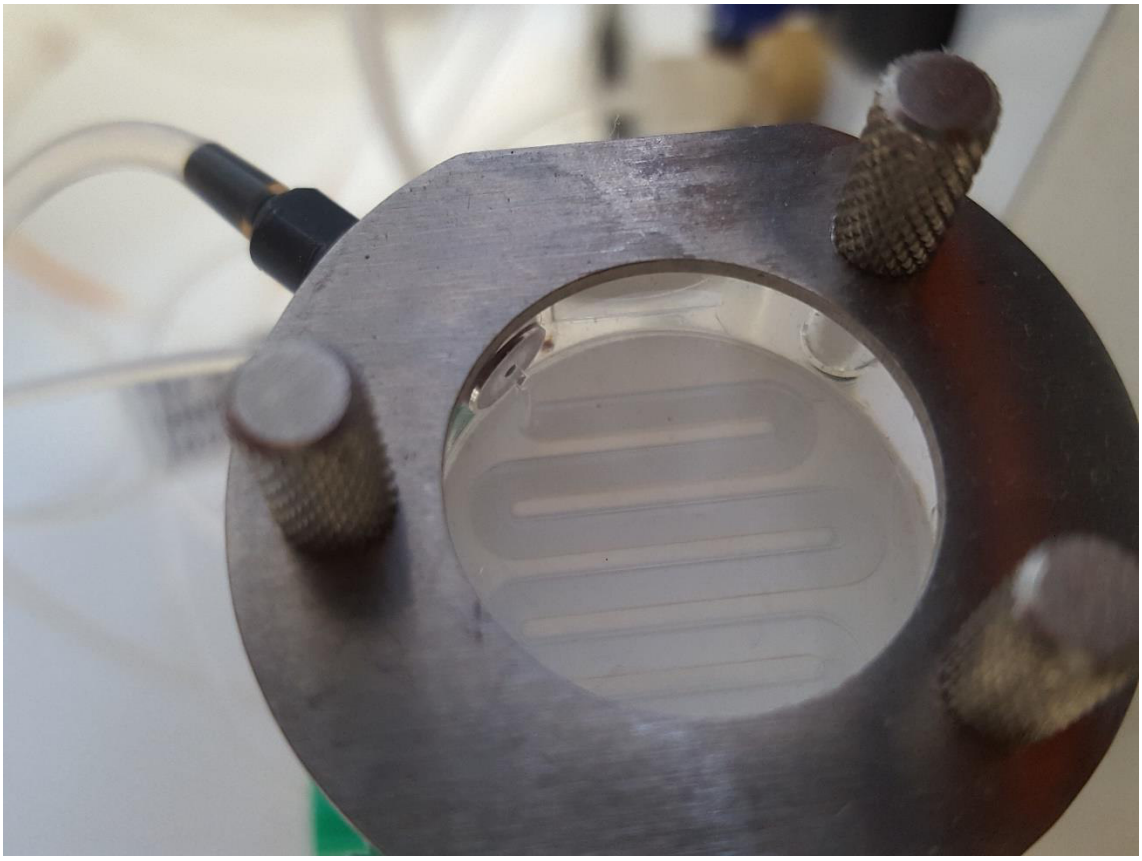


*Figure 31: CNSolution 3000 diffusion chamber side view*

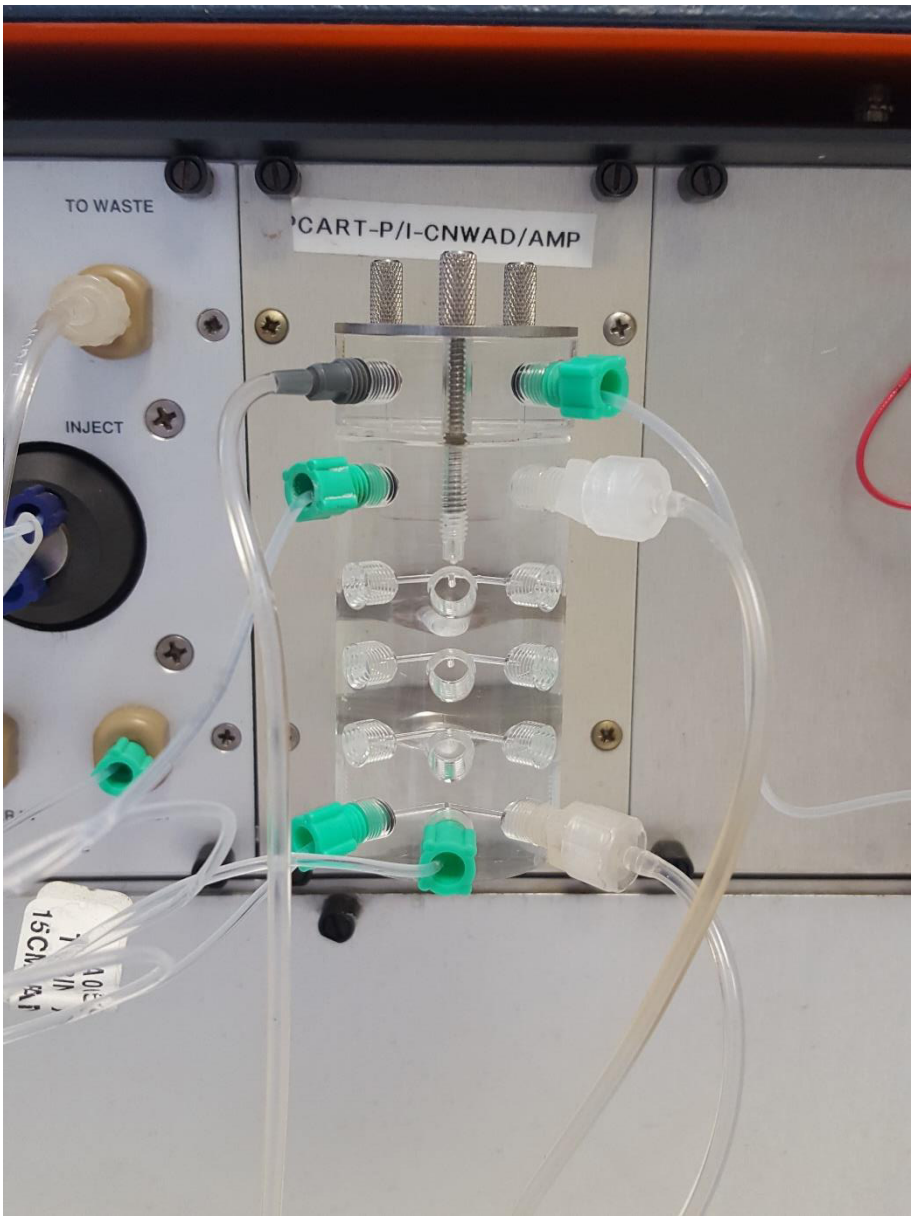



*Figure 32: MIxing cell and diffusion chamber module*


*Figure 33: 120-position autosmapler*


*Figure 34: CNSolution*

## 11.2. Ad CNSolution; examples for relative standard deviation of the calibration

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0928_04.RST
Ergebnisse fertiggestellt: 11:32 September 28, 2015.
Benutzer: moser

V1: Kalgerade pH12

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- | Benutzer Nachfrage: Datensammlung beginnen ---------- | | | | |
| 10:47 | 0 | Carryover | 628 | 0.000842 | LO |
| 10:47 | 0 | Baseline | 0 | 0.000000 | BL |
| 10:48 | 1 | Cal 0.200 mg | 144184 | 0.193293 | LO |
| 10:48 | 1 | Cal 0.200 mg | 156045 | 0.209192 | LOOL |
| 10:53 | 1 | Cal 0.200 mg | 149372 | 0.200247 | LO |
| 10:54 | 1 | Cal 0.200 mg | 147150 | 0.197268 | LO |
| | | !Zweck & RSD | 146902 | 0.196936 | 3.43% |
| 10:54 | 0 | Blank | 128 | 0.000171 | LO |
| 10:55 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:56 | 2 | 0,02 pH 12 | 15109 | 0.020255 | LO |
| 11:00 | 2 | 0,02 pH 12 | 15211 | 0.020391 | LO |
| 11:01 | 2 | 0,02 pH 12 | 15118 | 0.020267 | LO |
| | | !Zweck & RSD | 15146 | 0.020304 | .373% |
| 11:03 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:04 | 3 | 0,05 pH 12 | 37760 | 0.050620 | LO |
| 11:04 | 3 | 0,05 pH 12 | 37973 | 0.050906 | LO |
| 11:05 | 3 | 0,05 pH 12 | 38159 | 0.051155 | LO |
| | | !Zweck & RSD | 37964 | 0.050894 | .526% |
| 11:06 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:09 | 4 | 0,10 pH 12 | 75213 | 0.100830 | LO |
| 11:[illegible] | 4 | 0,10 pH 12 | 75733 | 0.101527 | LO |
| 11:[illegible] | 4 | 0,10 pH 12 | 76271 | 0.102248 | LO |
| | | !Zweck & RSD | 75739 | 0.101535 | .699% |
| 11:12 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:13 | 5 | 0,15 pH 12 | 114971 | 0.154129 | LO |
| 11:16 | 5 | 0,15 pH 12 | 119132 | 0.159708 | LOOL |
| 11:18 | 5 | 0,15 pH 12 | 116177 | 0.155746 | LO |
| | | !Zweck & RSD | 115574 | 0.154937 | 1.85% |
| 11:18 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:19 | 6 | 0,20 pH 12 | 155024 | 0.207824 | LO |
| 11:20 | 6 | 0,20 pH 12 | 156737 | 0.210120 | LO |
| 11:22 | 6 | 0,20 pH 12 | 156235 | 0.209447 | LO |
| | | !Zweck & RSD | 155999 | 0.209131 | .564% |
| 11:25 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:26 | 1 | cal. WH | -628 | -0.000841 | LOOL |
| 11:26 | 1 | cal. WH | -113 | -0.000151 | LO |
| 11:27 | 1 | cal. WH | 240 | 0.000321 | LO |
| | | !Zweck & RSD | 64 | 0.000085 | 686% |
| 11:28 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- | Benutzer Nachfrage: Lauf beenden ---------- | | | | |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0928_05.RST
Ergebnisse fertiggestellt: 12:26 September 28, 2015.
Benutzer: moser

V1: Kalibrierung pH12 ; WH 0,15; 0,20

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- Benutzer Nachfrage: Datensammlung beginnen ---------- | | | | | |
| 11:53 | 0 | Carryover | 732 | 0.001040 | LO |
| 11:54 | 0 | Baseline | 0 | 0.000000 | BL |
| 11:54 | 1 | Cal 0.200 mg | 139282 | 0.197739 | LO |
| 11:55 | 1 | Cal 0.200 mg | 141298 | 0.200601 | LO |
| 11:56 | 1 | Cal 0.200 mg | 141443 | 0.200808 | LO |
| 12:00 | 1 | Cal 0.200 mg | 141475 | 0.200853 | LO |
| | | !Zweck & RSD | 140874 | 0.200000 | .756% |
| 12:01 | 0 | Blank | -265 | -0.000376 | LO |
| 12:02 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 12:02 | 5 | 0,15 pH 12 | 108206 | 0.153621 | LO |
| 12:03 | 5 | 0,15 pH 12 | 109240 | 0.155089 | LO |
| 12:07 | 5 | 0,15 pH 12 | 108024 | 0.153362 | LO |
| | | !Zweck & RSD | 108490 | 0.154024 | .605% |
| 12:08 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 12:09 | 6 | 0,20 pH 12 | 144234 | 0.204770 | LO |
| 12:09 | 6 | 0,20 pH 12 | 144971 | 0.205815 | LO |
| 12:10 | 6 | 0,20 pH 12 | 145408 | 0.206436 | LO |
| | | !Zweck & RSD | 144871 | 0.205674 | .409% |
| 12:13 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 12:16 | 1 | cal. WH | 138065 | 0.196011 | LO |
| 12:[illegible] | 1 | cal. WH | 139152 | 0.197555 | LO |
| 12:[illegible] | 1 | cal. WH | 142006 | 0.201606 | LO |
| | | !Zweck & RSD | 139741 | 0.198391 | 1.46% |
| 12:17 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 12:19 | 5 | 0,15 pH 12 | 107541 | 0.152676 | LO |
| 12:23 | 5 | 0,15 pH 12 | 107650 | 0.152831 | LO |
| 12:23 | 5 | 0,15 pH 12 | 107969 | 0.153283 | LO |
| | | !Zweck & RSD | 107720 | 0.152930 | .206% |
| 12:24 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 12:25 | 6 | 0,20 pH 12 | 0 | 0.000000 | |
| 12:25 | 6 | 0,20 pH 12 | 0 | 0.000000 | |
| | | !Zweck & RSD | --- | --- | Kein |
| ---------- Benutzer Nachfrage: Lauf beenden ---------- | | | | | |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0930_01.RST
Ergebnisse fertiggestellt: 09:27 September 30, 2015.
Benutzer: moser

V1 Kala pH12

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- | Benutzer Nachfrage: Datensammlung beginnen | | | | ---------- |
| 08:42 | 0 | Carryover | 821 | 0.001233 | LO |
| 08:42 | 0 | Baseline | 0 | 0.000000 | BL |
| 08:43 | 1 | Cal 0.200 mg | 131379 | 0.197172 | LO |
| 08:44 | 1 | Cal 0.200 mg | 134066 | 0.201206 | LO |
| 08:44 | 1 | Cal 0.200 mg | 134080 | 0.201226 | LO |
| 08:48 | 1 | Cal 0.200 mg | 133526 | 0.200396 | LO |
| | | !Zweck & RSD | 133263 | 0.200000 | .962% |
| 08:50 | 0 | Blank | -270 | -0.000405 | LO |
| 08:50 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 08:51 | 6 | 0,2 | 136067 | 0.204208 | LO |
| 08:52 | 6 | 0,2 | 137378 | 0.206175 | LO |
| 08:54 | 6 | 0,2 | 137442 | 0.206271 | LO |
| | | !Zweck & RSD | 136962 | 0.205552 | .567% |
| 08:57 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 08:58 | 5 | 0,15 | 102141 | 0.153293 | LO |
| 08:58 | 5 | 0,15 | 103081 | 0.154703 | LO |
| 08:59 | 5 | 0,15 | 101977 | 0.153047 | LO |
| | | !Zweck & RSD | 102400 | 0.153681 | .582% |
| 09:00 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 09:[illegible] | 4 | 0,10 | 63828 | 0.095793 | LOOL |
| 09:[illegible] | 4 | 0,10 | 65896 | 0.098896 | LO |
| 09:05 | 4 | 0,10 | 65079 | 0.097670 | LO |
| | | !Zweck & RSD | 65487 | 0.098283 | 1.59% |
| 09:06 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 09:07 | 3 | 0,05 | 31913 | 0.047895 | LO |
| 09:11 | 3 | 0,05 | 32226 | 0.048364 | LO |
| 09:12 | 3 | 0,05 | 33149 | 0.049750 | LOOL |
| | | !Zweck & RSD | 32069 | 0.048130 | 2% |
| 09:13 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 09:13 | 2 | 0,02 | 13029 | 0.019553 | LO |
| 09:14 | 2 | 0,02 | 13243 | 0.019875 | LO |
| 09:18 | 2 | 0,02 | 13365 | 0.020058 | LO |
| | | !Zweck & RSD | 13212 | 0.019829 | 1.29% |
| 09:19 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 09:20 | 1 | cal. WH | 131722 | 0.197688 | LO |
| 09:21 | 1 | cal. WH | 135903 | 0.203963 | LOOL |
| 09:21 | 1 | cal. WH | 132489 | 0.198839 | LO |
| | | !Zweck & RSD | 132106 | 0.198263 | 1.68% |
| 09:24 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- | Benutzer Nachfrage: Lauf beenden | | | | ---------- |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0928_06.RST
Ergebnisse fertiggestellt: 13:43 September 28, 2015.
Benutzer: moser

V11: +PbCO3 pH7

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- | Benutzer Nachfrage: Datensammlung beginnen | ---------- | | | |
| 12:55 | 0 | Carryover | 765 | 0.001068 | LO |
| 12:59 | 0 | Baseline | 0 | 0.000000 | BL |
| 13:00 | 1 | Cal 0.200 mg | 141173 | 0.197128 | LO |
| 13:01 | 1 | Cal 0.200 mg | 145918 | 0.203752 | LOOL |
| 13:01 | 1 | Cal 0.200 mg | 142600 | 0.199120 | LO |
| | | !Zweck & RSD | 141887 | 0.198124 | 1.72% |
| 13:02 | 0 | Blank | -201 | -0.000280 | LO |
| 13:06 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:07 | 2 | 0,02 pb ph7 | 12975 | 0.018117 | LO |
| 13:08 | 2 | 0,02 pb ph7 | 13047 | 0.018218 | LO |
| 13:08 | 2 | 0,02 pb ph7 | 13048 | 0.018220 | LO |
| | | !Zweck & RSD | 13023 | 0.018185 | .323% |
| 13:09 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:13 | 3 | 0,05 pb ph7 | 32436 | 0.045291 | LO |
| 13:14 | 3 | 0,05 pb ph7 | 32588 | 0.045504 | LO |
| 13:15 | 3 | 0,05 pb ph7 | 32667 | 0.045614 | LO |
| | | !Zweck & RSD | 32563 | 0.045470 | .361% |
| 13:16 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:16 | 4 | 0,10 pb ph7 | 66900 | 0.093415 | LO |
| 13:20 | 4 | 0,10 pb ph7 | 66883 | 0.093393 | LO |
| 13:[illegible] | 4 | 0,10 pb ph7 | 66714 | 0.093156 | LO |
| | | !Zweck & RSD | 66832 | 0.093321 | .154% |
| 13:22 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:23 | 5 | 0,15 pb ph7 | 98868 | 0.138054 | LO |
| 13:23 | 5 | 0,15 pb ph7 | 99801 | 0.139357 | LO |
| 13:26 | 5 | 0,15 pb ph7 | 99576 | 0.139042 | LO |
| | | !Zweck & RSD | 99415 | 0.138818 | .49% |
| 13:29 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:30 | 6 | 0,20 pb ph7 | 130982 | 0.182898 | LO |
| 13:30 | 6 | 0,20 pb ph7 | 132520 | 0.185044 | LO |
| 13:31 | 6 | 0,20 pb ph7 | 132634 | 0.185204 | LO |
| | | !Zweck & RSD | 132045 | 0.184382 | .699% |
| 13:32 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 13:36 | 1 | cal. WH | 143686 | 0.200635 | LO |
| 13:37 | 1 | cal. WH | 145460 | 0.203114 | LO |
| 13:37 | 1 | cal. WH | 145697 | 0.203444 | LO |
| | | !Zweck & RSD | 144948 | 0.202398 | .758% |
| 13:38 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- | Benutzer Nachfrage: Lauf beenden | ---------- | | | |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0928_07.RST
Ergebnisse fertiggestellt: 14:39 September 28, 2015.
Benutzer: moser

VR.1+ $RCO_3$ pH11

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- Benutzer Nachfrage: Datensammlung beginnen ---------- | | | | | |
| 13:52 | 0 | Carryover | 598 | 0.000783 | LO |
| 13:52 | 0 | Baseline | 0 | 0.000000 | BL |
| 13:53 | 1 | Cal 0.200 mg | 151326 | 0.198070 | LO |
| 13:57 | 1 | Cal 0.200 mg | 153489 | 0.200900 | LO |
| 13:58 | 1 | Cal 0.200 mg | 153587 | 0.201029 | LO |
| | | !Zweck & RSD | 152801 | 0.200000 | .836% |
| 13:59 | 0 | Blank | 247 | 0.000323 | LO |
| 14:01 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:02 | 2 | 0,02 pb ph11 | 13568 | 0.017759 | LO |
| 14:03 | 2 | 0,02 pb ph11 | 13695 | 0.017925 | LO |
| 14:04 | 2 | 0,02 pb ph11 | 13608 | 0.017812 | LO |
| | | !Zweck & RSD | 13624 | 0.017832 | .476% |
| 14:04 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:08 | 3 | 0,05 pb ph11 | 34230 | 0.044803 | LO |
| 14:10 | 3 | 0,05 pb ph11 | 34542 | 0.045211 | LO |
| 14:10 | 3 | 0,05 pb ph11 | 34577 | 0.045258 | LO |
| | | !Zweck & RSD | 34450 | 0.045091 | .555% |
| 14:11 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:11 | 4 | 0,10 pb ph11 | 70661 | 0.092487 | LO |
| 14:15 | 4 | 0,10 pb ph11 | 71321 | 0.093351 | LO |
| 14[illegible] | 4 | 0,10 pb ph11 | 71078 | 0.093033 | LO |
| | | !Zweck & RSD | 71020 | 0.092957 | .47% |
| 14:17 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:18 | 5 | 0,15 pb ph11 | 103119 | 0.134971 | LO |
| 14:19 | 5 | 0,15 pb ph11 | 105058 | 0.137510 | LO |
| 14:21 | 5 | 0,15 pb ph11 | 105014 | 0.137452 | LO |
| | | !Zweck & RSD | 104397 | 0.136644 | 1.06% |
| 14:24 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:25 | 6 | 0,20 pb ph11 | 141770 | 0.185561 | LO |
| 14:25 | 6 | 0,20 pb ph11 | 144395 | 0.188997 | LO |
| 14:26 | 6 | 0,20 pb ph11 | 144233 | 0.188785 | LO |
| | | !Zweck & RSD | 143466 | 0.187781 | 1.03% |
| 14:27 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 14:31 | 1 | cal. WH | 152135 | 0.199129 | LO |
| 14:32 | 1 | cal. WH | 154328 | 0.201999 | LO |
| 14:32 | 1 | cal. WH | 154132 | 0.201742 | LO |
| | | !Zweck & RSD | 153532 | 0.200957 | .79% |
| 14:33 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- Benutzer Nachfrage: Lauf beenden ---------- | | | | | |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0930_03.RST
Ergebnisse fertiggestellt: 11:53 September 30, 2015.
Benutzer: moser

V2.2 pH11

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- | Benutzer Nachfrage: Datensammlung beginnen | ---------- | | | |
| 11:13 | 0 | Carryover | 699 | 0.000884 | LO |
| 11:14 | 0 | Baseline | 0 | 0.000000 | BL |
| 11:15 | 1 | Cal 0.200 mg | 157323 | 0.198832 | LO |
| 11:15 | 1 | Cal 0.200 mg | 158570 | 0.200408 | LO |
| 11:20 | 1 | Cal 0.200 mg | 158509 | 0.200330 | LO |
| 11:20 | 1 | Cal 0.200 mg | 158588 | 0.200430 | LO |
| | | !Zweck & RSD | 158247 | 0.200000 | .39% |
| 11:21 | 0 | Blank | -159 | -0.000201 | LO |
| 11:22 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:22 | 2 | 0,1pB ph11 | 117160 | 0.148072 | LO |
| 11:26 | 2 | 0,1pB ph11 | 118854 | 0.150213 | LO |
| 11:27 | 2 | 0,1pB ph11 | 118568 | 0.149852 | LO |
| | | !Zweck & RSD | 118194 | 0.149379 | .767% |
| 11:28 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:29 | 3 | 0,5pb ph11 | 130291 | 0.164667 | LO |
| 11:29 | 3 | 0,5pb ph11 | 131566 | 0.166279 | LO |
| 11:33 | 3 | 0,5pb ph11 | 132328 | 0.167242 | LO |
| | | !Zweck & RSD | 131395 | 0.166063 | .783% |
| 11:35 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:[illegible] | 4 | 1,0pb ph11 | 143840 | 0.181792 | LO |
| 11:[illegible] | 4 | 1,0pb ph11 | 144784 | 0.182984 | LO |
| 11:36 | 4 | 1,0pb ph11 | 145519 | 0.183914 | LO |
| | | !Zweck & RSD | 144715 | 0.182897 | .582% |
| 11:39 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:42 | 5 | 2,0pb ph11 | 146301 | 0.184902 | LO |
| 11:42 | 5 | 2,0pb ph11 | 147641 | 0.186595 | LO |
| 11:43 | 5 | 2,0pb ph11 | 146859 | 0.185607 | LO |
| | | !Zweck & RSD | 146934 | 0.185701 | .458% |
| 11:44 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:45 | 1 | cal. WH | 156738 | 0.198092 | LO |
| 11:49 | 1 | cal. WH | 157832 | 0.199475 | LO |
| 11:50 | 1 | cal. WH | 159390 | 0.201444 | LO |
| | | !Zweck & RSD | 157987 | 0.199670 | .844% |
| 11:50 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- | Benutzer Nachfrage: Lauf beenden | ---------- | | | |

Seite #1

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0930_02.RST
Ergebnisse fertiggestellt: 10:56 September 30, 2015.
Benutzer: moser

VL2 pH7

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- | Benutzer Nachfrage: Datensammlung beginnen | | | | ---------- |
| 10:15 | 0 | Carryover | 644 | 0.000820 | LO |
| 10:15 | 0 | Baseline | 0 | 0.000000 | BL |
| 10:16 | 1 | Cal 0.200 mg | 155703 | 0.198269 | LO |
| 10:20 | 1 | Cal 0.200 mg | 157126 | 0.200080 | LO |
| 10:21 | 1 | Cal 0.200 mg | 157583 | 0.200662 | LO |
| 10:22 | 1 | Cal 0.200 mg | 157839 | 0.200989 | LO |
| | | !Zweck & RSD | 157063 | 0.200000 | .607% |
| 10:23 | 0 | Blank | 164 | 0.000209 | LO |
| 10:23 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:27 | 2 | 0,1pB | 117678 | 0.149848 | LO |
| 10:29 | 2 | 0,1pB | 118837 | 0.151324 | LO |
| 10:29 | 2 | 0,1pB | 118414 | 0.150786 | LO |
| | | !Zweck & RSD | 118310 | 0.150653 | .496% |
| 10:30 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:30 | 3 | 0,5pb | 128578 | 0.163728 | LO |
| 10:33 | 3 | 0,5pb | 130084 | 0.165646 | LO |
| 10:36 | 3 | 0,5pb | 129479 | 0.164876 | LO |
| | | !Zweck & RSD | 129381 | 0.164750 | .586% |
| 10:36 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:[illegible] | 4 | 1,0pb | 144238 | 0.183668 | LO |
| 10:[illegible] | 4 | 1,0pb | 145667 | 0.185488 | LO |
| 10:39 | 4 | 1,0pb | 144922 | 0.184540 | LO |
| | | !Zweck & RSD | 144942 | 0.184566 | .493% |
| 10:43 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:44 | 5 | 2,0pb | 153565 | 0.195546 | LOOL |
| 10:44 | 5 | 2,0pb | 147278 | 0.187541 | LO |
| 10:45 | 5 | 2,0pb | 147764 | 0.188159 | LO |
| | | !Zweck & RSD | 147521 | 0.187850 | 2.37% |
| 10:46 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 10:50 | 1 | cal. WH | 158170 | 0.201410 | LO |
| 10:51 | 1 | cal. WH | 159595 | 0.203225 | LO |
| 10:54 | 1 | cal. WH | 159664 | 0.203313 | LO |
| | | !Zweck & RSD | 159143 | 0.202649 | .53% |
| 10:54 | 0 | Read Baselin | 0 | 0.000000 | BL |
| ---------- | Benutzer Nachfrage: Lauf beenden | | | | ---------- |

Seite #1

## 11.3. **Ad 7.2.4.1:** original measurement report “0922_03”

Ergebnisreport des Laufs
Ergebnisse: L:\LABOR\CN_ANA~1\1MOSER~1\REPORTS\0922_03.RST
Ergebnisse fertiggestellt: 11:51 September 22, 2015.
Benutzer: moser

V1 pH7 V1: pH7 vs. pH11

Kanal 2

| Zeit | Prob | Name | Höhe | Kalk. | Flagg |
|---|---|---|---|---|---|
| ---------- Benutzer Nachfrage: Datensammlung beginnen ---------- | | | | | |
| 11:16 | 0 | Carryover | 731 | 0.001341 | LO |
| 11:19 | 0 | Baseline | 0 | 0.000000 | BL |
| 11:21 | 1 | Cal 0.200 mg | 106851 | 0.195905 | LOOL |
| 11:21 | 1 | Cal 0.200 mg | 109915 | 0.201524 | LO |
| 11:22 | 1 | Cal 0.200 mg | 110486 | 0.202571 | LO |
| | | !Zweck & RSD | 110201 | 0.202047 | 1.77% |
| 11:23 | 0 | Blank | 158 | 0.000289 | LO |
| 11:25 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:28 | 4 | 0,10 pH 7 | 49732 | 0.091181 | LO |
| 11:29 | 4 | 0,10 pH 7 | 50320 | 0.092260 | LO |
| 11:29 | 4 | 0,10 pH 7 | 50442 | 0.092484 | LO |
| | | !Zweck & RSD | 50165 | 0.091975 | .757% |
| 11:30 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:32 | 5 | 0,15 pH 7 | 74608 | 0.136790 | LO |
| 11:35 | 5 | 0,15 pH 7 | 75755 | 0.138893 | LO |
| 11:36 | 5 | 0,15 pH 7 | 75220 | 0.137912 | LO |
| | | !Zweck & RSD | 75194 | 0.137865 | .763% |
| 11:36 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:37 | 6 | 0,20 pH 7 | 99553 | 0.182525 | LO |
| 11:38 | 6 | 0,20 pH 7 | 101160 | 0.185471 | LO |
| 11:39 | 6 | 0,20 pH 7 | 100870 | 0.184940 | LO |
| | | !Zweck & RSD | 100528 | 0.184312 | .852% |
| 11:43 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:44 | 1 | cal. WH | 108200 | 0.198380 | LO |
| 11:44 | 1 | cal. WH | 110252 | 0.202142 | LO |
| 11:45 | 1 | cal. WH | 110482 | 0.202563 | LO |
| | | !Zweck & RSD | 109645 | 0.201028 | 1.15% |
| 11:49 | 0 | Read Baselin | 0 | 0.000000 | BL |
| 11:50 | 6 | 0,20 pH 7 | 0 | 0.000000 | |
| ---------- Benutzer Nachfrage: Lauf beenden ---------- | | | | | |

Seite #1

## Ad 7.2.4.1: Validata plot for the comparison of calibration curves at pH 7, pH 11 and pH 12 (V 1)

## pH 7:

| 23.09.2015 | SOP | mOSER | | | | | | | | | Validata 3.02 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Beschreibung | Konzentrationsdaten aus Messung bei pH11; Signalhöhen aus Messung pH7; OHNE NIEDRIG | | | | | | pH7; c aus pH11; h aus pH7; OHNE NIEDRIGSTEN PUNKT.xls[Komponente1] | | | | |
| Verfahren | Verfahren | | | | | | | | | | |
| Kalibrationskurve | | | | | | | | | | | |
| | | | NORMGERECHT VALIDIERT | | | | | | | | |
| # Messung | # Rep. | # Konzstufen | Profil | | Arbeitsbereich | | | | | | |
| 12 | 3 | 4 | voest_01__ohne_Leerprobe | | 0,043887667 | 0,181421667 | | | | | |
| x | y1 | y2 | y3 | y4 | y5 | y6 | y7 | y8 | y9 | y10 | y_varianz | y_i_quer |
| mg/l | pA | | | | | | | | | | | |
| 0,043887667 | 23047 | 24093 | 23570 | | | | | | | | 273529 | 23570 |
| 0,088977333 | 49732 | 50320 | 50442 | | | | | | | | 144121,3333 | 50164,66667 |
| 0,135015667 | 74608 | 75755 | 75220 | | | | | | | | 329396,3333 | 75194,33333 |
| 0,181421667 | 99553 | 101160 | 100870 | | | | | | | | 733506,3333 | 100527,6667 |

| Datenblatt (Linear (normgerecht)) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Konzentration | Meßwerte | geschätzte Werte | Residuen | Vertrauens-intervall (-) | Vertrauens-intervall (+) | Prognose-intervall (-) | Prognose-intervall (+) | Gewichte | berechnete Konzentration | % Abweichung |
| 0,043887667 | 23047 | 24183,27852 | -1136,27852 | 0,042317405 | 0,045457928 | 0,041435739 | 0,046339595 | | 0,041850927 | -4,640802211 |
| 0,043887667 | 24093 | 24183,27852 | -90,27852014 | 0,042317405 | 0,045457928 | 0,041435739 | 0,046339595 | | 0,043725846 | -0,368716603 |
| 0,043887667 | 23570 | 24183,27852 | -613,2785201 | 0,042317405 | 0,045457928 | 0,041435739 | 0,046339595 | | 0,042788386 | -2,504759407 |
| 0,088977333 | 49732 | 49338,39141 | 393,6085919 | 0,087942753 | 0,090011913 | 0,086828709 | 0,091125957 | | 0,089682863 | 0,792931988 |
| 0,088977333 | 50320 | 49338,39141 | 981,6085919 | 0,087942753 | 0,090011913 | 0,086828709 | 0,091125957 | | 0,090736833 | 1,977469162 |
| 0,088977333 | 50442 | 49338,39141 | 1103,608592 | 0,087942753 | 0,090011913 | 0,086828709 | 0,091125957 | | 0,090955513 | 2,22324048 |
| 0,135015667 | 74608 | 75022,75676 | -414,756758 | 0,133986036 | 0,136045298 | 0,132869421 | 0,137161912 | | 0,13427223 | -0,550630242 |
| 0,135015667 | 75755 | 75022,75676 | 732,243242 | 0,133986036 | 0,136045298 | 0,132869421 | 0,137161912 | | 0,136328187 | 0,972124662 |
| 0,135015667 | 75220 | 75022,75676 | 197,243242 | 0,133986036 | 0,136045298 | 0,132869421 | 0,137161912 | | 0,135369218 | 0,261859733 |
| 0,181421667 | 99553 | 100912,24 | -1359,239981 | 0,179841717 | 0,183001616 | 0,178963523 | 0,183879811 | | 0,178985276 | -1,342943502 |
| 0,181421667 | 101160 | 100912,24 | 247,7600195 | 0,179841717 | 0,183001616 | 0,178963523 | 0,183879811 | | 0,181865768 | 0,244789524 |
| 0,181421667 | 100870 | 100912,24 | -42,23998051 | 0,179841717 | 0,183001616 | 0,178963523 | 0,183879811 | | 0,181345953 | -0,041733548 |

| Test der Varianzen | | |
|---|---|---|
| | unten | oben |
| s(rel) | 2,218922359 | 0,851954364 |
| Freiheitsgrade | 2 | 2 |
| Varianz | 273529 | 733506,3333 |
| Prüfwert | 2,681640094 | |
| F_95Var | 19 | |
| F_99Var | 99 | |
| Ok, kein signifikanter Unterschied auf Niveau 95% | | |
| Ok, kein signifikanter Unterschied auf Niveau 99% | | |

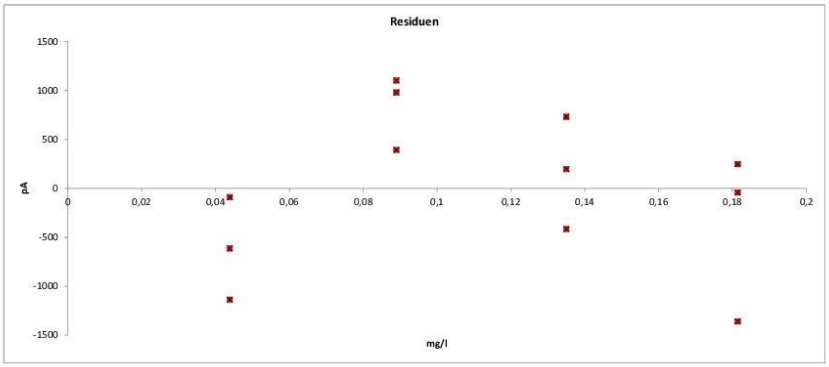
| Linearitätstest | |
|---|---|
| Prüfwert | 7,175302689 |
| F_99 | 10,56143105 |
| Ok, kein signifikanter Unterschied (99% Niveau) | |

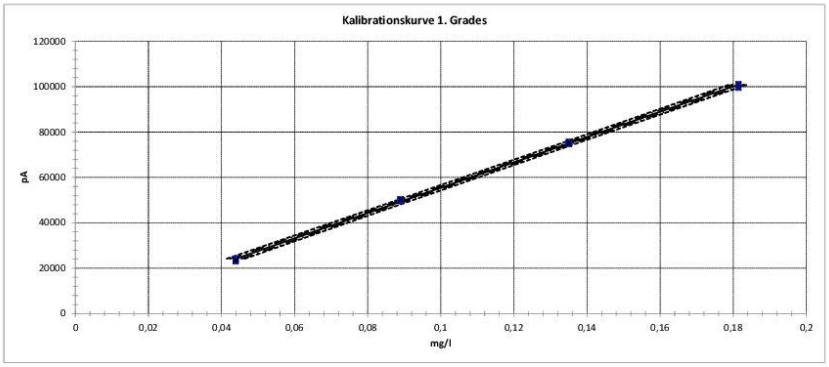
| Kalibrierfunktion 1. Grades (y=a+b*x) | | |
|---|---|---|
| Steigung | 557890,8594 | pA/(mg/l) |
| VB(Steigung) | 547646,9404 568134,7784 | pA/(mg/l) |
| Achsenabschnitt | -301,2495548 | pA |
| VB(Achsenabschnitt) | -1566,136556 963,6374463 | pA |
| Mittelwert(x) | 0,112325583 | mg/l |
| Mittelwert(y) | 62364,16667 | pA |
| Reststandardabweichung | 816,6783641 | pA |
| Verfahrensstd.abweichung | 0,001463868 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,30323616 | % |
| t-Wert (95%) | 2,228138852 | |
| Qx | 0,031553993 | (mg/l)^2 |

| Kalibrierfunktion 2. Grades (y=a+b*x+c*x^2) | | |
|---|---|---|
| a | -2684,405862 | pA |
| b | 611210,9433 | pA/mg/l |
| c | -236516,2282 | |
| Empfindlichkeit | 558077,2967 | pA/(mg/l) |
| Mittelwert(x) | 0,112325583 | mg/l |
| Mittelwert(y) | 62364,16667 | pA |
| Reststandardabweichung | 642,132782 | pA |
| Verfahrensstd.abweichung | 0,001150616 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,024358096 | % |
| t-Wert (95%) | 2,262157163 | |
| Prüfwert (Lösung) | 1,292112063 | mg/l |
| Ok, kein Extremwert innerhalb des Arbeitsbereiches | | |

| Nachweisgrenze - Kalibrationsmethode | | |
|---|---|---|
| Ergebnisunsicherheit (k) | 3 | |
| Konzentration (0) | 0 | |
| Geschätzter Meßwert (0) | -301,2495548 | pA |
| Wiederholungen (Meßprobe) | 3 | |
| Entscheidungsniveau NWG | 0,95 | |
| t-Werte (1/2-seitig) | 1,812461123 2,228138852 | |
| Entscheidungsniveau VB | 0,95 | |
| Faktoren VB | 0,698717043 1,754933527 | |
| Kritischer Wert | 1036,281055 | pA |
| Nachweisgrenze | 0,002397477 | mg/l |
| Schnellschätzung NWG | 0,003337618 | mg/l |
| VB Nachweisgrenze | 0,001675158 0,004207413 | mg/l |
| Erfassungsgrenze | 0,004794954 | mg/l |
| Schnellschätzung EG | 0,006675236 | mg/l |
| VB Erfassungsgrenze | 0,003350316 0,008414826 | mg/l |
| Bestimmungsgrenze | 0,008569394 | mg/l |
| Schnellschätzung BG | 0,010012855 | mg/l |
| VB Bestimmungsgrenze | 0,005987582 0,015038717 | mg/l |
| Ok, Arbeitsbereich abgesichert | | |

| ANOVA für Lineare Regression | | | | | |
|---|---|---|---|---|---|
| Quelle | FG | QS | QS/FG | F-Verhältnis | Wahrsch. |
| Modell | 1 | 9820934700 | 9820934700 | 14724,8447 | 3,54402E-17 |
| Residuen | 10 | 6669635,504 | 666963,5504 | | |
| LOF | 2 | 3708529,504 | 1854264,752 | 5,009654506 | 0,038851466 |
| PE | 8 | 2961106 | 370138,25 | | |




xrm003.10.08.201618:06

## Ergebnis Validierung Verfahren

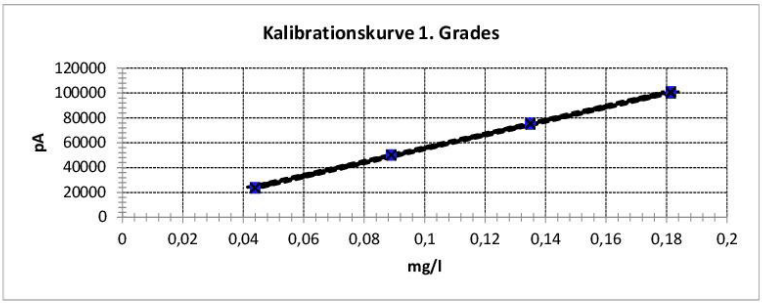
| | | | |
|---|---|---|---|
| Datum | 23.09.2015 | | |
| Beschreibung | Konzentrationsdaten aus Messung bei pH11; Signalhöhen aus Messun | | |
| Bearbeiter | mOSER | | |
| # Messung | 12 | Einheit Konz.: | mg/l |
| # Rep. | 3 | Einheit Mess.: | pA |
| # Konz.stufen | 4 | | |

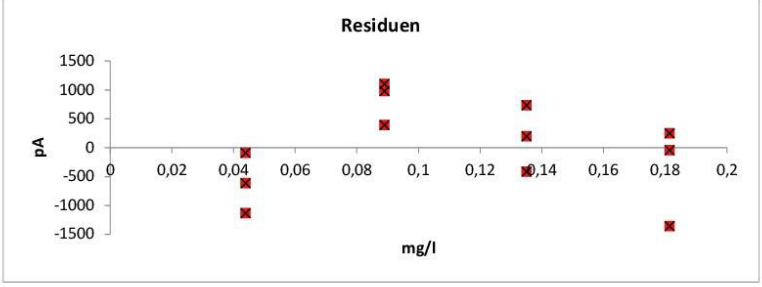
| | |
|---|---|
| **Modell** | Linear (normgerecht) |
| **y[pA] = 557890,85943[pA/(mg/l)] * x [mg/l] -301,24955[pA]** | |

| | | | |
|---|---|---|---|
| Varianzcheck | 95% Ok, 99% Ok | | |
| Linearität | Ok | | |
| Varianz unten | 273529 | | |
| Varianz oben | 733506,3333 | | |
| VB(Steigung) | 547646,9404 | 568134,7784 | pA/(mg/l) |
| VB(Achsenabschnitt) | -1566,136556 | 963,6374463 | pA |
| Reststd.abweichung | 816,6783641 | | pA |
| Verfahrensstd.abweichung | 0,001463868 | | mg/l |
| Rel. Verfahrensstd.abw. | 1,30323616 | | % |

| **Nachweis- und Bestimmungsgrenze** | | | |
|---|---|---|---|
| | Leerwertmeth. | Kalibriermeth. | |
| Entscheidungsniveaus (VB) | 0,95 | 0,95 | |
| Nachweisgrenze | N/A | 0,002397477 | mg/l |
| Erfassungsgrenze | N/A | 0,004794954 | mg/l |
| Bestimmungsgrenze | | 0,008569394 | mg/l |

**Kalibrierkurve**



## pH 12:

| 01.10.2015 | SOP | moser | | | | | | | | | | Validata 3.02 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Beschreibung | ph12 Kalibrierung | | | | | | V1 pH11.xls[Komponente1] | | | | | |
| Verfahren | ANTEC nach ISO Methode | | | | | | | | | | | |

**Kalibrationskurve**

**NICHT NORMGERECHT!**

| # Messung | # Rep. | # Konzstufen | Profil | | Arbeitsbereich | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 3 | 5 | voest_01__ohne_Leerprobe | | 0,02 | 0,2 | | | | | | |
| x | y1 | y2 | y3 | y4 | y5 | y6 | y7 | y8 | y9 | y10 | y_varianz | y_i_quer |
| mg/l | pA | | | | | | | | | | | |
| 0,02 | 15109 | 15211 | 15118 | | | | | | | | 3189 | 15146 |
| 0,05 | 37760 | 37973 | 38159 | | | | | | | | 39861 | 37964 |
| 0,1 | 75213 | 75733 | 76271 | | | | | | | | 279868 | 75739 |
| 0,15 | 114971 | 119132 | 116177 | | | | | | | | 4583397 | 116760 |
| 0,2 | 155024 | 156737 | 156235 | | | | | | | | 775482,3333 | 155998,6667 |

**Datenblatt (Linear (normgerecht))**

| Konzentration | Meßwerte | geschätzte Werte | Residuen | Vertrauens-intervall (-) | Vertrauens-intervall (+) | Prognose-intervall (-) | Prognose-intervall (+) | Gewichte | berechnete Konzentration | % Abweichung |
|---|---|---|---|---|---|---|---|---|---|---|
| 0,02 | 15109 | 14439,23014 | 669,7698562 | 0,018564202 | 0,021435798 | 0,017561936 | 0,022438064 | | 0,020853957 | 4,269786057 |
| 0,02 | 15211 | 14439,23014 | 771,7698562 | 0,018564202 | 0,021435798 | 0,017561936 | 0,022438064 | | 0,020984007 | 4,920036548 |
| 0,02 | 15118 | 14439,23014 | 678,7698562 | 0,018564202 | 0,021435798 | 0,017561936 | 0,022438064 | | 0,020865432 | 4,327161101 |
| 0,05 | 37760 | 37968,62414 | -208,6241401 | 0,04885651 | 0,05114349 | 0,047721797 | 0,052278203 | | 0,049734004 | -0,531991959 |
| 0,05 | 37973 | 37968,62414 | 4,375859912 | 0,04885651 | 0,05114349 | 0,047721797 | 0,052278203 | | 0,050005579 | 0,011158451 |
| 0,05 | 38159 | 37968,62414 | 190,3758599 | 0,04885651 | 0,05114349 | 0,047721797 | 0,052278203 | | 0,050242729 | 0,485458809 |
| 0,1 | 75213 | 77184,2808 | -1971,280801 | 0,09911714 | 0,10088286 | 0,097840814 | 0,102159186 | | 0,097486615 | -2,513384919 |
| 0,1 | 75733 | 77184,2808 | -1451,280801 | 0,09911714 | 0,10088286 | 0,097840814 | 0,102159186 | | 0,098149616 | -1,850384418 |
| 0,1 | 76271 | 77184,2808 | -913,2808005 | 0,09911714 | 0,10088286 | 0,097840814 | 0,102159186 | | 0,098835566 | -1,1644339 |
| 0,15 | 114971 | 116399,9375 | -1428,937461 | 0,148922095 | 0,151077905 | 0,147753999 | 0,152246001 | | 0,148178103 | -1,214597759 |
| 0,15 | 119132 | 116399,9375 | 2732,062539 | 0,148922095 | 0,151077905 | 0,147753999 | 0,152246001 | | 0,153483382 | 2,322254912 |
| 0,15 | 116177 | 116399,9375 | -222,9374609 | 0,148922095 | 0,151077905 | 0,147753999 | 0,152246001 | | 0,149715755 | -0,189496985 |
| 0,2 | 155024 | 155615,5941 | -591,5941213 | 0,198433195 | 0,201566805 | 0,197482557 | 0,202517443 | | 0,199245717 | -0,377141537 |
| 0,2 | 156737 | 155615,5941 | 1121,405879 | 0,198433195 | 0,201566805 | 0,197482557 | 0,202517443 | | 0,201429794 | 0,714896788 |
| 0,2 | 156235 | 155615,5941 | 619,4058787 | 0,198433195 | 0,201566805 | 0,197482557 | 0,202517443 | | 0,200789743 | 0,394871546 |

**Test der Varianzen**

| | unten | oben |
|---|---|---|
| s(rel) | 0,372845845 | 0,564501458 |
| Freiheitsgrade | 2 | 2 |
| Varianz | 3189 | 775482,3333 |
| Prüfwert | 243,1741403 | |
| F_95Var | 19 | |
| F_99Var | 99 | |

WARNUNG: Signifikanter Unterschied auf Niveau 95%
WARNUNG: Signifikanter Unterschied auf Niveau 99%

**Linearitätstest**

| | |
|---|---|
| Prüfwert | 3,71915874 |
| F_99 | 9,330212103 |

Ok, kein signifikanter Unterschied (99% Niveau)

**Kalibrierfunktion 1. Grades (y=a+b*x)**

| | | |
|---|---|---|
| Steigung | 784313,1332 | pA/(mg/l) |
| VB(Steigung) | 773728,8982 794897,3682 | pA/(mg/l) |
| Achsenabschnitt | -1247,03252 | pA |
| VB(Achsenabschnitt) | -2546,783478 52,71843779 | pA |
| Mittelwert(x) | 0,104 | mg/l |
| Mittelwert(y) | 80321,53333 | pA |
| Reststandardabweichung | 1239,04145 | pA |
| Verfahrensstd.abweichung | 0,001579779 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,51901831 | % |
| t-Wert (95%) | 2,160368656 | |
| Qx | 0,06396 | (mg/l)^2 |

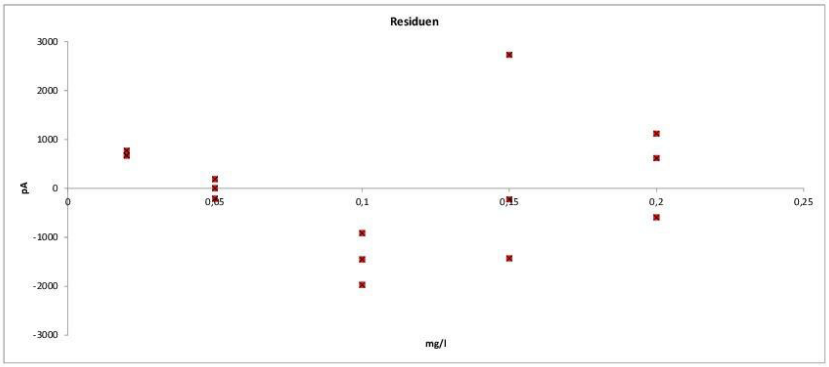
**Kalibrierfunktion 2. Grades (y=a+b*x+c*x^2)**

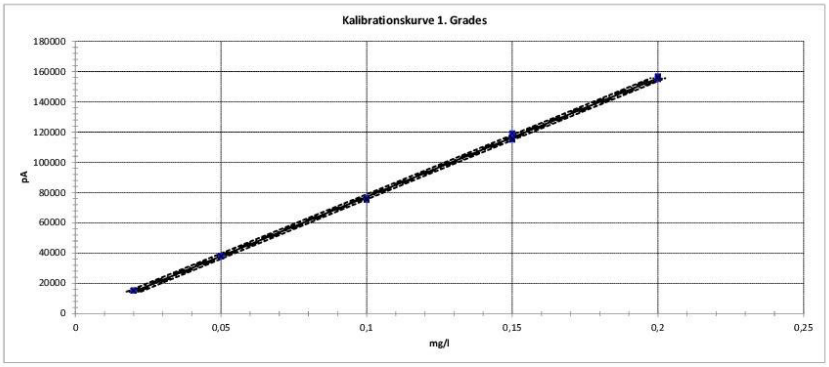
| | | |
|---|---|---|
| a | 61,36418633 | pA |
| b | 747039,0038 | pA/mg/l |
| c | 170299,2539 | |
| Empfindlichkeit | 782461,2486 | pA/(mg/l) |
| Mittelwert(x) | 0,104 | mg/l |
| Mittelwert(y) | 80321,53333 | pA |
| Reststandardabweichung | 1126,789682 | pA |
| Verfahrensstd.abweichung | 0,001440058 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,38467128 | % |
| t-Wert (95%) | 2,17881283 | |
| Prüfwert (Lösung) | -2,193312615 | mg/l |

Ok, kein Extremwert innerhalb des Arbeitsbereiches.

| Nachweisgrenze - Kalibrationsmethode | | |
|---|---|---|
| Ergebnisunsicherheit (k) | 3 | |
| Konzentration (0) | 0 | |
| Geschätzter Meßwert (0) | -1247,03252 | pA |
| Wiederholungen (Meßprobe) | 3 | |
| Entscheidungsniveau NWG | 0,95 | |
| t-Werte (1/2-seitig) | 1,770933396 2,160368656 | |
| Entscheidungsniveau VB | 0,95 | |
| Faktoren VB | 0,724953932 1,611042417 | |
| Kritischer Wert | 408,2972567 | pA |
| Nachweisgrenze | 0,002110547 | mg/l |
| Schnellschätzung NWG | 0,003412323 | mg/l |
| VB Nachweisgrenze | 0,001530049 0,003400181 | mg/l |
| Erfassungsgrenze | 0,004221094 | mg/l |
| Schnellschätzung EG | 0,006824645 | mg/l |
| VB Erfassungsgrenze | 0,003060099 0,006800362 | mg/l |
| Bestimmungsgrenze | 0,007587308 | mg/l |
| Schnellschätzung BG | 0,010236968 | mg/l |
| VB Bestimmungsgrenze | 0,005500449 0,012223475 | mg/l |
| Ok, Arbeitsbereich abgesichert | | |

| ANOVA für Lineare Regression | | | | | |
|---|---|---|---|---|---|
| Quelle | FG | QS | QS/FG | F-Verhältnis | Wahrsch. |
| Modell | 1 | 39344807935 | 39344807935 | 25628,06159 | 8,30363E-23 |
| Residuen | 13 | 19957908,3 | 1535223,715 | | |
| LOF | 3 | 8594313,635 | 2864771,212 | 2,521007917 | 0,117113856 |
| PE | 10 | 11363594,67 | 1136359,467 | | |

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## Ergebnis Validierung ANTEC nach ISO Methode

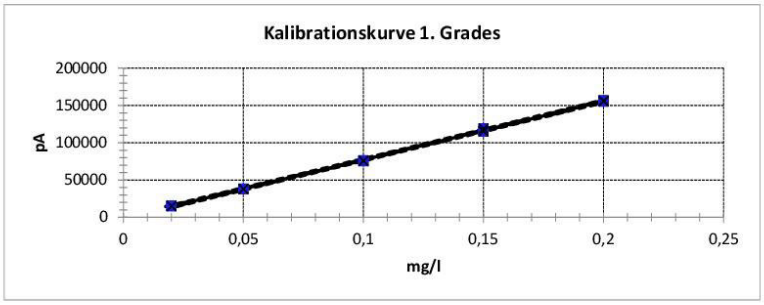
| | | | |
|---|---|---|---|
| Datum | 01.10.2015 | | |
| Beschreibung | ph12 Kalibrierung | | |
| Bearbeiter | moser | | |
| # Messung | 15 | Einheit Konz.: | mg/l |
| # Rep. | 3 | Einheit Mess.: | pA |
| # Konz.stufen | 5 | | |

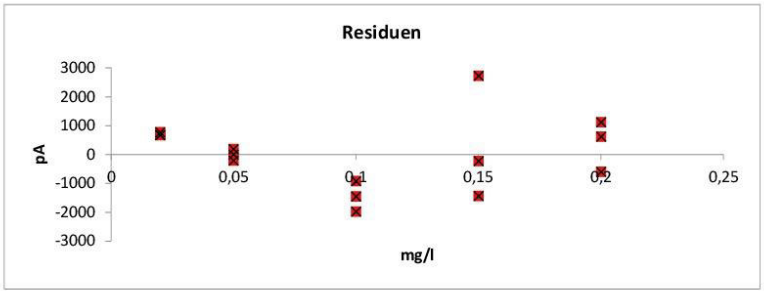
| | |
|---|---|
| **Modell** | Linear (normgerecht) |
| **y[pA] = 784313,13321[pA/(mg/l)] * x [mg/l] -1247,03252[pA]** | |

| | | | |
|---|---|---|---|
| Varianzcheck | 95% nicht ok! 99% nicht ok! | | |
| Linearität | Ok | | |
| Varianz unten | 3189 | | |
| Varianz oben | 775482,3333 | | |
| VB(Steigung) | 773728,8982 | 794897,3682 | pA/(mg/l) |
| VB(Achsenabschnitt) | -2546,783478 | 52,71843779 | pA |
| Reststd.abweichung | 1239,04145 | | pA |
| Verfahrensstd.abweichung | 0,001579779 | | mg/l |
| Rel. Verfahrensstd.abw. | 1,51901831 | | % |

| **Nachweis- und Bestimmungsgrenze** | | | |
|---|---|---|---|
| | Leerwertmeth. | Kalibriermeth. | |
| Entscheidungsniveaus (VB) | 0,95 | 0,95 | |
| Nachweisgrenze | N/A | 0,002110547 | mg/l |
| Erfassungsgrenze | N/A | 0,004221094 | mg/l |
| Bestimmungsgrenze | | 0,007587308 | mg/l |

**Kalibrierkurve**



## Ad 7.2.4.2. Validata report for 0.02 – 0.2 mg/L Cyanide + 0.2 g PbCO3/100mL (V 2.1)

| 01.10.2015 | SOP | moser | | | | | | | | | Validata 3.02 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Beschreibung | PbCO3 Behandlung; Kalibrationsgerade | | | | | V2.1 PbCO3 Behandlung.xls[Komponente1] | | | | | |
| Verfahren | Verfahren | | | | | | | | | | |
| **Kalibrationskurve** | | | | | | | | | | | |
| | | | NICHT NORMGERECHT! | | | | | | | | |
| # Messung | # Rep. | # Konzstufen | Profil | | Arbeitsbereich | | | | | | |
| 15 | 3 | 5 | voest_01__ohne_Leerprobe | | 0,02 | 0,2 | | | | | |
| x | y1 | y2 | y3 | y4 | y5 | y6 | y7 | y8 | y9 | y10 | y_varianz | y_i_quer |
| mg/l | pA | | | | | | | | | | | |
| 0,02 | 14552,48991 | 14633,24361 | 14634,36519 | | | | | | | | 2204,329956 | 14606,69957 |
| 0,05 | 35967,2662 | 36135,81424 | 36223,41487 | | | | | | | | 16949,07656 | 36108,83177 |
| 0,1 | 71968,75975 | 71950,47172 | 71768,66723 | | | | | | | | 12237,38991 | 71895,96624 |
| 0,15 | 108531,6589 | 109555,8532 | 109308,861 | | | | | | | | 285670,346 | 109132,1244 |
| 0,2 | 139505,0617 | 141143,1401 | 141264,5582 | | | | | | | | 965645,1478 | 140637,5867 |

**Datenblatt (Linear (normgerecht))**

| Konzentration | Meßwerte | geschätzte Werte | Residuen | Vertrauens-intervall (-) | Vertrauens-intervall (+) | Prognose-intervall (-) | Prognose-intervall (+) | Gewichte | berechnete Konzentration | % Abweichung |
|---|---|---|---|---|---|---|---|---|---|---|
| 0,02 | 14552,48991 | 15152,76846 | -600,2785585 | 0,018181624 | 0,021818376 | 0,016912297 | 0,023087703 | | 0,019150026 | -4,249869077 |
| 0,02 | 14633,24361 | 15152,76846 | -519,5248572 | 0,018181624 | 0,021818376 | 0,016912297 | 0,023087703 | | 0,019264371 | -3,678146745 |
| 0,02 | 14634,36519 | 15152,76846 | -518,4032781 | 0,018181624 | 0,021818376 | 0,016912297 | 0,023087703 | | 0,019265959 | -3,670206157 |
| 0,05 | 35967,2662 | 36339,7232 | -372,4570046 | 0,048551819 | 0,051448181 | 0,047114754 | 0,052885246 | | 0,049472614 | -1,054772644 |
| 0,05 | 36135,81424 | 36339,7232 | -203,9089573 | 0,048551819 | 0,051448181 | 0,047114754 | 0,052885246 | | 0,049711272 | -0,577456156 |
| 0,05 | 36223,41487 | 36339,7232 | -116,3083274 | 0,048551819 | 0,051448181 | 0,047114754 | 0,052885246 | | 0,049835311 | -0,329377191 |
| 0,1 | 71968,75975 | 71651,31443 | 317,445324 | 0,098881896 | 0,101118104 | 0,097265484 | 0,102734516 | | 0,100449492 | 0,449491672 |
| 0,1 | 71950,47172 | 71651,31443 | 299,1572983 | 0,098881896 | 0,101118104 | 0,097265484 | 0,102734516 | | 0,100423596 | 0,423596456 |
| 0,1 | 71768,66723 | 71651,31443 | 117,3528081 | 0,098881896 | 0,101118104 | 0,097265484 | 0,102734516 | | 0,100166168 | 0,166167544 |
| 0,15 | 108531,6589 | 106962,9057 | 1568,753259 | 0,14863488 | 0,15136512 | 0,147155536 | 0,152844464 | | 0,152221301 | 1,480867145 |
| 0,15 | 109555,8532 | 106962,9057 | 2592,947515 | 0,14863488 | 0,15136512 | 0,147155536 | 0,152844464 | | 0,153671525 | 2,447683065 |
| 0,15 | 109308,861 | 106962,9057 | 2345,955331 | 0,14863488 | 0,15136512 | 0,147155536 | 0,152844464 | | 0,153321792 | 2,2145281 |
| 0,2 | 139505,0617 | 142274,4969 | -2769,435129 | 0,198015709 | 0,201984291 | 0,196811767 | 0,203188233 | | 0,196078575 | -1,960712497 |
| 0,2 | 141143,1401 | 142274,4969 | -1131,356729 | 0,198015709 | 0,201984291 | 0,196811767 | 0,203188233 | | 0,198398038 | -0,80098113 |
| 0,2 | 141264,5582 | 142274,4969 | -1009,938694 | 0,198015709 | 0,201984291 | 0,196811767 | 0,203188233 | | 0,198569962 | -0,715019247 |

**Test der Varianzen**

| | unten | oben |
|---|---|---|
| s(rel) | 0,321429849 | 0,698726759 |
| Freiheitsgrade | 2 | 2 |
| Varianz | 2204,329956 | 965645,1478 |
| Prüfwert | 438,067425 | |
| F_95Var | 19 | |
| F_99Var | 99 | |

WARNUNG: Signifikanter Unterschied auf Niveau 95%
WARNUNG: Signifikanter Unterschied auf Niveau 99%

**Linearitätstest**

| | |
|---|---|
| Prüfwert | 11,09244484 |
| F_99 | 9,330212103 |

WARNUNG: Signifikanter Unterschied (99% Niveau)!

**Kalibrierfunktion 1. Grades (y=a+b*x)**

| | | |
|---|---|---|
| Steigung | 706231,8245 | pA/(mg/l) |
| VB(Steigung) | 694161,8107 718301,8383 | pA/(mg/l) |
| Achsenabschnitt | 1028,131974 | pA |
| VB(Achsenabschnitt) | -454,0735841 2510,337532 | pA |
| Mittelwert(x) | 0,104 | mg/l |
| Mittelwert(y) | 74476,24172 | pA |
| Reststandardabweichung | 1412,973857 | pA |
| Verfahrensstd.abweichung | 0,002000722 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,923771574 | % |
| t-Wert (95%) | 2,160368656 | |
| Qx | 0,06396 | (mg/l)^2 |

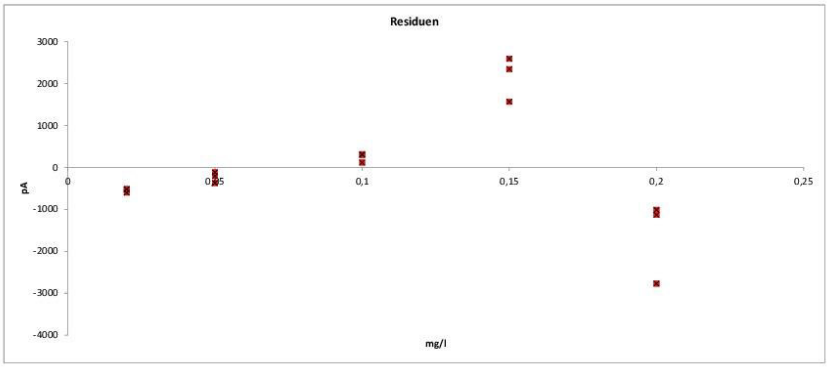
**Kalibrierfunktion 2. Grades (y=a+b*x+c*x^2)**

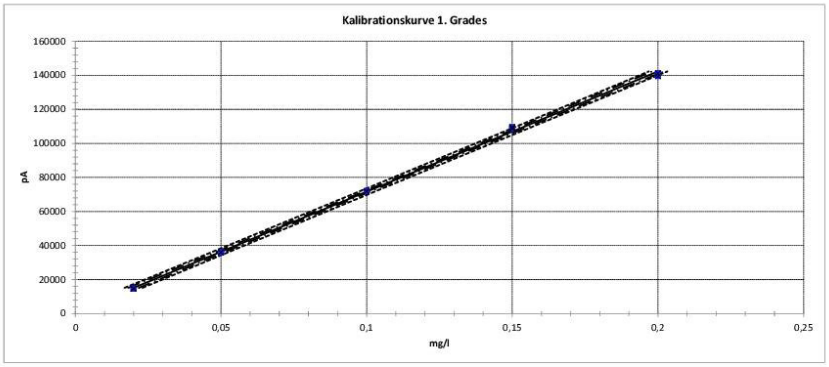
| | | |
|---|---|---|
| a | -1097,845738 | pA |
| b | 766797,529 | pA/mg/l |
| c | -276714,5594 | |
| Empfindlichkeit | 709240,9007 | pA/(mg/l) |
| Mittelwert(x) | 0,104 | mg/l |
| Mittelwert(y) | 74476,24172 | pA |
| Reststandardabweichung | 1060,158611 | pA |
| Verfahrensstd.abweichung | 0,001494779 | mg/l |
| Rel. Verfahrensstd.abweich. | 1,43728778 | % |
| t-Wert (95%) | 2,17881283 | |
| Prüfwert (Lösung) | 1,385538822 | mg/l |

Ok, kein Extremwert innerhalb des Arbeitsbereiches.

| Nachweisgrenze - Kalibrationsmethode | | |
|---|---|---|
| Ergebnisunsicherheit (k) | 3 | |
| Konzentration (0) | 0 | |
| Geschätzter Meßwert (0) | 1028,131974 | pA |
| Wiederholungen (Meßprobe) | 3 | |
| Entscheidungsniveau NWG | 0,95 | |
| t-Werte (1/2-seitig) | 1,770933396 2,160368656 | |
| Entscheidungsniveau VB | 0,95 | |
| Faktoren VB | 0,724953932 1,611042417 | |
| Kritischer Wert | 2915,831291 | pA |
| Nachweisgrenze | 0,002672917 | mg/l |
| Schnellschätzung NWG | 0,00432156 | mg/l |
| VB Nachweisgrenze | 0,001937742 0,004306183 | mg/l |
| Erfassungsgrenze | 0,005345835 | mg/l |
| Schnellschätzung EG | 0,008643121 | mg/l |
| VB Erfassungsgrenze | 0,003875484 0,008612367 | mg/l |
| Bestimmungsgrenze | 0,009564205 | mg/l |
| Schnellschätzung BG | 0,012964681 | mg/l |
| VB Bestimmungsgrenze | 0,006933608 0,015408341 | mg/l |
| Ok, Arbeitsbereich abgesichert | | |

| ANOVA für Lineare Regression | | | | | |
|---|---|---|---|---|---|
| Quelle | FG | QS | QS/FG | F-Verhältnis | Wahrsch. |
| Modell | 1 | 31900906421 | 31900906421 | 15978,45449 | 1,78705E-21 |
| Residuen | 13 | 25954436,56 | 1996495,12 | | |
| LOF | 3 | 23389023,98 | 7796341,328 | 30,39020463 | 2,44649E-05 |
| PE | 10 | 2565412,58 | 256541,258 | | |

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## Ergebnis Validierung Verfahren

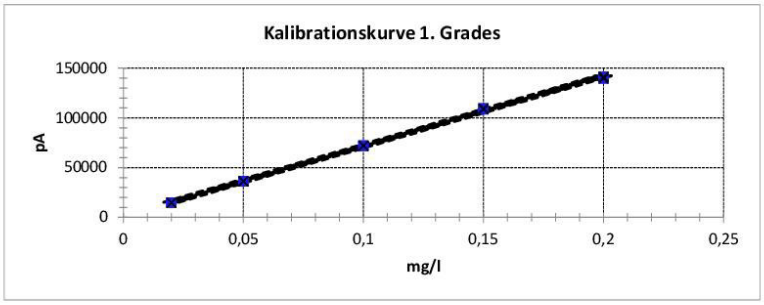
| | | | |
|---|---|---|---|
| Datum | 01.10.2015 | | |
| Beschreibung | PbCO3 Behandlung; Kalibrationsgerade | | |
| Bearbeiter | moser | | |
| # Messung | 15 | Einheit Konz.: | mg/l |
| # Rep. | 3 | Einheit Mess.: | pA |
| # Konz.stufen | 5 | | |

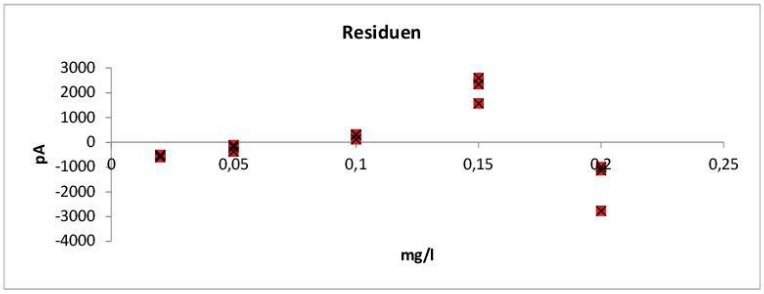
| | |
|---|---|
| **Modell** | Linear (normgerecht) |
| **y[pA] = 706231,82451[pA/(mg/l)] * x [mg/l] + 1028,13197[pA]** | |

| | | | |
|---|---|---|---|
| Varianzcheck | 95% nicht ok! 99% nicht ok! | | |
| Linearität | nicht ok! | | |
| Varianz unten | 2204,329956 | | |
| Varianz oben | 965645,1478 | | |
| VB(Steigung) | 694161,8107 | 718301,8383 | pA/(mg/l) |
| VB(Achsenabschnitt) | -454,0735841 | 2510,337532 | pA |
| Reststd.abweichung | 1412,973857 | | pA |
| Verfahrensstd.abweichung | 0,002000722 | | mg/l |
| Rel. Verfahrensstd.abw. | 1,923771574 | | % |

| **Nachweis- und Bestimmungsgrenze** | | | |
|---|---|---|---|
| | Leerwertmeth. | Kalibriermeth. | |
| Entscheidungsniveaus (VB) | 0,95 | 0,95 | |
| Nachweisgrenze | N/A | 0,002672917 | mg/l |
| Erfassungsgrenze | N/A | 0,005345835 | mg/l |
| Bestimmungsgrenze | | 0,009564205 | mg/l |

**Kalibrierkurve**



# List of figures

# List of tables

# Literature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Datum

Unterschrift