Final Report

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on
The H2S/pH2S Electrode Cell WT-573-H2S-SX

(Water Test Co.,Ltd. Bangkok/Thailand)

Dipl.-Geookol. Axel Heimann & Prof. Dr. Stefan Peiffer
Chair of Hydrology
University of Bayreuth
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1 Introduction

Accurate determination of dissolved sulfide concentration with analytically sufficient precision is a vital goal in many scientific fields and everyday life, due to its well-known toxic and corrosive properties [1], and the role of sulfide in metal precipitation [2].

Since the introduction of sulfide selective electrodes (Ag^0,Ag_2S) in environmental studies [3] some 40 years ago, much progress has been made on the potentiometric determination of sulfide. Applications of these methods have been numerous during the past decades, virtually covering all scales from micrometers recorded with microelectrodes [4-14], over studies in bacterial suspensions [15-19] to large scale anthropogenically influenced systems [20-26]. A combined glass//Ag°,Ag_2S electrode cell has been developped that allows measurements of the activity of dissolved H_2S [27] and at pH values below 5, also total sulfide directly [28], its potentiometric signal of electro-motoric force (emf) being proportional to the pH_2S value [27]:

$$pH_2S = -\log a(H_2S)$$

The pH_2S value of a sample can be calculated from a calibration line of the type:

$$pH_2S = (emf_{sample} - emf°)/S \qquad (1)$$

emf_{sample}: potentiometric signal as measured in the sample [mV]

$emf°$: intercept with the y-axis corresponding to pH_2S = 0 obtained from a linear regression analysis pH_2S vs. *emf* [mV]

S: slope of the calibration line, theoretically ~ 29 mV at 25 °C

The pH_2S value was used to establish a master variable for predicting trace metal speciation in the leachate of anaerobic waste waters [2].

Theoretical "Nernstian" behaviour of the glass//Ag°,Ag_2S electrode cell was demonstrated in metal sulfide buffers of low hydrogen sulfide activity down to 10^{-18} mol L^{-1} (i. e. pH_2S 18) [Peiffer & Frevert, 1987] [29]. This observation could be explained by relating the formation of a residual signal at the Ag_2S membrane to the half reaction:

$$Ag^\circ \leftrightarrow Ag^+ + e^-$$

As a consequence the suggestion was made to use silver ion buffers for the calibration of the pH_2S electrode cell (Peiffer et al, 1986 [30]; Klemm & Peiffer, 1991) [31]. The corresponding Ag^+-ion activity electrochemically generates a similar potentiometric signal as an H_2S activity provided by the addition of a sulfide standard solution.

Thus, today potentiometric sulfide determination is a well-established alternative to classic analytical methods, like the spectrophotometric methylene-blue method or iodometric titration. Nevertheless, only few studies on the direct comparison of those methods can be found in the literature, comparing either the iodometric method with potentiometric titration and direct potentiometry [32, 33], spectrophotometric with iodometric method [34], or redox titration with direct potentiometry and potentiometric titration [35].

In this study, however, we will present the first rigorous comparison of all three methods (direct potentiometry, iodometry, spectrophotometry) in various synthetic and natural solutions artificially enriched in sulfide. Moreover different calibration procedures for the H_2S electrode will be evaluated and intricacies will be pointed out. Thus, our contribution to this research topic is twofold, as we will

- provide a comparison of the use of sulfide-selective electrodes to two alternative standard methods for the determination of dissolved sulfide, as to precision, accuracy, and overall performance
- delineate a procedure that allows the correct handling and calibration of H_2S electrode cells

2 Methods

2.1 Experiments

2.1.1 Comparison of Calibration vessels

Calibrations were carried out in potassium hydrogen phthalate buffer, pH 5. Two calibration procedures were compared:

a) calibration procedure according to Peters et al, 1985.

A gas-tight glass vessel (Figure 1) with a volume of about 170 mL (with two electrodes inserted) was filled with 100 mL of the buffer solution and purged with N_2 for 1 hour prior to the calibration procedure. Therefore a gas volume of ca. 70 mL remains to which loss of H_2S may occur. Theoretically, according to Henry's law, this accounts for an error of 21.7 % at 20 °C.

$$c(H_2S)_{sol} = c(H_2S)_{exp} \frac{V_{aq} \cdot R \cdot T \cdot K_H}{V_{aq} \cdot R \cdot T \cdot K_H + V_{gas}}$$

$c(H_2S)_{sol}$: Concentration of H_2S in solution after equilibration between the solution and the gas phase [mol L^{-1}]

$c(H_2S)_{exp}$: Expected concentration of H_2S according to injection [mol L^{-1}]

V_{aq}, V_{gas}: Volume of solution and gas, resp. [L]

K_H: Henry constant: 0,105 mol L^{-1} atm^{-1} (Stumm & Morgan, 1996)

R: Gas constant: 0,082 L atm mol^{-1} K^{-1}

T: Absolute temperature [K]

b) calibration procedure according using BOD-type ("Karlsruhe") bottles [36].

A gas-tight glass vessel with a volume of about 110 mL (with one electrode inserted) was completely filled with buffer solution and purged with N_2 for 1 hour prior to the calibration procedure. The exact volume was determined by weighing the calibration vessel before and after filling with solution

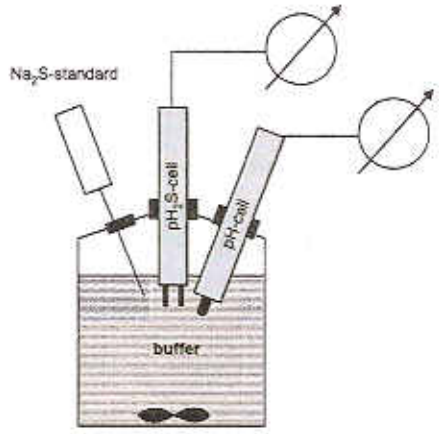

Figure 1 Calibration vessel containing a pH buffer solution to which a sulfide standard is added using a syringe.

Increasing volumes of a Na_2S stock solution (c(Na_2S) ~0.5 mol L^{-1}; exact concentration determined iodometrically) were injected by a syringe through a septum. Injected volumes ranged from 5 µL to 500 µL. Each calibration was performed as three replicates for each of the two electrodes

2.1.2 Comparison of calibration solutions for the potentiometric method

Calibrations of the pH_2S electrode cell were performed in three different buffer solutions:

- Merck pH 5 buffer, citrate-NaOH (I = 0,11 mol L^{-1})
- Ammonium Fluoroborate buffer, pH 2.65 (I = 0,02 mmol L^{-1})
- Potassium hydrogen phthalate buffer, pH 5 (according to [37])
  (I = 0,145 mol L^{-1})

2.1.3 Determination of isotherms of the pH_2S electrode cell

Calibrations were carried out in potassium hydrogen phthalate buffer solutions (pH 5) of a volume of 300 mL and a small head space of 42,82 mL. The closed calibration vessel had a cooling jacket through which thermostated water circulated. The temperature of the heating solution was adapted to obtain a final temperature of 293 K, 313 K and 333 K. The electrodes were inserted into the thermostated solutions. Three replicates were performed for each temperature so that we finally obtained three regression lines from the mean values of the replicates, of which the intercepts were calculated.

2.1.4 Effect of chloride on electrode response

Calibrations were carried out in Potassium hydrogen phthalate buffer, pH 5, to which NaCl was added at two different concentrations (0.1 and 0.55 mol L^{-1}). The calibration was performed using closed vessels ("Karlsruhe" bottles) as described above

2.1.5 Calibration in silver ion (Ag+) buffer solutions

Calibration was performed in AgI buffers, that theoretically mimic various pH_2S values and allow for a sulfide-free calibration. Buffer solutions were prepared as follows: An aliquot of KI (c = 0,1 mol L^{-1}) was added to 10 mL HNO_3 (c = 0,1 mol L^{-1}) in a volumetric flask and filled to 100 mL. To each solution four drops of $AgNO_3$-solution (c = 0,1 mol L^{-1}) were added, which produced a white precipitate. The concentrations were chosen such that the resulting measuring values fitted into the range of values obtained using the conventional calibration procedure (Section 2.1.1).

2.1.6 Comparison of analytical methods to determine dissolved sulfide in synthetic and natural solutions

In these experiments the performances of three analytical methods to determine sulfide (potentiometry, spectral photometry and iodometry) were compared. All reagents were of analytical grade (Merck, Germany). The following solutions were used for the experiments,

- KNO_3 (c = 0,01 mol L^{-1})
- KNO_3 (c = 0,2 mol L^{-1}), $MgSO_4$ (c = 0,3 mol L^{-1}), $NaHCO_3$ (c = 0,001 mol L^{-1}), $CaCl_2$ (c = 0,001 mol L^{-1})
- Potassium hydrogen phthalate $C_8H_5KO_4$ (c = 0,001 mol L^{-1}, buffered to pH 7)
- bog water (pH 4.4; 95 µS/cm)
- waste water (pH 7.4; 1230 µS/cm)

the latter two being samples from a Northeastern Bavarian mountain bog and from the intake of the municipal sewage treatment plant at Bayreuth City, Germany, respectively.

A volume of V = 600...700 mL of solution was injected into the reaction vessel (V = 1L), containing two openings for the pH_2S electrode cells and one opening sealed by a septum (cf. Figure 2). The solution was bubbled with N_2 for 1 h prior to all experiments.

Sulfide was produced electrochemically by a H_2S generator (G200, Analysenmeßtechnik GmbH). A continous flow of approximately 0.85 mL min^{-1} with a H_2S concentration of c_{H2S} = 670...720 µmol L^{-1} was directed into the reaction vessel via a needle penetrating the septum for about 2 hours to obtain a final concentration of ~ 10^{-4} mol L^{-1} total sulfide. A second needle penetrating the septum was used for pressure compensation to prevent electrode damage. The H_2S generator is feeded with a H_2SO_4 solution (c = 5 mmol L^{-1}), which leads to a decrease of the pH in the sample solution. Therefore, the measured pH_2S values were converted to total sulfide by considering the final pH values.

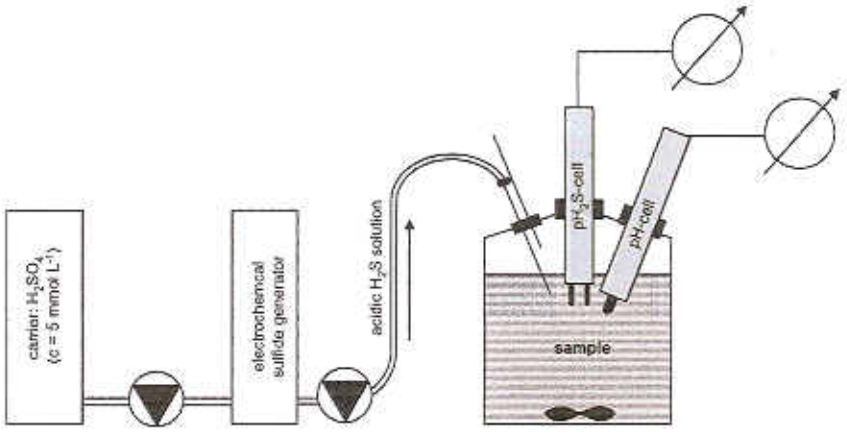

Figure 2 Electrochemical generation of hydrogen sulfide that is transported into the reaction vessel containing the sample

2.2 Analytical

Prior to sulfide analysis the pH of all sample solutions was determined using a commercial pH glass electrode (Mettler) to calculate total dissolved sulfide concentrations from H_2S concentrations (neglecting activity corrections for hydrogen sulfide, i.e., $a_{H2S} = c_{H2S}$) and the first dissociation constant for H_2S (pK_{a1} = 7.03 at 25°C, [38]). Below pH 5 this calculation was omitted as all ionized sulfide species (HS^-, S^{2-}) were assumed to be negligible.

The following methods for the determination of dissolved sulfide were applied:

- Direct potentiometry using two glass//Ag^0,Ag_2S electrodes
- Iodometric titration (according to [36])
- Methylene Blue Method (according to [37])

Direct potentiometry

Sulfide concentrations were determined with a combined glass//Ag^0,Ag_2S electrode cell (Water Test WT-573-H_2S). *Emf* readings were obtained either from two high impedance laboratory mV-meters (Metrohm Ion Activity Meter E 580, Knick Microprocessor pH-meter 764, high-ohmic input resistance > 10^{12} Ohm, manufacturer's estimate 10^{14} Ohm) with a precision of 0,1 mV (WTW pH 91), in some cases also battery-driven pH-meters of the same properties but with lower reading precision of 1 mV were used. A high impedance cable with coaxial connecting plug (Mettler-Toledo) was used as connecting cable.

Iodometric titration

200 mL of the sample were withdrawn and added to a mixture of 2.5 mL 10% KI and 2.5 mL 0.1N KIO_3. The titration was performed with 0.025 N $Na_2S_2O_3$ solution against starch solution as an indicator. Two parallels were analyzed for each experiment.

Methylene Blue Method

This method was carried out according to [37]. A 45 mL subsample was taken and added to a 50 mL volumetric flask containing 5 mL ascorbate solution (pH 10). This sample was analyzed within the next hour in all experiments. The 50 mL solution was added to 25 mL potassium hydrogen phthalate buffer (pH 4, same as for electrode calibration) and was bubbled with nitrogen for 30 minutes. The N_2 stream leaving the sample was led into a Zn-acetate solution (20 g $Zn(CH_3COO)_2 2H_2O$ L^{-1}). After the bubbling stopped, the color reagents were added to the Zn-acetate solution (see [37] for details) and the absorption was measured at a Cary 1E UV/VIS spectrophotometer. Two parallels were analyzed for each experiment.

3 Results and Discussion

3.1 Comparison of Calibration vessels

Table 1 shows the statistical data of slopes and intercepts of the two electrodes calibrated in two different calibration vessels at room temperature (20 °C).

Electrode I

	Slope (mV/pH_2S)	Intercept (mV)
Calibration vessel <u>with</u> head space		
Mean (n=3)	-28.5	676.9
Standard deviation	0.57	3.0
Calibration vessel <u>without</u> head space		
Mean (n=3)	-27.4	669.4
Standard deviation	1.6	1.9

Electrode II

	Slope (mV/pH_2S)	Intercept (mV)
Calibration vessel <u>with</u> head space		
Mean (n=3)	-29.4	679.4
Standard deviation	0.4	1.8
Calibration vessel <u>without</u> head space		
Mean (n=3)	-28.6	675.2
Standard deviation	1.6	3.1

Table 1 Statistical parameters of the comparison of the effect of the calibration vessel on the calibration line

Fig. 3 shows a plot of the calibration lines calculated by use of mean values of measured *emf.*'s at the corresponding pH_2S-values for the calibration vessels with and without gas volume for three independent calibrations in each vessel.

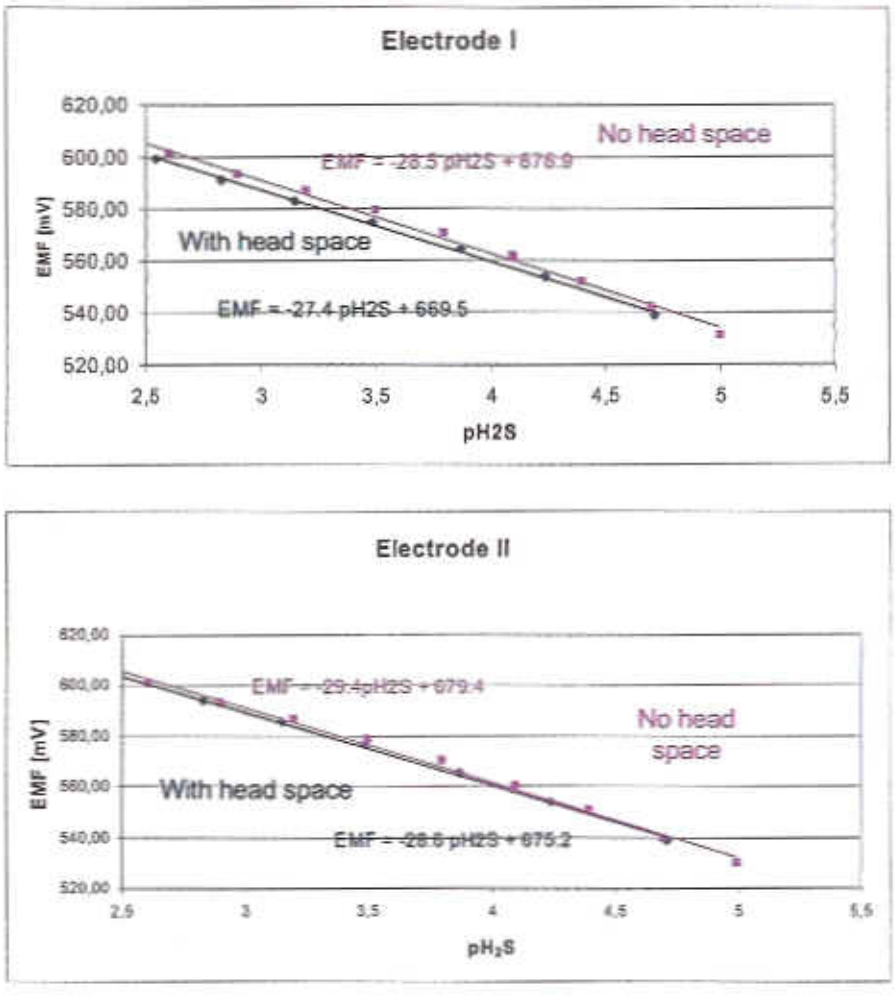

Figure 3 Mean Calibration line for two different calibration vessels with and without gas volume

The difference between the two calibration procedures is statistically significant (two-side test of the slopes, α = 0.05). However, use of a head space is advantageous because injection of large volumes of Na_2S solutions lead to an overpressure within the vessel without gas volume, which squeezed out some solution. Also, handling with respect to weigh the complete vessel including electrodes seems not to be straight forward with respect to a convenient and user-friendly calibration procedure. Since the effect of the head space appears to be not very large, we recommend the use of a calibration vessel with a head space significantly lower than that described by Peters et al, 1984 [23]. A convenient gas volume would be 10 mL instead of the 70 mL used, that is a solution-gas phase ratio of 160 mL to 10 mL, which leads to a theoretical loss of only 2.4 % of the expected concentration to the gas phase.

3.2 Comparison of calibration-buffer solutions

Calibration graphs obtained for the three buffer solutions and the two electrode cell are shown in Fig. 4.

The *emf* reading is reproducibly and significantly highest for the potassium hydrogen phthalate buffer, followed by ammonium fluoroborate and citrate-NaOH buffer, respectively. The *emf* differences are on the order of 5...10 mV. This has severe implications concerning the calculation of H_2S concentrations from these different regressions, as c_{H2S} variations up to 100% between different calibrations are feasible. This effect will be perceptible in a later section of this text when the results of different sulfide determination methods will be shown.

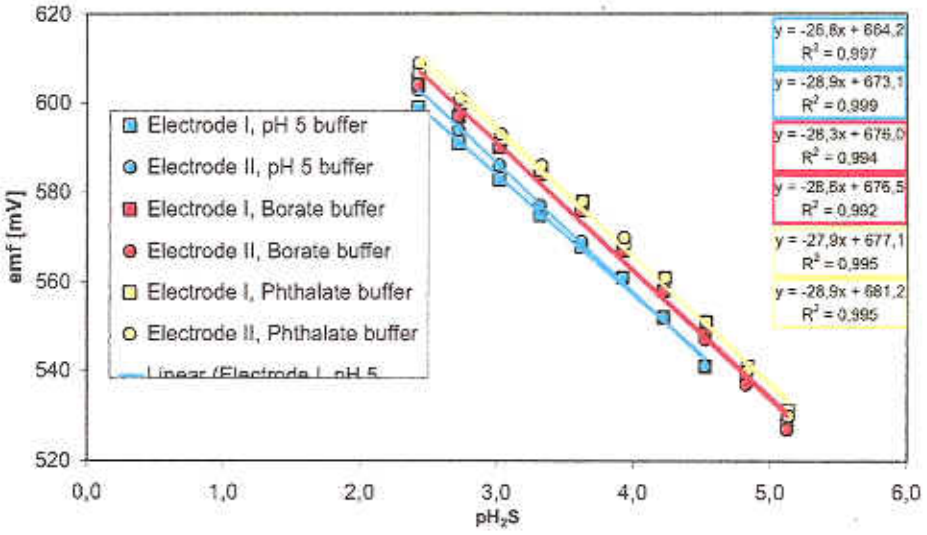

Figure 4 Calibration of two pH_2S electrode cells ("Electrode I & II") in three different acid buffer media

The differences cannot be attributed to ionic strength because the borate buffer has the lowest ionic strength. They rather may reflect the different chemical composition of the buffer solutions.

Also the variation of calibration parameters (intercept, slope) were recorded over time (Tab. 2).

Combination		Intercept [mV]			Slope [mV pH_2S^{-1}]		
Electrode cell	Buffer	Day 1	Day 5	Day 12	Day 1	Day 5	Day 12
Electrode I	cit	664.2	674.4	681.8	-26.8	-29.7	-31.6
	bor	676.0	686.5	681.0	-28.3	-31.3	-29.1
	pht	677.1	682.7	678.0	-27.9	-29.1	-28.4
Electrode II	cit	673.1	680.0	682.7	-28.9	-31.2	-32.6
	bor	676.5	692.9	679.9	-28.6	-33.7	-29.6
	pht	681.2	684.0	680.5	-28.9	-29.7	-29.4

Table 2 Comparison of calibration parameters over a 12-day period (Buffer media: cit=citrate-NaOH, bor=ammonium fluoroborate, pht=potassium hydrogen phthalate)

A considerable fluctuation of the regression parameters occurs, even within a relatively short time of a few days, which makes frequent recalibration on a daily base necessary.

It should be noted that the electrode cell requires some pre-treatment prior to use after delivery from the manufacturer and after it had been kept in a nearly sulfide-free solution for a longer period of about one month. In both cases, the electrode cells did not show linear pH_2S-behavior and had a slower response time. These difficulties could be overcome by pre-conditioning the electrode cells in a solution of approximately pH_2S = 4 for about 72 h. Application of the procedure is highly recommened in case the cell might be immersed in aqueous solutions containing no or very low sulfide for a long period of time.

The analytical range that can be reliably calibrated lies between 20 and 5000 µmol L^{-1} (i. e. 0.7 .... 170 mg L^{-1}) of dissolved H_2S. Effectively, also lower values should be measurable, however, the calibration technique described above does not allow generation of lower sulfide standards.

3.3 Isotherms of the pH_2S electrode cell

Table 3 shows the parameters of the isotherms

	Electrode I		Electrode II	
T (K)	Slope (mV)	Intercept (mV)	Slope (mV)	Intercept (mV)
293	-24.9	657.6	-25.9	658.2
313	-28.5	684.8	-28.3	678.2
333	-31.7	709.5	-32.1	704.2

Table 3 slopes and intercepts of calibration lines obtained isotherms

The resulting intercepts between the three isotherms lines were:

	Electrode I		Electrode II	
Isotherms intersected	Intercept pH_2S axis [-]	Intercept *emf* axis (mV)	Intercept pH_2S axis	Intercept *emf* axis
293/313	7.61	468.0	8.18	446.6
313/333	7.76	463.9	6.83	484.8
293/333	7.68	466.3	7.36	467.8
Mean value	7.68 ±0.07	466.1 ± 2.0	7.46 ± 0.96	466.4 ± 27.0

Table 4 electrode parameters of isotherms

The change of the electrode characteristics with temperatrure is significant. The electrode has its isotherm intercept at a pH_2S value that corresponds to very low H_2S concentrations. Therefore calibration at the temperature of the sample is recommended.

3.4 Effect of Chloride on electrode response

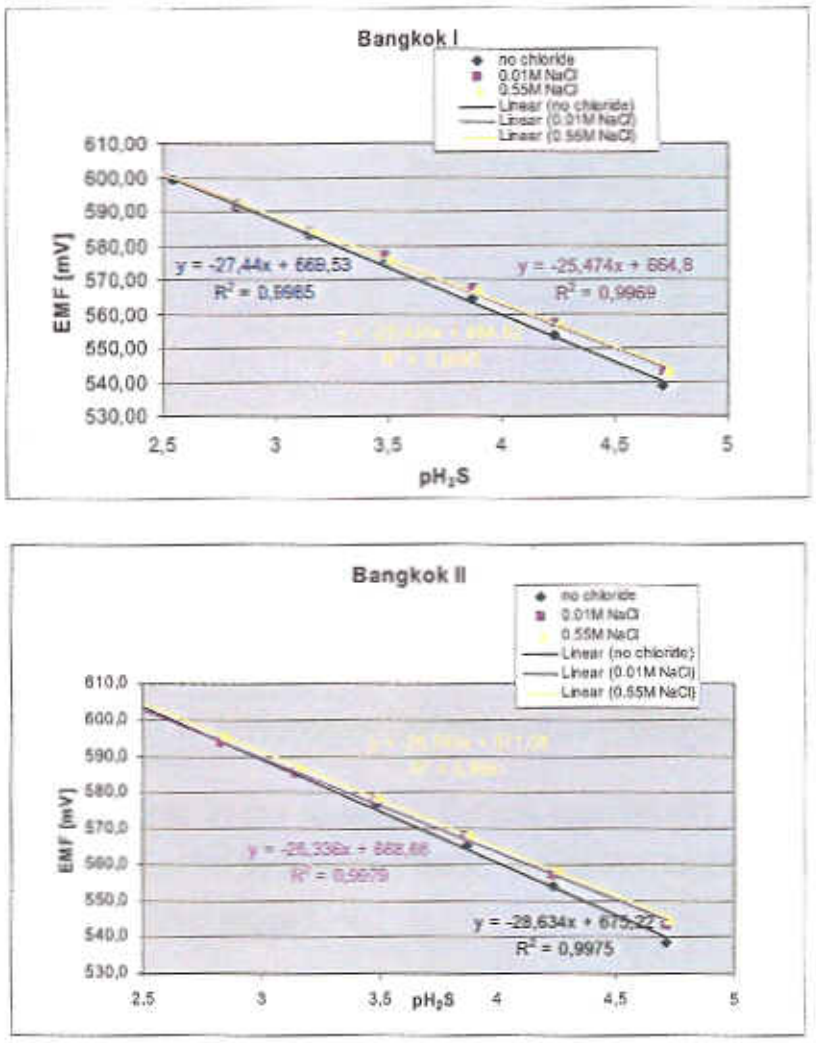

Figure 5 Effect of chloride concentration on calibration lines

Fig. 5 shows the effect of chloride on the calibration signal. Obviously, the sensitivity, expressed as the slope of the electrode cell, is somewhat lower in the presence of chloride. The difference between no chloride and 0.1 mol/L chloride and 0.55 mol/L chloride, however, is significant for both electrodes (α = 0.05). The effect of ionic strength seems to be of minor importance because the ionic strength of the initial phthalate concentration is already 0.145 mol/L. Addition of 0.01 mol L^{-1} of NaCl only slightly effects ionic strength (I = 0.155 mol L^{-1}). However, it appears that the reproducibility of the calibration seems to be better after addition of chloride, which we see as some kind of a buffering effect at the Ag_2S-membrane due to the formation of a mixed AgCl/Ag_sS precipitate. We, therefore, suggest to add chloride at the expected sample concentration in order to cope for the chloride effect and also to improve signal stability.

3.5 Calibration in silver ion (Ag^+) buffer solutions

Table 5 shows the parameters of regression lines –log a(I^-) versus *emf* obtained for the various silver ion buffers. The slope matches only 82 % and 90 %, resp. of the theoretical value of 59.1 mV.

Electrode I

	Slope (mV/pH_2S)	Intercept (mV)
Mean (n=3)	49.1	624.8
Standard deviation	1.2	1.8

Electrode II

	Slope (mV/pH_2S)	Intercept (mV)
Mean (n=3)	52.5	645.3
Standard deviation	0.8	2.3

Table 5 Parameters of the regression line –log a(I) versus emf obtained for the various silver ion buffers.

The *emf* values measured in the silver ion buffers theoretically correspond to pH_2S values that can be calculated by inserting these values into calibration lines obtained from conventional calibration procedure:

$$pH_2S_{buffer} = (emf_{buffer} - emf^{\circ})/S \qquad (2)$$

emf° and S were taken from the calibration lines obtained from calibration in phthalate buffer and 0.55 mol L^{-1} NaCl (cf. Section 3.3), where we observed the highest precision. The error for each pH_2S value was calculated using the Gauss error propagation law, considering the variances of each parameter in equation (2) calculated from replicate measurements. Table 6 shows the results for the two electrodes:

Electrode I

Activity of Iodide in silver buffers (mol L^{-1})	Mean value of *emf* measured in silver buffers (mV)	Variance of *emf* measured in silver buffers (mv^2)	pH_2S values calculated using eq. (2)	Error calculated using the error propagation law
0.00078	475.7	5.0	7.44	0.17
0.0016	486.6	1.4	7.01	0.14
0.0039	504.0	0.4	6.32	0.12
0.0078	519.8	0.4	5.70	0.11
0.015	534.0	0.2	5.14	0.10
0.038	555.7	0.4	4.29	0.09
0.075	572.0	0.0	3.64	0.08

Electrode II

Activity of Iodide in silver buffers (mol L^{-1})	Mean value of *emf* measured in silver buffers (mV)	Variance of *emf* measured in silver buffers (mv^2)	pH2S values calculated using eq. (2)	Error calculated using the error propagation law
0.00078	484.4	0.1	7.29	0.14
0.0016	498.0	0.0	6.76	0.13
0.0039	516.3	0.5	6.04	0.13
0.0078	533.4	0.4	5.37	0.12
0.015	548.9	1.5	4.77	0.12
0.038	571.2	1.6	3.90	0.10
0.075	587.9	1.3	3.24	0.10

Table 6 pH_2S values calculated from emf values measured in silver ion buffers that were inserted into a conventional calibration line obtained from the experiments in Section 3.3. The activities of I⁻ were calculated using the Davies approximation

Table 6 demonstrates that the precision, particularly at high iodide acitivities corresponding to high pH_2S values, may be acceptable with errors of ± 0.1 pH_2S units (i. e. 20 % error in terms of H_2S activities). The accuracy, however, remains inconclusive, since both electrodes provide rather different pH_sS values in apparently identical silver ion buffers. The silver ion buffer method, therefore, can not be recommended as referred to the results of the experimental setting used in this study.

3.6 Comparison of dissolved sulfide determination in synthetic and natural solutions

3.6.1 Synthetic solutions

The results of sulfide determination for the three different synthetic solutions are shown in Figures 6-8. The final pH values of the synthetic solutions are shown in Table 7

solution composition	pH
KNO_3 (c = 0,01 mol L^{-1})	2.94
KNO_3 (c = 0,2 mol L^{-1}), $MgSO_4$ (c = 0,3 mol L^{-1}), $NaHCO_3$ (c = 0,001 mol L^{-1}), $CaCl_2$ (c = 0,001 mol L^{-1});	3.66
$C_8H_5KO_4$ (c = 0,001 mol L^{-1}, buffered to pH 7))	6.42

Table 7 Final pH values in synthetic solutions after addition of H_2S

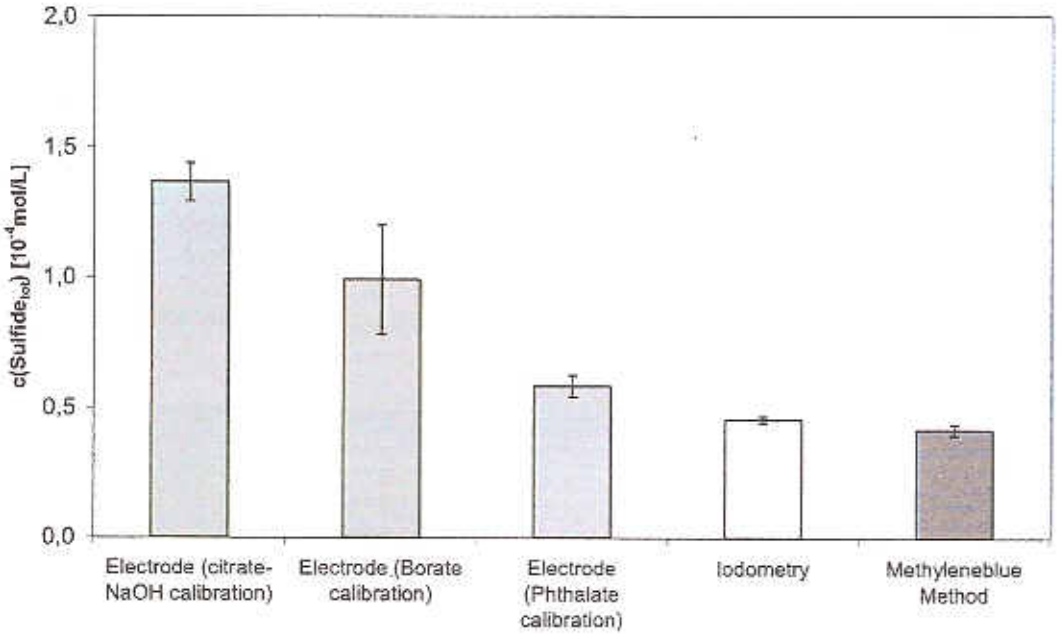

Figure 6 Total dissolved sulfide concentration in a KNO_3 solution at pH 2.94, determined with three different methods.

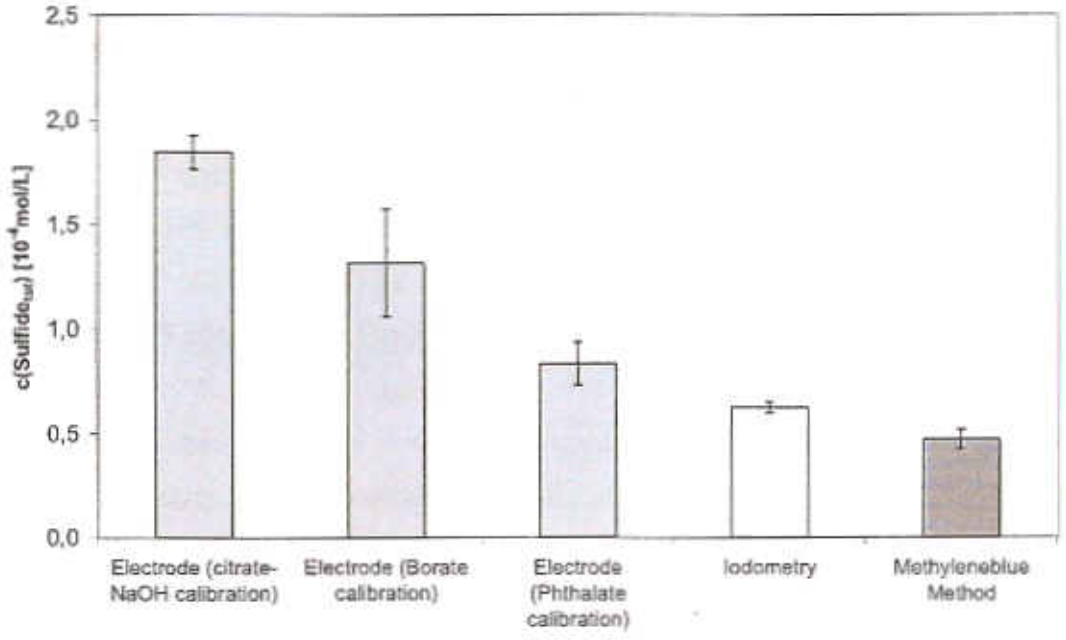

Figure 7 Total dissolved sulfide concentration in a solution of the composition KNO_3 (c = 0,2 mol L^{-1}), $MgSO_4$ (c = 0,3 mol L^{-1}), $NaHCO_3$ (c = 0,001 mol L^{-1}), $CaCl_2$ (c = 0,001 mol L^{-1}) at pH 3 66, determined with three different methods.

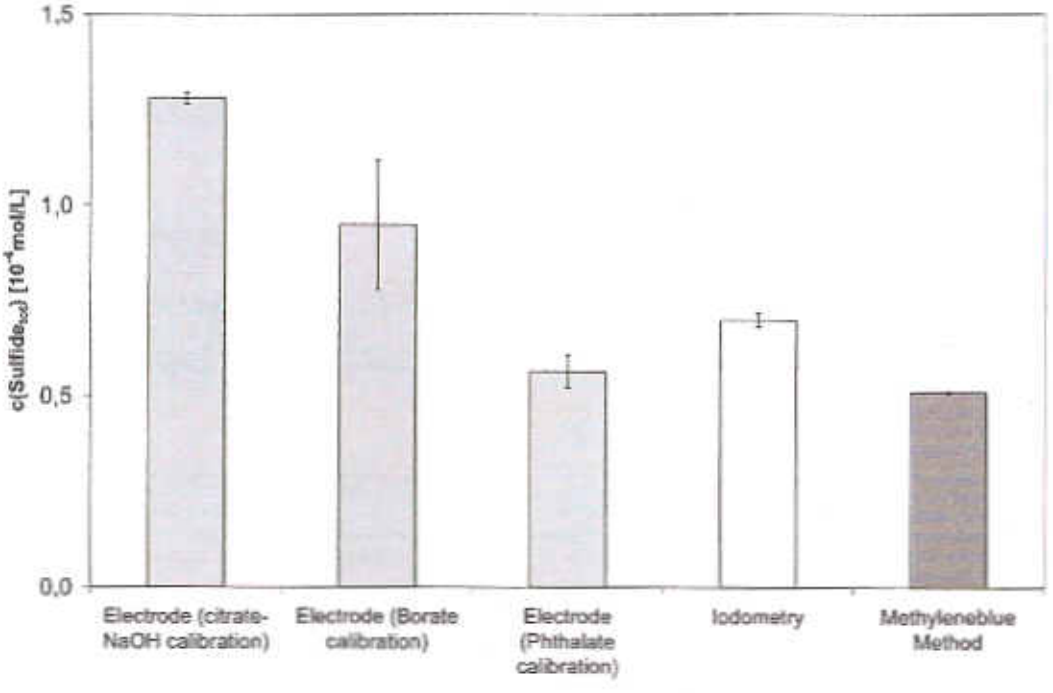

Figure 8 Total dissolved sulfide concentration in a potassium hydrogen phthalate solution (c = 0,001 mol L^{-1}) at pH 6.42, determined with three different methods.

In all three solutions, the electrode measurements follow the same pattern, i. e. the citrate-NaOH calibration provides the highest values, followed by the ammonium

fluoroborate and the potassium phthalate calibration. This is, of course, a direct consequence from the calibration differences discussed in the previous section.

The lowest value of all electrode measurements (i.e. phthalate calibration) seems to be the most accurate as compared to the results from iodometric titration and the Methylene Blue Method. This is especially the case for the potassium hydrogen phthalate sample solution (Fig. 8), where the value obtained by the electrode falls just into the range spanned by the iodometric and the Methylene Blue value. Supposedly, this is due to the similar composition of sample solution and calibration medium (although the calibration solution is more concentrated and has a lower pH). However, the low accuracy of the citrate-NaOH calibration and to lower degree also the borate calibration is striking. Compared to the other two methods they yield sulfide concentrations that are double or even threefold.

The precision as indicated by error bars is representative of the standard deviation between two different electrode cell readings for the potentiometric method and of two parallels for the titrimetric and the spectrophotometric method each. On this basis the two latter methods seem to be more precise ($1.2 \cdot 10^{-6}$ mol L^{-1} and $2.3 \cdot 10^{-6}$ mol L^{-1}, respectively) than the potentiometric method ($7.4 \cdot 10^{-6}$ mol L^{-1}, $2.1 \cdot 10^{-5}$ mol L^{-1}, and $4.1 \cdot 10^{-6}$ mol L^{-1}).

3.6.2 Natural samples

The results of sulfide determination for the three different synthetic solutions are shown in Figures 9 and 10. The initial and the final pH values after addition of H_2S are shown in Table 8.

Sample type	$pH_{initial}$	pH_{final}
Bog water	4.40	2.90
Waste water	7.41	7.30

Table 8 Initial and final pH value of samples after addition of H_2S

The pattern is different from the synthetic solutions, but strikingly similar within the both runs. For the Methylene Blue method we also included two unfiltered parallels to study the effect of sample filtration. The unfiltered subsamples show a higher sulfide concentration than the filtered ones in the domestic waste water experiment, which is exactly opposite in the bog water run. One explanation could be an interaction of

sulfide with and incorporation into particulate organic matter, which is retained when the bog water sample is filtered.

The concentrations determined by iodometric titration exceed all the other values. In the waste water sample it exceeds the expected value of 100 µmol L^{-1} by a factor of 1.3, which we interpret by the detection of interfering reduced compounds other than sulfide being already in the sample (e. g. organic sulfur ompounds). In the bog water sample the iodometric method almost matches the expected value, while the other methods (except the citrate-NaOH calibration) determine significantly lower concentrations. We interprete this difference by the oxidation of sulfide by the highly oxidized organic substances in the bog water (e. g. S° or organic sulfide), which cannot be detected neither by the Methylene Blue nor by the potentiometric method. . The agreement between potentiometry and methylene blue method is good. The precision of the potentiometric method seems to have slightly increased compared to synthetic solutions and compares favorably to the other two methods.

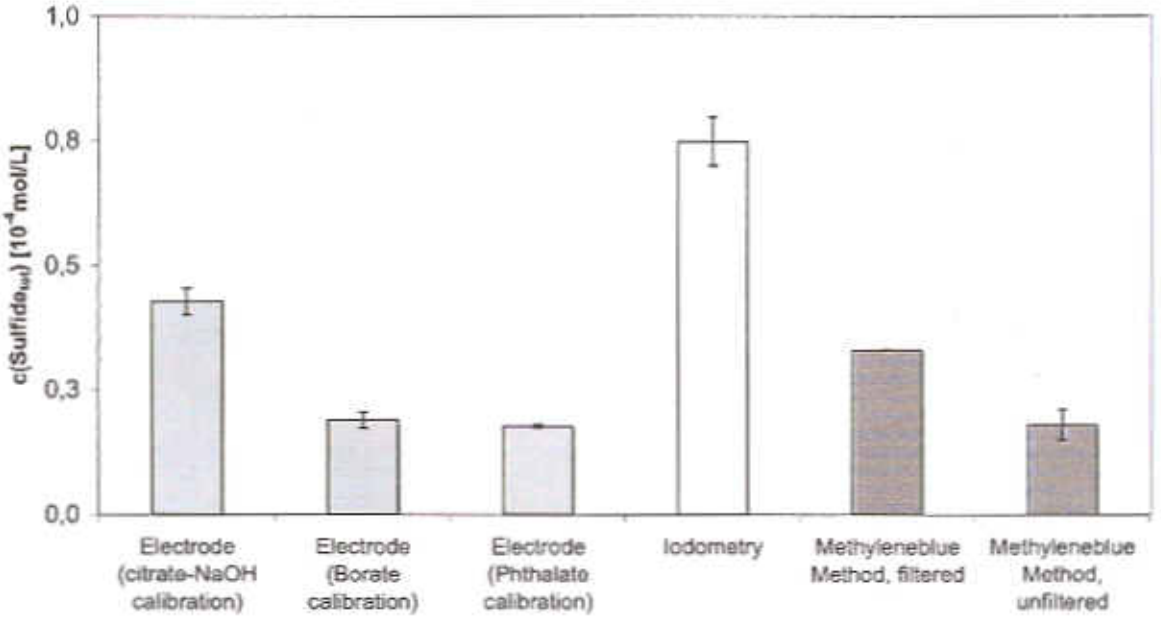

Figure 9 Total dissolved sulfide concentration in a bog water sample, determined with three different methods

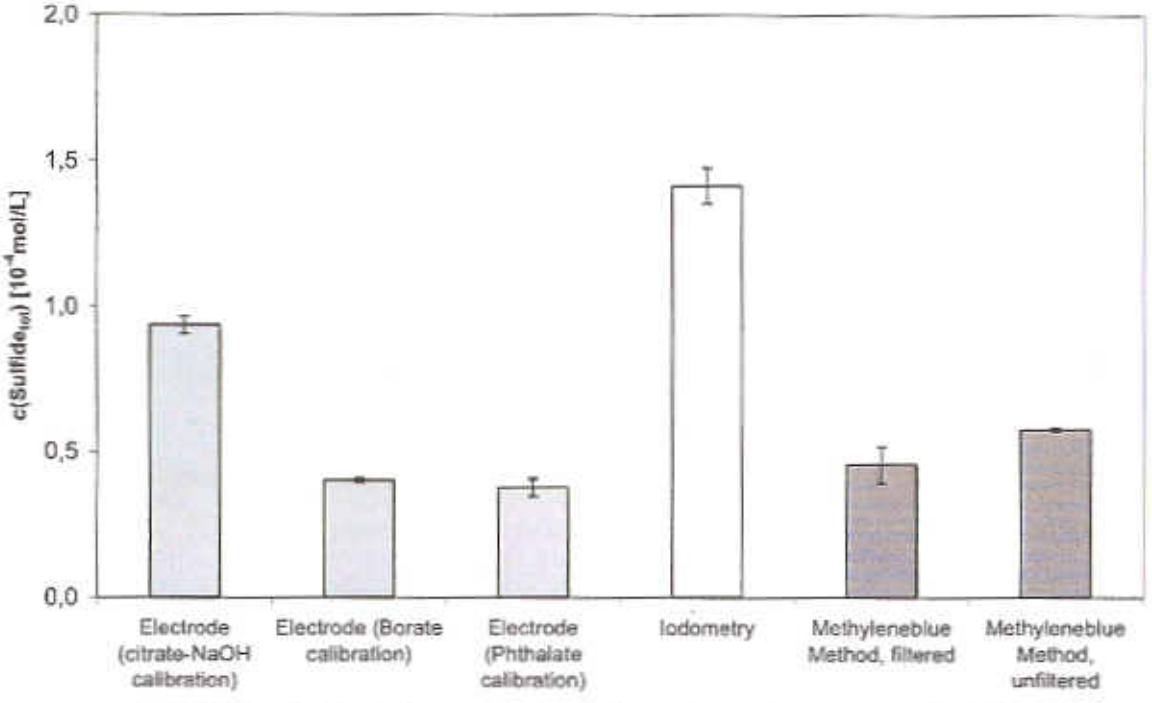

Figure 10 Total dissolved sulfide concentration in domestic waste water sample, determined with three different methods

In order to compare the analytical precision we calculated the confidence intervals for the concentrations measured in waste water by potentiometry (Phthalate method) and the Methylene Blue method. The precision of the mV-meters in these experiments were ± 1 mV. The confidence interval for the logarithmic potentiometric calibration line was calculated by subtracting (lower value) or adding (upper value) the error from the measured pH_2S value, taking the anti-log value and relate it to the non-logarithmic measured H_2S concentration.

	c(sample I) [µmol L^{-1}]	Conf. interval [%]	C(sample II) [µmol L^{-1}]	Conf. interval [%]
Potentiometry Electrode I	40	58 (upper) 37 (lower)		
Potentiometry Electrode II	35	62 (upper) 40 (lower)		
Methylene Blue	50	5,3	41	6,5

Table 9 Comparison of confidence intervals calculated by use of the statistical parameters from the regression lines after Funk (1985).

Table 9 shows that the analytical precision is by a factor 10 higher for the methylene blue method. The analytical precision of the potentiometric method is limited by its logarithmic nature, combined with a low slope (only ~ 29 mV). It can be increased by a high precision mV-meter (± 0,1 mV) to ~ 20 % (as calculated with calibration lines obtained using high precision meters in experiments described e. g. in Section 2.1.1).

3.7 Evolution of turbidity during calibration

In all potentiometric calibration procedures conducted in this study the evolution of turbidity in the buffer medium could be observed especially at high total dissolved sulfide concentrations. Also, the color of the turbidity was actually indicative of a certain buffer solution, being yellowish in the citrate-NaOH buffer, and white in the other two media. Supposedly, this effect could be due to elemental sulfur (S^0), or polysulfide precipitation. In order to get a more quantitative grasp on this problem an absorption spectrum of this turbid solution was recorded and the wavelength of maximum absorbance was determined. Then, a classic calibration was performed and for each step an aliquot was removed from the reaction vessel and its absorption at 562 nm was determined. The results are depicted in Fig. 11.

Although the process responsible for the turbidity evolution can not be determined with this procedure it shows at which concentration range this process becomes relevant. Measurable absorption occur only at pH_2S values below 3.5. However, a quantitative estimate of how severely these precipitates interfere with precise calibration has to be further evaluated.

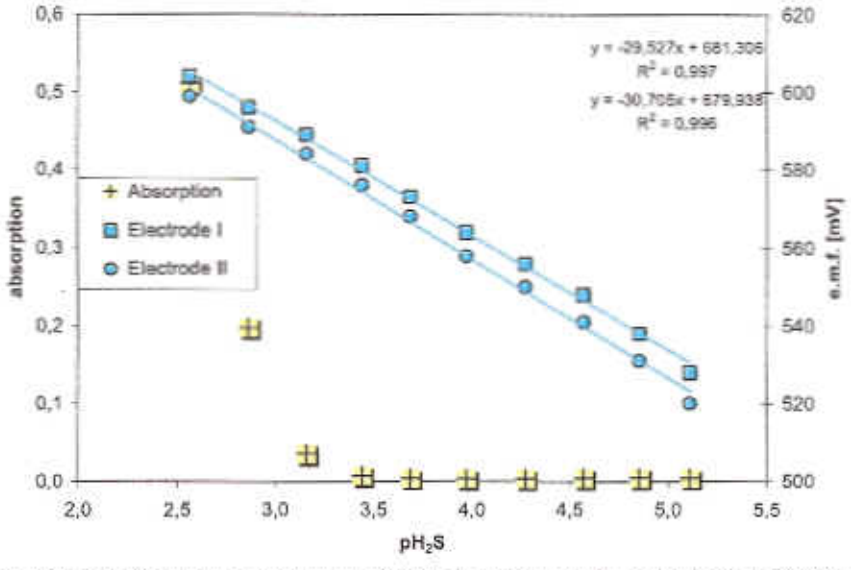

Figure 11 Calibration in potassium hydrogen phthalate buffer, absorption at 562 nm

4 Summary

The potentiometric method to detect hydrogen sulfide can be regarded as a robust and reliable tool to rapidly measure dissolved sulfide. It detects sulfide selectively and is therefore advantageous compared to iodometry. It is, however, not competitive to the standard Methylene Blue Method due to its lower analytical precision and the low stability of the calibration line.

The pH_SS electrode cell can be recommended for use in all those cases, where precision is not a major requirement, e. g. monitoring or control systems, because its physical signal can be easily used to be continuously recorded. Then the following recommendations are given:

Calibration should be performed at the sample temperature using the calibration technique described in Section 2.1.1a using potassium phthalate buffer at pH 5 and NaCl (c = 0,1 mol L^{-1}) in a calibration vessel with a head space that is small compared to the solution volume. The analytical range that can be reliably calibrated with this method lies between 20 and 5000 µmol L^{-1}. The calibration should be repeated on a weekly base at minimum, if possible daily. If a high precision mV meter (± 0.1 mV) is used, an analytical precision of ~ 20 % (as confidence interval) can be obtained.

The calibration procedure using silver ion buffers can not be recommended due due its low accuracy. Rather then using silver ion buffers for a rapid calibration procedure, it appears to be recommendable to think about sulphide containing buffers that are added to some antioxidizing solution.

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