

Chapter 4

Comparison of Different Methods for Redox Potential Determination in Natural Waters

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4.1 Introduction

In geochemical equilibrium model programs such as PHREEQE (PARKHURST et al., 1990) PHREEQC (PARKHURST, 1995) the redox potential is a major variable strictly affecting the species distribution and mineral stability of both, redox-sensitive dissolved species and solid phases. It is therefore necessary to assess the accuracy of p_e determinations by redox probes. In addition, there are often inconsistencies to be found in calculated p_e values. In different geochemical computer model programs, the p_e may be calculated from the concentrations of various redox couples. These values often vary by hundreds of millivolts in one single water analysis. Therefore, the reliability of p_e calculations is discussed.

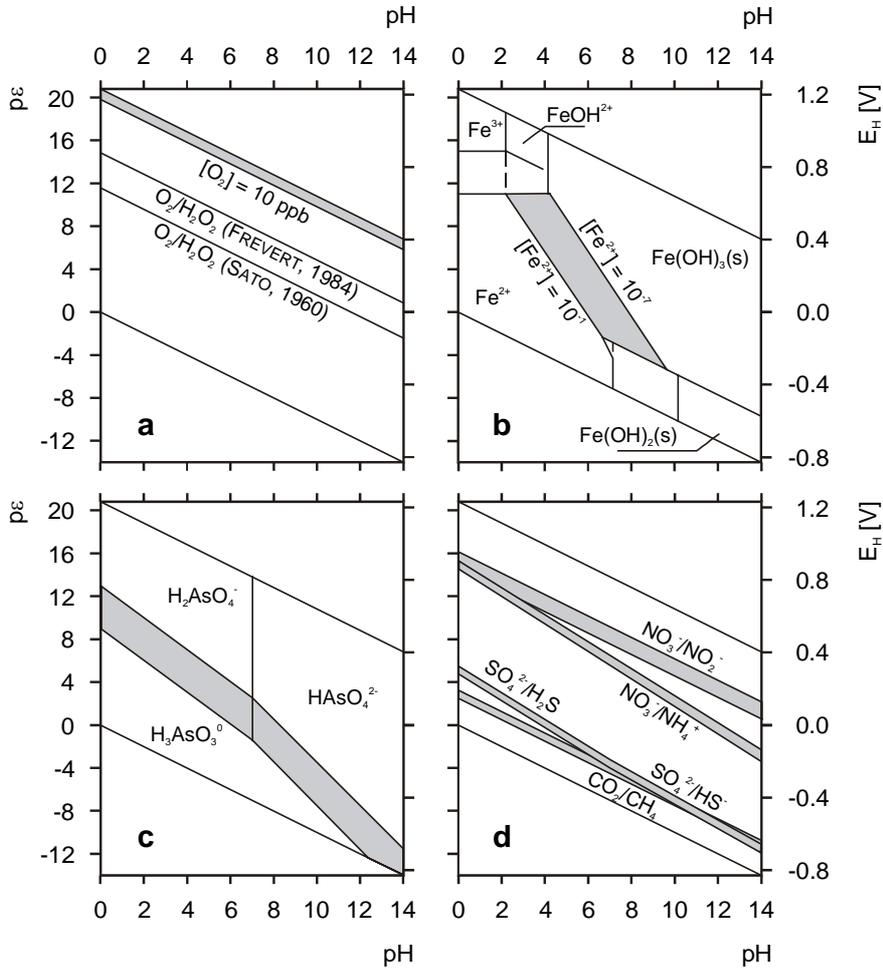


Fig. 4.1: “Redox windows” (shaded areas) for different redox couples: (a) Oxygen = 10 ppb to saturation; (b) $[\text{Fe}^{2+}] = 10^{-1}$ to 10^{-7} mol/L, $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = 10^{-2}$ to 10^2 ; (c) $[\text{As(V)}]/[\text{As(III)}] = 10^4$ to 10^{-4} ; (d) $[\text{NO}_3^-]/[\text{NO}_2^-] = 10^4$ to 10^1 , $[\text{NO}_3^-]/[\text{NH}_4^+] = 10^{-3}$ to 10^3 , $[\text{CO}_2]/[\text{CH}_4] = 10^{-3}$ to 10^3 , $[\text{SO}_4^{2-}]/[\text{H}_2\text{S}] = 10^3$ to 10^{-3} (modified from KÖLLING, 1986).

4.2 Redox Potential Calculations

In natural waters there are numerous ions that participate in different redox reactions. Theoretically, the redox potential calculated from the activity ratio of

different redox couples using the appropriate NERNST-equations should yield identical redox potentials, if the chemical components are in thermodynamic equilibrium. Real calculations usually produce values that differ strongly from each other for two major reasons:

- Redox couples react to changes in the redox environment very differently. Some systems (e.g. $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$) rapidly equilibrate and may cause sampling artefacts while others might take years. In both cases the calculated value will not reflect the redox state of the water sample regardless of the analytical accuracy.
- On the other hand, the possibilities in redox potential calculation are limited by naturally occurring concentrations and detection limits. Assuming a redox potential of 20 mV ($\text{p}\epsilon = 3.4$) for a water with a Fe^{2+} activity of 1 ppm the Fe^{3+} -activity theoretically should be $10^{-9.6}$ ppm according to the NERNST-equation of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ -couple:

$$\text{p}\epsilon = 13.0 + \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (4.1)$$

Using a detection limit for Fe^{3+} (e.g. 1 ppb) instead of the correct value, the calculated redox potential becomes 590 mV ($\text{p}\epsilon = 10$) which differs dramatically from the correct value. It is therefore critically important for such calculations that the concentrations of both redox partners are well above the detection limits.

For redox couples present in natural waters, the possible range of calculated redox potentials is limited by the detection limits of the redox species involved and by the maximum of the naturally occurring concentrations. Using these boundary conditions we can plot "redox windows" for redox couples. They represent areas of the pH- $\text{p}\epsilon$ diagrams, to which all meaningful redox values calculated from the concentrations of the relevant redox species will be allocated (Figure 4.1).

4.2.1

The $\text{H}_2\text{O}/\text{O}_2$ -Couple

The standard potential of the $\text{H}_2\text{O}/\text{O}_2$ -couple is very high ($E_{\text{H}}^0 = 1230$ mV, $\text{p}\epsilon^0 = 20.78$).

$$\text{p}\epsilon = 20.78 - \text{pH} + \frac{1}{4} \log \text{pO}_2 \quad (4.2)$$

Assuming a detectable amount of oxygen (i.e. 10 ppb) the calculated redox potential at pH = 7 becomes 760 V ($\text{p}\epsilon = 12.9$). Since such high redox values are usually not observed, SATO (1960) stated that the oxygen reduction in water occurs via a metastable H_2O_2 phase which controls the redox potential of the solution.

The NERNST-equation for this couple is:

$$pe = 11.7 - pH + \frac{1}{2} \log \frac{pO_2}{[H_2O_2]} \quad (4.3)$$

The activity of the metastable H_2O_2 is not detected in routine analyses but the activity ratio may not become smaller than unity since H_2O_2 is formed from O_2 , hence

$$pe \geq 11.7 - pH \quad (4.4)$$

should be the minimum redox potential of water containing oxygen (Figure 4.1a).

According to FREVERT (1984) measurements in well aerated waters show pe values which may be explained with a predominance of the O_2/H_2O_2 -couple assuming a H_2O_2 activity of 10^{-7} M estimated on the basis of available data. On the basis of this estimate the measured pe values should follow

$$pe = 14.9pH + \frac{1}{2} \log pO_2 \quad [H_2O_2] = 10^{-7} \text{ M} \quad (4.5)$$

The calculation of redox potentials from the oxygen concentration “according to SATO (1960)” is erroneous in some geochemical equilibrium model programs inasmuch as 11.7 is used instead of 20.78 as the pe^0 for the H_2O/O_2 -couple, a value which has never been proposed by SATO (1960).

4.2.2 Fe-Species

In Figure 4.1b the redox windows of some Fe-redox couples are shown. In natural waters with normal pH the pe may be calculated from:

$$pe = 16.5 - 3pH - \log[Fe^{2+}] \quad (4.6)$$

4.2.3 As-Species

CHERRY et al. (1979) introduced the calculation of redox potentials from the concentrations of As (III) and As(V). Using an appropriate method as described by SHAIK & TALLMANN (1978) species-specific analyses of As(III) and As(V) down to ng-concentration levels allow reliable calculations of redox potentials. Arsenic responds to changes in redox conditions within days or weeks. This allows sampling and preservation of redox states but also assures sufficiently quick adaptation to changes of redox conditions. The As-“redox window” is in a region where measured values are often found (Figure 4.1c).

$$\begin{aligned}
 p\varepsilon &= 11 - \frac{3}{2}pH + \frac{1}{2} \log \frac{[\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_3]} && \text{for } pH < 7 \\
 p\varepsilon &= 14.5 - 2pH + \frac{1}{2} \log \frac{[\text{HAsO}_4^{2-}]}{[\text{H}_3\text{AsO}_3]} && \text{for } pH > 7
 \end{aligned}
 \tag{4.7}$$

4.2.4 S-Species

Under reducing conditions sulfate is reduced to sulfide. The redox potential may be calculated with the NERNST-equations:

$$\begin{aligned}
 p\varepsilon &= 5.12 - \frac{5}{4}pH + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{S}]} && \text{for } pH < 7 \\
 p\varepsilon &= 4.25 - \frac{9}{8}pH + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{HS}^-]} && \text{for } pH > 7
 \end{aligned}
 \tag{4.8}$$

The sulfate/sulfide-couple is often far from equilibrium. From the NERNST-equations it may be seen that, due to eight electron transfers, the changes in the calculated redox potential only amount to 1/8 pε unit or 7 mV per order of magnitude change in the sulfate to sulfide ratio. As a consequence, the sulfur “redox window” (Figure 4.1d) is very narrow (pε = 3.2 to 4 or E_H = 190 to 235 mV at pH = 7).

4.2.5 N-Species

Several redox reactions may be formulated for nitrogen species. In natural waters the nitrate/nitrite-couple and the nitrate/ammonia-couple are often used:

$$\begin{aligned}
 p\varepsilon &= 14.15 - pH + \frac{1}{2} \log \frac{[\text{NO}_3^-]}{[\text{NO}_2^-]} \\
 p\varepsilon &= 14.9 - \frac{5}{4}pH + \frac{1}{8} \log \frac{[\text{NO}_3^-]}{[\text{NH}_4^+]}
 \end{aligned}
 \tag{4.9}$$

4.2.6 The CO₂/CH₄-Couple

In strong reducing environments CO₂ is reduced to CH₄ and the redox potential may be calculated with the following equation:

$$p\varepsilon = 2.87 - \text{pH} + \frac{1}{8} \log \frac{[\text{CO}_2]}{[\text{CH}_4]} \quad (4.10)$$

4.3 Redox Potential Measurements

The redox potential is measured by using redox probes. The potential difference is determined between a metal electrode and a reference electrode whereby both are immersed in the solution to be measured. The redox potential is generated by transfer of electrons from the metal electrode into the solution and vice versa. The net current from this process depends on the redox species, its concentration in solution and the material of the electrode. The redox potential equilibrates where the absolute values of the cathodic and anodic currents are equal and the net current becomes zero. Net current graphs drawn for different redox couples should theoretically meet at one redox potential. (Figure 4.2a). In natural waters, redox couples are usually far from equilibrium. In this case electrodes show mixed potentials. The mixed potential is determined by redox couples with the steepest net current curve (Figure 4.2b). Redox couples with a smaller slope in this curve produce a net current close to zero over a wide redox potential range, which results in a poor stability as far as the measurements are concerned.

Natural waters are usually very dilute solutions in terms of the concentration of redox-sensitive species. Redox probes only respond to processes which quickly and reversibly occur at the metal electrode surface. According to STUMM & MOR-

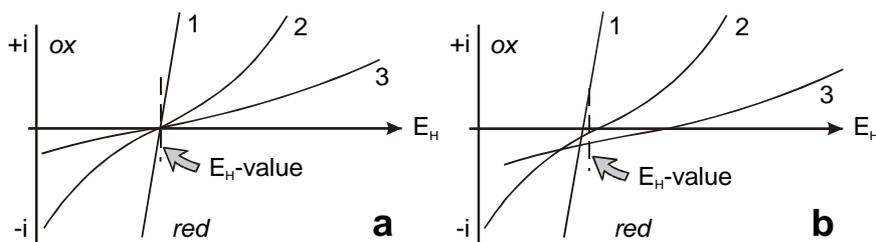


Fig. 4.2: Net current graphs for a set of three redox couples: (a) equilibrium between redox couples; (b) natural situation of non-equilibrium between redox couples. The redox probe will show the potential, where the sum of all three net current curves becomes zero (dashed lines, modified from KÖLLING, 1986).

GAN (1996), this condition does not hold for nitrate, nitrite, sulfide, ammonia and the CO₂/CH₄-system.

FREVERT (1984) clearly distinguishes between the log of the electron activities calculated from electrode measurements which he refers to as *pe*, and the *pe* which is conceptually defined as the redox intensity. The *pe* and *pe* values are equal when equilibria exist between different redox couples (Figure 4.2a) and between the solution and the electrode. A detailed theoretical background on the interactions between electrode, aqueous electron activities, and redox potentials is given by HOSTETTLER (1984).

4.3.1 Metal Electrodes

Redox probes often use platinum as the metal electrode. In solutions with high oxygen concentrations chemi-sorption of oxygen to the platinum surface results in a redox reaction Pt/Pt-O which is induced by the electrode itself and affects the measured values (WHITFIELD, 1974)

4.3.2 Reference Electrodes

The reference to which all potentials are related is the standard hydrogen electrode (SHE). Today, a Ag/AgCl electrode is used in most laboratory and field measurements. The Ag/AgCl reference system has its own potential related to the SHE. This potential has to be added to all measured values

$$E_{\text{H}}(\text{SHE}) = E_{\text{H}(\text{measured})} + E_{\text{H}(\text{reference})} \quad (4.11)$$

$$\text{Ag/AgCl: } E_{\text{H}(\text{reference})} [\text{mV}] = 207 + 0.7(25 - t)$$

where *t* is the temperature in [°C].

Most combined redox probes do not have a durable label showing the reference system or the appropriate electrolyte solution to be used.

4.3.3 Calibration Solutions

Redox probes are not calibrated but the probe function may be checked using calibration solution of known potential. Common solutions contain 3 mmol/L K₃Fe(CN)₆ and 3 mmol/L K₄Fe(CN)₆ dissolved in 100 mmol/L KCl with

$$E_{\text{H}}(\text{SHE}) [\text{mV}] = 428 + 2.2(25 - t) \quad (4.12)$$

pH buffer solutions saturated with chinhydronium may also be used, with

$$E_{\text{H}}(\text{SHE}) [\text{mV}] = 699 - 59 \text{pH} \quad t = 25^{\circ}\text{C} \quad (4.13)$$

Common reasons for malfunctions of redox probes are aged electrolyte solutions in the reference electrode, broken cables, surface-contaminated metal electrodes or corroded plugs. In contrast to other potentiometric sensors malfunctions are usually not detected right away since some mV-meters often show stable values which differ well from zero even without a probe connected.

4.4 Materials and Methods

4.4.1 The Artesian Well “Schierensee”

An artesian well in Northern Germany was chosen as a test site for measurements. The well is reported to have discharged oxygen-free water from Tertiary brown coal sands for years. Therefore water samples of homogenous composition could be taken directly without pumping and changes in hydraulics.

Measurements were performed using flow-through cells (KÄSS, 1984) which allow an oxygen-free application of probes. Up to three cells were arranged in serial order. The water flow was adjusted between 0.4 and 0.7 l/min. The flow-through cells were equipped with probes for oxygen, temperature, pH, and with up to six different redox probes.

4.4.2 Electrodes

Four different types of combination electrodes were used (Probes 1 to 4). Additionally, two types of double junction Ag/AgCl reference electrodes were applied in combination with platinum electrodes 5 and 6 (see Table 4.1).

Tab. 4.1: Electrode characteristics.

<i>Probe #</i>	<i>Type</i>	<i>Reference</i>	<i>Manufacturer</i>
1	combination with Pt-tip	Hg/HgCl ₂	Schott Pt-61
2	combination with Pt-ring	Ag/AgCl	Ingold Pt4805-KN
3	micro-combination with Pt-cone	Ag/AgCl	Ingold Pt4805-M6
4	combination with Pt-ring	Ag/AgCl	Ingold Pt4805-88-NS
5 and 6	massive Pt-tip	(none)	Ingold Pt800-6317
Ref. I	double-junction reference	Ag/AgCl	Orion 90-02-00
Ref. II	double-junction reference	Ag/AgCl	Ingold 373-90-W-NS-S7

4.4.3 Instruments

Oxygen was measured using an *Orbisphere Model 2711* system which is capable of detecting oxygen >50 ppb. pH was measured using a standard *Schott pH 61* probe and a *Knick Portamess 902*. The same instrument was used to measure redox potentials together with a *WTW pH 191*.

4.5 Results

4.5.1 Redox Potential Measurements

Figure 4.3 shows the results of five measurements as difference from the mean measured value. Measurement A was performed using two probes without preparation. Prior to measurement B, all probes were filled with fresh electrolyte solutions and the platinum surface was polished. Measurements C and D were performed without refilling the electrolyte solutions.

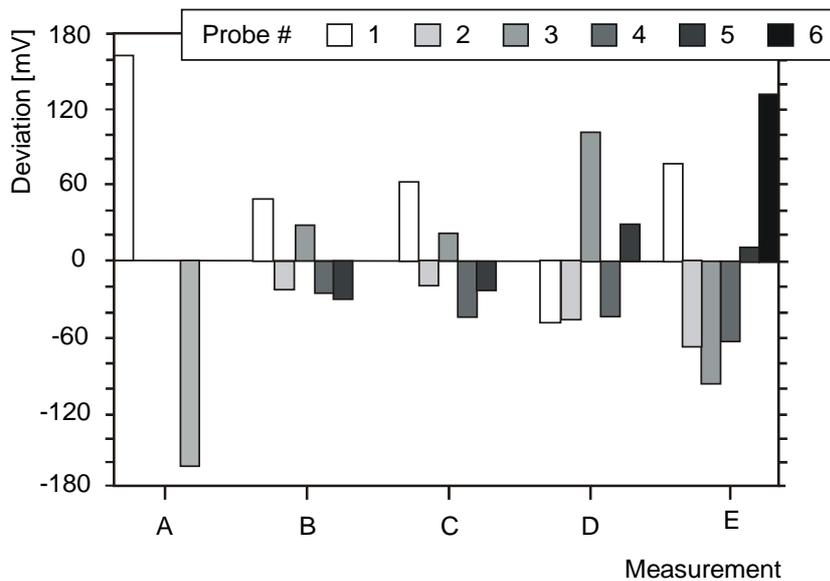


Fig. 4.3: Deviations from mean E_H -values. Results of five measurements at the artesian well “Schierensee” with up to six redox probes (modified from KÖLLING, 1986).

After changing the electrolyte a second time a fifth measurement (E) was performed with all probes. From the results obtained from the measurements B, C and D ageing of the electrolyte solutions was assessed. Yet, differences in measured values became even greater after the probes were refilled prior to measurement E. It should be noted that deviations from the mean are at least ± 50 mV even when probes were carefully prepared. Most interesting are the differences observed between probes 5 and 6 which are metal electrodes connected to a separate double-junction reference electrode. We changed the cables the instruments and the reference electrodes and we tried both metal electrodes connected to the same reference. Yet, the difference in potentials between the two identical metal electrodes was still over 100 mV!

Similar deviations from mean values of even more than ± 50 mV were observed in sewage water, sea water, tap water and in well waters either saturated or unsaturated with calcite.

4.5.2 Calculation of Redox Potentials

Non-referenced analyses of deep groundwaters were used to compare the calculated redox potentials to the measured values. There was no detailed information on both sampling and measuring conditions, which is normal for many real situations.

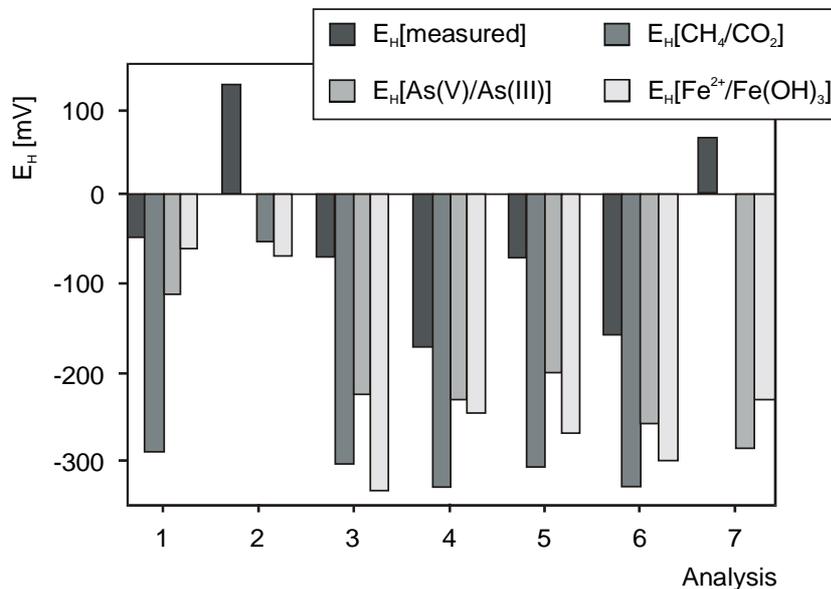


Fig. 4.4: Redox potential calculations for analyses from deep groundwaters (modified from KÖLLING, 1986).

The calculated values are much lower than the measured ones indicating an oxygen contamination of the samples prior to or during measurements. Calculations for the $\text{H}_2\text{O}/\text{O}_2$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ -couples were left out since the results are theoretically much too high as discussed above.

Redox values calculated on the basis of the $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3^-$ and $\text{As}(\text{V})/\text{As}(\text{III})$ -couples differ by less than 100 mV. The absolute values calculated on the basis of the CO_2/CH_4 -couple is generally very low due to the low standard potential and the narrow “redox window” (Figure 4.1d). Therefore, agreement with other values is only good when the latter are very low.

4.6 Discussion

4.6.1 Redox Potential Measurements

There are no clear correlations between the probes used and the measurements' accuracy. Great differences among the measured values which might be due to aged electrolyte solution and coated surface of the metal electrode have been suggested, but even with freshly refilled probes and carefully polished electrode surfaces these differences remain. One criterion for the quality of the redox probe might be the measurement dynamics. There were probes that showed differences of only 50 mV between a reduced and an oxic water while others showed differences as high as 260 mV in the same experiment.

Metal electrodes, together with a double-junction reference electrode are recommended since double-junction electrodes are not contaminated by sulfide and the metal electrodes of the type we used may be easily polished whereas other electrodes utilise only thin platinum tips which should not be polished too often to avoid damage to the electrode. Yet, with the metal electrode/double-junction reference combination, there were differences between two identical set-ups as high as 100 mV so that this combination should not be recommended as the ideal redox probe.

We recommend measurements with the same electrode for all samples which should be prepared as follows:

- refill fresh electrolyte solution and check the working condition of the probe with calibration solution from time to time,
- clean and refill fresh electrolyte solution one day prior to measurement campaign, especially after using the probe with calibration solution,
- polish the metal surface prior to each measurement campaign,
- immerse probe in 2% ascorbic acid solution for a few seconds and rinse with pure water prior to every measurement in order to reduce equilibration time.
- Whenever possible, measurements should be performed in flow-through cells without contamination of ambient oxygen.

4.6.2 Redox Potential Calculations

By using the $\text{H}_2\text{O}_2/\text{O}_2$ -couple only a minimum redox potential of a solution may be calculated regardless of the oxygen concentration. A calculation “according to SATO (1960)” is not possible as long as the concentration of the metastable H_2O_2 is not known. Redox potential calculations from the $\text{SO}_4^{2-}/\text{H}_2\text{S}$ -couple are usually faulty due to the slow equilibration of this system and the narrow “redox window”, thus showing that the calculations are quite insensitive to measured concentrations. Redox potentials can be determined in natural water with an arsenic content above 10 ppb if species-specific analyses of arsenic are performed. The redox values calculated from the $\text{Fe}^{2+}/\text{Fe}(\text{OH})_3$ -couple usually agree well with the values calculated from $\text{As}(\text{V})/\text{As}(\text{III})$ and with the measured values as long as the measurements have been performed without oxygen contamination.

4.7 Conclusions

It has to be stated that the redox potential of most natural waters cannot be detected more accurately than ± 50 mV. Similar deviations have been determined with two identical metal electrodes connected to one and the same reference electrode. Redox probes have to be carefully prepared to reach this “accuracy”. From the $\text{As}(\text{V})/\text{As}(\text{III})$ -couple and from the Fe^{2+} -concentration of the solution, redox potentials may be calculated at the same “accuracy”-level. This uncertainty of measured redox potentials needs to be carefully considered in thermodynamic calculations.

The determination of redox potentials is usually not interesting in terms of the value itself, but for the geochemical predictions that may be made for the behaviour of a system. It is therefore suitable to measure analytically important redox species as indicators of the redox status of the waters (STUMM, 1984).

4.8 References

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