

Establishing a Total Dissolved Solids: Electrical Conductivity Ratio for Mine Waters

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ABSTRACT

Total dissolved solids (TDS) expresses the sum of all dissolved ions in water. In a given water, the TDS content in mg/L and electrical conductivity κ_{25} at 25 °C in $\mu\text{S}/\text{cm}$ are related to each other by the equation $\text{TDS} = \kappa_{25} \times f$, where f is a constant, commonly referred to be in the range of 0.55 – 0.9. Mine water with elevated TDS contents rapidly causes scaling or corrosion, as high TDS values are often associated with lower pH-values. TDS is also used to calculate the potential amount of sludge in mine water treatment, which makes TDS a crucial parameter.

For accurate TDS determinations, filtered water samples are oven dried and the mass of the residue is the TDS-content. As this procedure is time consuming, the TDS is commonly estimated from EC measurements using the above equation and laboratory and field conductometers are manufactured with a programmable conversion factor. Normally TDS is reported without further considering the conversion factor or its way of measurement.

In this paper, we describe TDS/EC conversion factors for 45 South African, mining impacted waters. It can be shown that the conversion factor ranges from 0.25 to 1.34 with a mean of 0.86 and a standard deviation of 0.19. No correlation with other on-site parameters was found, though there is a tendency to higher conversion factors at lower pH-values and higher electrical conductivities.

Based on our work we conclude that prior to using the TDS/EC conversion equation, the conversion factor for the single mine water, not only site specific but also time depended, must be determined in the lab and the conductometer be programmed with this conversion factor. In addition, the conversion factor 0.65 recommended in the South African Water Quality Guidelines should no longer be used for mining impacted water.

Keywords: mine water, South Africa, electrical conductivity, total dissolved solids (TDS)

INTRODUCTION

When electrolytes or salts are dissolved in aqueous solutions their ions dissociate and increase both the amounts of dissolved solids in the solution and their conductivity (Hölting and Coldewey, 2013). Consequently, both parameters are relevant in characterizing the chemistry of aqueous solutions. Electrical conductivity (EC) and total dissolved solids (TDS) are commonly analysed in water samples to provide an indication for the waters' mineralization or salinity. Both parameters are related to each other, as each charged ion of the dissolved constituents contributes to the conductivity of the aqueous solution. EC measurements are therefore commonly used for estimating the TDS (Gustafson and Behrman, 1939).

Electrical conductivity is measured with a probe that determines the resistivity of the aqueous solution. Because the resistivity is the reciprocal of the conductance, the conductivity of the aqueous solution can be calculated based on the resistivity measurement (American Public Health Association et al., 2005, Hölting and Coldewey, 2013):

$$G = \kappa \frac{A_c}{l_c}$$

where G is the conductance in S, κ the electrical conductivity in S/cm, A_c the cross section of the conductor in m² and l_c the characteristic length in m. The electrical conductivity κ is calculated as follows:

$$\kappa = \frac{l}{A \cdot R}$$

where κ is the electrical conductivity in S/cm, l the distance between the electrodes in cm, A the cross section of the electrodes in cm² and R the electrical resistance in $\Omega = \frac{1}{S}$.

Because the electrical conductivity is temperature dependent (Smith, 1962), the measured value has to be temperature compensated, usually to 25 °C.

TDS is determined analytically by evaporating the aqueous solution and measuring the weight of the dry residue (Hem, 1985). Accurate determination of the total dissolved solids for filtered or unfiltered samples is achieved by evaporating the aqueous solution at predetermined temperatures, which are in the range of 105 to 110 °C and at 180 °C (American Public Health Association et al., 2005). When comparing the sum of all analysed ions and molecules with the analytically determined TDS, the latter frequently exceeds the sum of ions, as not all water constituents are usually included in the analysis (Howard, 1933).

Problems with this method occur when water contains considerable amounts of sulphate, as the minerals that precipitate during evaporation of the water are Ca, Mg or Na sulphates which contain water in their crystal structure (Howard, 1933). Even at a temperature of 180 °C, not all of the crystal water is released from the crystal and consequently, the determined TDS is greater than the sum of all analysed ions in the aqueous solution.

It can be shown that EC and TDS are related with each other by the following equation

$$\text{TDS} = \kappa_{25} \cdot f \quad [\text{mg/L}]$$

where TDS are the total dissolved solids in mg/L, κ_{25} the temperature compensated electrical conductivity in $\mu\text{S}/\text{cm}$ at 25 °C and f a conversion factor in (10 g m)/(L S). Commonly, the value of this factor is given to be in the range of 0.55 – 0.9 (American Public Health Association et al., 2005, Wolkersdorfer, 2008) and many probes are pre-set to a factor in this range. If the water contains elevated concentrations of SiO_2 , this relationship is no longer accurate and corrections for SiO_2 need to be applied (Day and Nightingale, 1984).

However, there are cases where those values can't be used to precisely calculate the TDS and as each aqueous solution contains different ions the factor f changes with the water's chemistry. Ali et al. (2012), for example, determined factors between 0.41 and 2.01 for industrial waste water in Korea and based on the data of Atekwana et al. (2004) for a contaminated aquifer in Michigan/USA a conversion factor of 0.50 to 1.21 can be calculated. For South African rivers, van Niekerk et al. (2014) determined factors between 0.48 and 0.86 ($n = 144\ 643$) and based on the data of Day and Nightingale (1984) the ratio for SiO_2 -rich waters in California is between 0.56 and 0.82, while Weiner (2010) provides a range of 0.55 to 0.7 for surface and ground waters and 0.5 for seawater. Department of Water Affairs and Forestry (1996) recommends a single conversion factor of 0.65 for South African waters, while Hobbs (2013) inconsistently used 0.7 or 0.77 while he determined a factor of 0.73 from 1045 EC measurements and TDS lab analysis. In a personal communication, Hobbs reports TDS/EC ratios of 0.46 to 1.29 for a variety of surface, ground and waste waters with an average of 0.83 ($n = 16$).

Because high TDS values are often associated with lower pH-values, water with elevated TDS concentrations rapidly causes scaling or corrosion. Besides, TDS is used to calculate the potential amount of sludge in mine water treatment. Consequently, the effective and low cost evaluation of TDS becomes a crucial parameter. In this paper, we present first results of determining the TDS/EC-ratio for 45 South African mine water samples taken at various locations in the Witwatersrand gold fields, the Mpumalanga coal mines and various other locations in Gauteng, Mpumalanga and Limpopo.

METHODOLOGY

Unfiltered and unacidified water samples at 45 locations in the South African provinces Gauteng, Mpumalanga and Limpopo were taken in 1-L-PE bottles (Figure 1). On-site, the parameters temperature (Hach CDC401), pH (Hach PHC201), redox-potential (Hach MTC101), electrical conductivity (Hach CDC401) and oxygen saturation (Hach LDO101) connected to a Hach HQ40d were determined. pH was calibrated at the start of each sampling day with pH 4, 7, and 10 standard solutions. Electrical conductivity was calibrated with a 1413 $\mu\text{S}/\text{cm}$ 0.01 M KCl standard solution. Samples were kept in a cooler box with cooling elements and stored in a cooling room at TUT until further analysis. Sample aliquots were allowed to warm to room temperature before each lab analysis.

TDS was determined in the lab using standard method 2540 (American Public Health Association et al., 2005) after filtering the sample through a 0.45 μm cellulose nitrate membrane filter. All samples were analysed in duplicates and if necessary in triplicates when the deviation of the duplicates was too high.

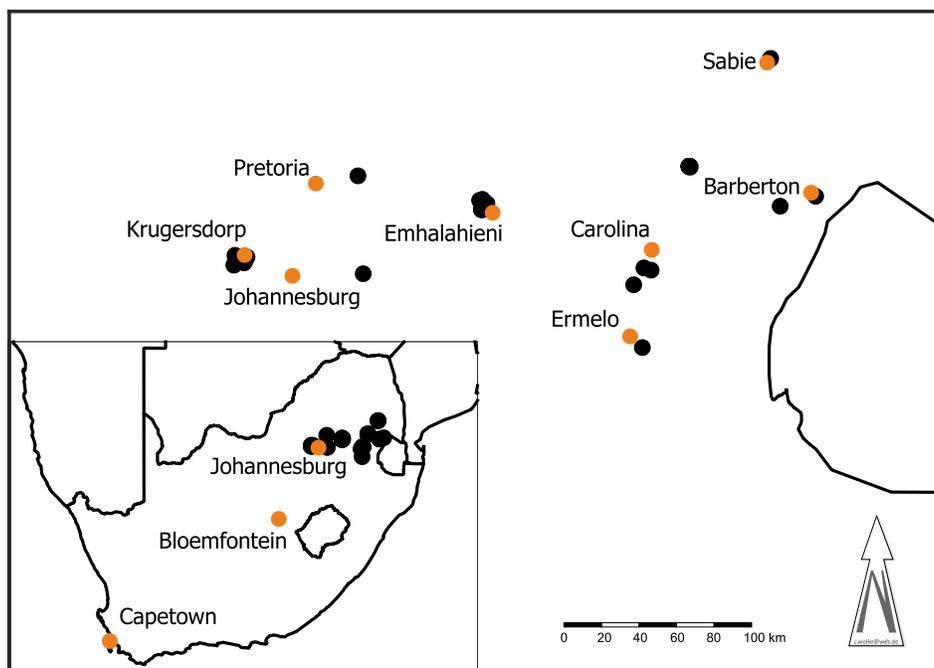


Figure 1 Map of the sampling locations (dark dots) within Nord-Eastern South Africa.

Electrical conductivity was measured in the lab with a daily calibrated EC probe (Hach CDC401) attached to a Hach HQ40d. All data was temperature corrected to 25 °C with a compensation factor individually determined for each sample from measurements of the EC while heating a cooled sample aliquot. This temperature correction factor ranged between 1.16 and 2.16 % with an average of 1.92 %. After measuring the EC and determining the TDS, the conversion factor was determined according to this equation:

$$f = \frac{\text{TDS}}{\kappa_{25}}$$

where f is the correlation factor for EC and TDS in (10 g m)/(L S), TDS is the total dissolved solids in mg/L and κ_{25} the temperature compensated electrical conductivity in $\mu\text{S}/\text{cm}$ at 25 °C. Then the averages of the correlation factors f determined for one sample by duplicate or triplicate measurements were calculated.

Both, the geological setting and the climatic conditions of the sampled sites vary. Geologically, the sites are located in the Karoo Supergroup (eMmahlaheni, Carolina, Ermelo), the Transvaal Supergroup (Sabie, Krugersdorp, Edendale) and the Barberton Greenstone Belt (Barberton). Climatically, all the sites are within the humid subtropical climate zone (Köppen Climate Classification) with hot, rainy summers and cool dry winters and precipitation between 600 and 800 mm/a (Johnson et al., 2006, Lynch, 2004).

RESULTS AND DISCUSSION

Field pH of the 45 samples ranged between 2.45 and 7.85 and the electrical conductivity between 45 and 16 369 $\mu\text{S}/\text{cm}$ with average values of 3.92 and 5 091 $\mu\text{S}/\text{cm}$, respectively (Table 1). As can be

seen, most pH-values are in the range of the iron buffer, some in the aluminium buffer and those at higher pH-values in the carbonate buffer range (Figure 2).

Consequently, the water samples represent a wide range of mining impacted waters in South Africa from the low pH-values indicative for AMD, high pH-values for well buffered mine water and one surface water sample. As expected, the general trend of all samples is that lower pH-values often relate to higher electrical conductivities (Figure 2). Exceptions from the general trend are samples from the abandoned Transvaal and Delagoa Bay Colliery near eMalahleni, which show an exceptionally high electrical conductivity. Reason for this behaviour is that this mine was closed several decades ago, is very close to the surface, the coal was mined underground as well as strip mined and the pyrite oxidation is consequently higher than in the flooded mines with low pH-values. A similar situation occurred in the case of the Yorkshire No 1 and the Shoff mines in the US where the up-dip and strip mined Shoff mine also shows higher contamination loads than the down dip Yorkshire No 1 mine (Mentz et al., 1975).

Lab determined TDS ranged between 50 and 13 984 mg/L with an average of 4 279 mg/L and a standard deviation of 4 422 mg/L (Table 1). Using those analytically determined total dissolved solids concentrations, the calculated TDS/EC ratio is in the range of 0.25 to 1.34 with an average of 0.86 and a standard deviation of 0.19 (Figure 3). This result is unexpected as an e-mail poll revealed that most South African mine water researchers ($n = 38$) either use the factor 0.65 from Department of Water Affairs and Forestry (1996) or the factory programmed factor of the EC meters.

To identify which other on-site parameter can be used to estimate the TDS, statistical investigations were conducted. Yet, no dependency on another on-site parameter could be found for the 45 analysed samples. Most of the TDS/EC factors increase with increasing TDS of the sample, but the abandoned tailings dam and the Transvaal and Delagoa Bay Colliery samples deviate from this general trend (Figure 3).

Table 1 Field and lab parameters of the analysed mine water samples. Average of the pH calculated from the $\{H^+\}$ activity. TDS from lab analyses.

	pH, –	κ_{25} , $\mu\text{S}/\text{cm}$	TDS, mg/L
n	45	45	45
Minimum	2.45	67	50
Maximum	7.85	16 369	13 948
Median	3.76	3 059	2 832
Average	3.92	4 769	4 279
σ	1.93	5 091	4 422
σ , %	40	107	103

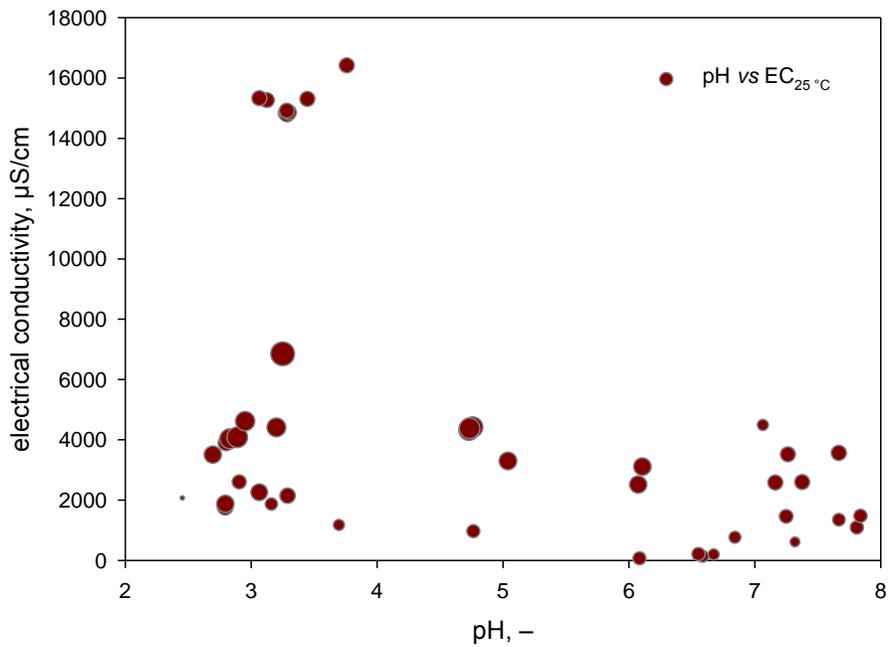


Figure 2 Scatter plot of the measured pH-values and electrical conductivities of all samples. The radius of the circles represents the TDS/EC ratio, $n = 45$.

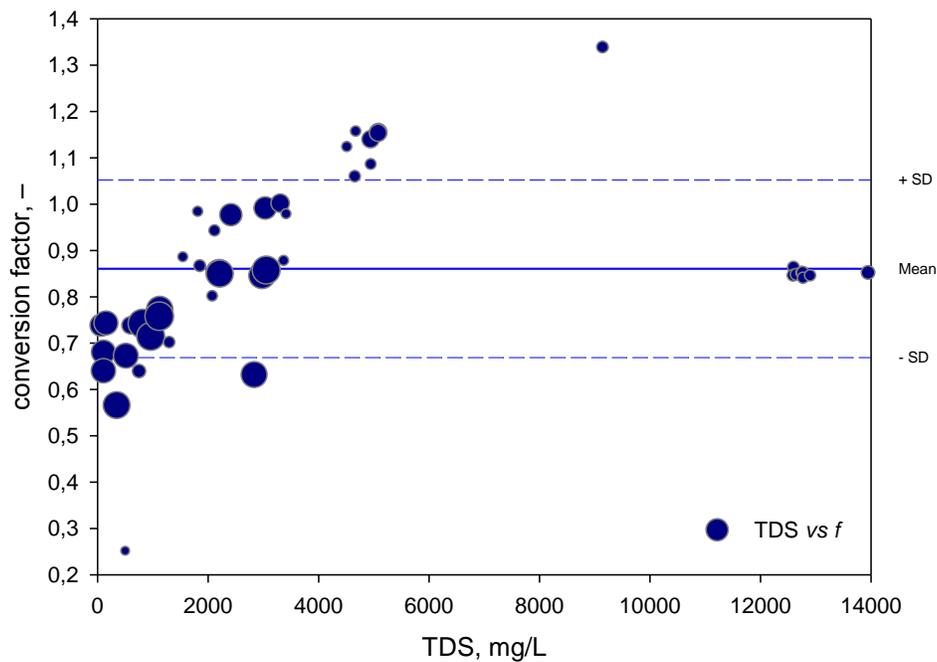


Figure 3 Scatter plot of the lab determined TDS and the TDS/EC ratios. The radius of the circles is proportional to the pH-value of the sample; $n = 45$.

CONCLUSIONS AND RECOMMENDATIONS

As can be seen from the above data, it is not possible to use a single conversion factor from EC to TDS to estimate the total dissolved solids of a mine water sample. The range of the ratio is too high to use it as a reliable tool for TDS estimations. Consequently, prior to using the TDS/EC conversion equation, the conversion factor for the single mine water, which might change with local, diel or seasonal variations, must be determined in the lab and the conductometer be programmed with this conversion factor. Together with the results, the applied conversion factors should be mentioned. In addition, the conversion factor 0.65 recommended in the South African Water Quality Guidelines (Department of Water Affairs and Forestry, 1996) should no longer be used for mining impacted water and the guidelines might need to be updated in this regard.

Future work will investigate a larger set of samples and will include chemical analyses as well. This shall determine how the TDS can be more reliably estimated from the EC without its lengthy lab determination.

ACKNOWLEDGEMENTS

We thank our colleagues at Tshwane University of Technology (TUT) who provided us with equipment and facilities for analysing the water samples and our colleagues at various mines and governmental institutions who provided us with locations, water samples and data. This work was financed by a SARChI (South African Research Chair Initiative) research grant of the NRF (National Research Foundation). Special thanks to Henk Coetzee who introduced us to the “heavily toxic” mine water situation in South Africa.

A more comprehensive paper with all the relevant data is currently under review in the Journal Water SA in will be available during the year 2015.

NOMENCLATURE AND ABBREVIATIONS

A	cross section of electrodes, [cm ²]
A_c	cross section of conductor, [m ²]
EC	electrical conductivity
f	conversion factor from EC to TDS, [(10 g m)/(L S)]
G	conductance [S]
l	distance of electrodes, [cm]
l_c	characteristic length of conductor, [m]
R	resistance, [Ω]
TDS	total dissolved solids
κ_{25}	electrical conductivity at 25 °C [S/cm, μ S/cm]

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