# THE SENSIBILITY ANALYSIS OF C<sup> $1^{-1}</sup> AND SO<sub>4</sub><sup>2-</sup> TITRATION IN GROUNDWATER SAMPLES</sup>$

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## Introduction

The dominant cations in groundwater are  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$  and the anions are  $HCO_3^-$ ,  $Cl^-$  and  $SO_4^{-2-}$ . Here the method for determination concentration of anions used in project "Establishment of interdisciplinary scientist group and modelling system for groundwater research" is described. The concentration of ions in groundwater can wary across several orders of magnitude, e.g. in case of Cl<sup>-</sup> from several mg/L to more than 100 g/L. Particularly difficult can be the measuring the low concentrations of SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>.

## **C**hlorides

Cl<sup>-</sup> concentration is measured using argentometric method. Potassium chromate is used to indicate the end point of the silver nitrate titration of chloride [1]. Measuring chloride with low concentration, solution colour changes later. The accuracy of both methods in low concentration range was tested and procedures to improve it developed.

# **T**he principle of the method

In a neutral or slighly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

## **S**ulphates

The turbidimetric method is used to measure concentration of sulphate ion. By adding barium chloride the barium sulphate is obtained. BaSO<sub>4</sub> solubility is about 1 mg/ L and it defines the determination limit of the method. If  $SO_4^{2-}$  concentration is lower than 5 mg/L it can not be measured, because it the linear dependence of light absorption to  $SO_4^{2-}$  concentration is breaking down.

## **T**he principle of the method

Sulfate ion  $(SO_4^{2})$  is precipitated in an acetic acid medium with barium chloride (BaCl<sub>2</sub>) so as to form barium sulfate (BaSO<sub>4</sub>) crystals of uniform size. Light absorbance of the BaSO<sub>4</sub> suspension is measured by a spectrophotometer and the  $SO_4^{2-}$  concentration is determined by comparison of the reading with a standart curve.



Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions

interfere but can be removed by treatment with hydrogen peroxide. Orthophosphate in excess of 25 mg/L interferes by precipitating as silver phosphate. Iron in excess of 10 mg/L interferes by masking the end point [1].

### **P**roblem and its solution

Using test solutions it has been found that in the solutions with chloride concentration less than about 40 mg/L, the measured results are higher than the theoretical concentration known for the test solutions.

Cl<sup>-</sup>standards at 5 mg/L increments in the 0 to 50 mg/L range are preapared and the obtained solutions are analyzed and the curve is obtained (Fig. 1.).





Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. Waters containing large quantitatives of organic material it may not be possible to precipitate BaSO<sub>4</sub> satisfactorily [1].

## **P**roblem and its solution

Sulphates can not be measured if the concentration is less than 5 mg/L as there is no linear dependence of the light absorption by the precipitated BaSO<sub>4</sub>. It is possible to add Na<sub>2</sub>SO<sub>4</sub> to shifting sulphate concentration in the range of linear absorption. Exactly knowing the amount of extra  $SO_4^{2-}$  ions introduced in the solution, it is possible to calculate the initial  $SO_4^{2-}$  concentration. This approach can be used if the  $SO_4^{2-}$  concentration is lower than 10 mg/L. The offset of the results is demonstrated in the Fig. 2.



Concentration, mg/L Without additives

Fig. 1. Comparison of measured and theoretical Cl<sup>-</sup> concentration

Using mathematical regression the best fit curve can be found that is described by the equation:

$$\gamma_{Obt.} = 0,00195\gamma_{Cl} + 0,83677\gamma_{Cl} + 3,35979 \tag{1}$$

Solving the equation (1) the Cl<sup>-</sup> concentration corrected value can be found by the equation:

$$\gamma_{CL} = \frac{-0.83677 + \sqrt{0.67397 + 0.0078\gamma_{Obt.}}}{0.0039} mg/L$$
(2)

where,  $\gamma_{Obt.}$  – measured result and  $\gamma_{CI}$  – corrected value, that should represent the reality more closely. The equation (2) can be used to correct the measurement accuracy if the  $Cl^{-}$  concentration is less than 35 mg/L.

2. Fig. Calibration curves for  $SO_4^{2}$  measurement with and without additives extra added  $Na_2SO_4$ The calibration curve with extra added  $Na_2SO_4$  can be used to measure  $SO_4^{2-}$  concentration less than 10 mg/L



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This study is supported by the European Social Fund project "Establishment of interdisciplinary scientist group and modelling system for groundwater research". Project No. 2009/0212/1DP/1.1.1.2.0/09/APIA/VIAA/060



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