



# Ion-selective electrodes in potentiometric titrations; a new method for processing and evaluating titration data



Kim Granholm <sup>a, \*</sup>, Tomasz Sokalski <sup>a</sup>, Andrzej Lewenstam <sup>a, b</sup>, Ari Ivaska <sup>a</sup>

<sup>a</sup> Process Chemistry Centre, c/o Laboratory of Analytical Chemistry, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Åbo-Turku, Finland

<sup>b</sup> AGH - University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30-059 Krakow, Poland

## HIGHLIGHTS

- A new method to convert the potential to concentration or activity is proposed.
- The standard potential and the slope of the calibration curve do not have to be known.
- The new method gave accurate results when using synthetic and real samples.
- A complexometric titration model was also developed.

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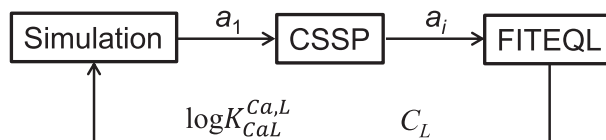
Simulation

Calcium

Black liquor

## GRAPHICAL ABSTRACT

Iteration procedure for obtaining the stability constant



## ABSTRACT

A new method to convert the potential of an ion-selective electrode to concentration or activity in potentiometric titration is proposed. The advantage of this method is that the electrode standard potential and the slope of the calibration curve do not have to be known. Instead two activities on the titration curve have to be estimated e.g. the starting activity before the titration begins and the activity at the end of the titration in the presence of large excess of titrant. This new method is beneficial when the analyte is in a complexed matrix or in a harsh environment which affects the properties of the electrode and the traditional calibration procedure with standard solutions cannot be used. The new method was implemented both in a method of linearization based on the Grans's plot and in determination of the stability constant of a complex and the concentration of the complexing ligand in the sample. The new method gave accurate results when using titrations data from experiments with samples of known composition and with real industrial harsh black liquor sample. A complexometric titration model was also developed.

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## 1. Introduction

Ion selective electrodes have successfully been used in potentiometric titrations [1–3]. The matrices can sometimes be complicated and challenging like the black liquor in the pulping

process [4]. By linearization of the titration curve a better detection of the equivalence point is possible. The first method for a linearization was introduced by Gran in 1950 [5]. This method is simply based on plotting  $\Delta V/\Delta E$  vs. the volume of the added titrant ( $V$ ), which creates two differential curves intersecting at the equivalence point. In 1951 Sørensen published a paper showing that by plotting the antilogarithm of the potential against the volume of the titrant a similar linearized curve was obtained for neutralization titrations of strong and weak acids with strong bases and the

\* Corresponding author.

E-mail address: [kim.granholm@abo.fi](mailto:kim.granholm@abo.fi) (K. Granholm).

titration of chloride ions with silver ions [6]. Gran further investigated Sørensen's method for more complicated titrations such as ion combination titrations including ions of different valences [7]. Sørensen/Gran's second method is today commonly referred to as Gran's method and is still widely used in evaluating potentiometric titration curves. The Gran's second method has further been developed [8–10]. The main drawback with the Gran's second method is that it requires the knowledge of the slope of the electrode response [11]. However, when the Gran's first method is used the knowledge of the slope is not needed but the method in itself is an approximation and does not give accurate results [12]. The Gran's first method has also been modified in order to minimize the approximations needed in this method [12]. Although Gran's first method has the advantage of not requiring the knowledge of the slope it, however, has some other limitations. The points quite close to the equivalence point must be used, and the points after the equivalence point are also needed. When ion-selective electrodes (ISEs) are used in potentiometric titrations those points are perhaps not possible to obtain due to interference of other ions in the sample and due to the detection limit of the electrode [13]. Today the Gran's second method is almost exclusively used.

The need of the value of the slope of the electrode response in the linearization process does not possess any difficulty for well behaving electrodes like for instance the pH glass electrodes. However, in the case of plastic polymeric membrane electrodes and especially with the solid-contact electrode, the standard potential and the slope of the electrode may change with time and due to the exposure to a harsh environment of the sample [4]. The problem then arises if calibration of the ISE in the pure metal ion solutions is any more valid when the electrode is used in such a sample [14]. The uncertainty of the slope influences the result obtained by the Gran's second method. Therefore determination of stability constants depends on the assumed electrode slope and standard potential.

In this work a new method is proposed which does neither require the knowledge of the slope nor the standard potential of ISE and is of general analytical validity. As will be demonstrated in this paper the method is useful especially when linear titration curves are used and when stability constants of metal-ligand complexes are determined in demanding matrices. This method is general and can be used in demanding matrices illustrated later using a black liquor sample.

## 2. Method for circumvention of slope and standard potential (CSSP)

In the proposed CSSP method the values of the standard potential of the cell and the electrode slope do not have to be known. This is advantageous in complex matrices and harsh environments where these values can change over time.

When an ion selective electrode is used as the indicator electrode, the response will be obtained as a potential. This potential is proportional to the logarithm of activity of the specific ion according to the Nernst equation:

$$E = E^0 + S \cdot \log(a) \quad (1)$$

where  $E^0$  is the standard potential of the cell and  $a$  is the activity of the measured ion.  $S$  is the slope of the electrode response and can be calculated theoretically using the following equation:

$$S = \frac{2.303RT}{zF} \quad (2)$$

$R$  is the universal gas constant,  $T$  is the temperature (K),  $F$  is the Faraday constant and  $z$  is charge of the ion. The values of  $S$  and  $E^0$ , however, depend on the electrode and may vary between individual electrodes and over time, especially if the sample is a harsh solution.  $S$  and  $E^0$  are usually found experimentally by performing a calibration.

The principles of the CSSP method are described below.

The potential of an ISE at consecutive titration points is described as:

$$\begin{aligned} E_1 &= E^0 + S \cdot \log(a_1) \\ E_2 &= E^0 + S \cdot \log(a_2) \\ &\dots \\ E_n &= E^0 + S \cdot \log(a_n) \end{aligned} \quad (3)$$

where  $n$  is the number of titration points. If we subtract the last potential from the potentials obtained at all the other points of the titration curve we will obtain the following equations:

$$\begin{aligned} E_1^* &= E_1 - E_n = S \cdot \log\left(\frac{a_1}{a_n}\right) \\ E_2^* &= E_2 - E_n = S \cdot \log\left(\frac{a_2}{a_n}\right) \\ &\dots \\ E_n^* &= E_n - E_n = S \cdot \log\left(\frac{a_n}{a_n}\right) \end{aligned} \quad (4)$$

When the potentials obtained by Eq. (4) are divided by an arbitrary chosen potential from the titration curve, e.g.  $E_1^*$ , we obtain:

$$\begin{aligned} E_1^{**} &= \frac{E_1^*}{E_1^*} = \frac{\log\left(\frac{a_1}{a_n}\right)}{\log\left(\frac{a_1}{a_n}\right)} \\ E_2^{**} &= \frac{E_2^*}{E_1^*} = \frac{\log\left(\frac{a_2}{a_n}\right)}{\log\left(\frac{a_1}{a_n}\right)} \\ &\dots \\ E_n^{**} &= \frac{E_n^*}{E_1^*} = \frac{\log\left(\frac{a_n}{a_n}\right)}{\log\left(\frac{a_1}{a_n}\right)} \end{aligned} \quad (5)$$

After rearrangement of terms the following equation can be obtained:

$$\log(a_i) = E_i^{**} \cdot \log\left(\frac{a_1}{a_n}\right) + \log(a_n) \quad (6)$$

where  $i$  is an index (an integer number), in the range  $i \in (1, n)$ . By using this equation the experimental constants  $S$  and  $E^0$  are not needed. Instead two activities,  $a_1$  and  $a_n$ , on the titration curve have to be estimated. The simplest points to be used in the estimation are perhaps the starting activity (before the titration begins) and the activity at the end of the titration in the presence of large excess of titrant.

The CSSP method is thus useful if the activity of the measured ion both at the start and at the end of the titration can be estimated without knowing the constants  $S$  and  $E^0$ . In order to obtain reliable values for  $a_1$  and  $a_n$  the sample composition has to be known quite well. This can make the method quite arduous and is recommended only when the standard electrode potential and the slope are difficult to obtain.

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