Facile Density Measurement Method for High-Concentration Sulfate Determination

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In this study, a fast, facile and high accuracy method for high concentration sulfate determination is presented. The method is based on precipitation of sulfate ions with barium ions. The sulfate amount is quantified by measurement of the density of the barium and sulfate ion solutions before mixing, and the density of the supernatant after mixing. A calibration curve for sulfate concentration between 2.5 and 5.5 M in vanadium electrolyte was performed, obtaining a precision better than 0.7%, in agreement with a propagation-of-error analysis. Accuracy is determined by one-point calibration against a sample with known sulfate concentration and is at best the same as the precision. Within the precision of the method, no systematic effect of the presence of other ions/interferents (vanadium, phosphate) on the sulfate determination is observed.

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Vanadium Redox Flow Batteries (VRFBs) is a promising technology for large scale Energy Storage Systems (ESS) because of their low-cost potential and long life-time.1,2 In VRFBs, electricity is chemically stored in liquid electrolyte solutions composed of redox active vanadium ions. Vanadium electrolyte typically contains 1.6–1.8 M vanadium ions dissolved in 1.8–3.2 M sulfuric acid.3–6 With a total sulfate concentration of 3.4–5 M. Moreover, additives such as phosphoric acid or ammonium sulfate are often added to the electrolyte to prevent precipitation of V2O5 at temperatures above 40 °C.7 Different vanadium-containing raw materials might be used for the production of vanadium electrolyte,8,9 but V2O5 entails a lower price and is the most widely used precursor at industrial level.8,10

Although VRFBs sometimes are stated to have an infinite chemical lifetime, there are several (reversible) degradation mechanisms. This includes thermal instability, external oxidation, and vanadium, sulfate and volumetric crossover through the membrane in the stack. Regarding crossover, mainly Cation Exchange Membranes (CEMs) or Anion Exchange Membranes (AEMs) are used. If CEMs and AEMs were 100% selective, only protons and sulfate ions, respectively, would migrate across the membrane during charging/discharging.11,12 However, due to the very high ionic strength of the vanadium solution, both the CEMs and AEMs lose significant part of the ion selectivity.13,14 In practice, water, sulfates, protons and vanadium ions in different oxidation states, are transported by diffusion, migration and convection across the membrane.15,16 Because of the many transport mechanisms and types of membranes, there is, to date, no consolidated understanding in the literature on the detailed transport mechanisms.12,16–19

The widely used methods for the determination of vanadium/ sulfate concentration and trace impurities in vanadium electrolyte are Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively Coupled Plasma Mass Spectroscopy (ICP-MS).20–22 However, ICP instruments are costly, both at initial capital expenditure and ongoing operating costs levels.23 Also, ICP is excellent for detection of trace amount but, unless carefully calibrated the technique loses accuracy and precision, and the measurement of concentrations >1 M requires large dilution of the sample. For this reason, many researchers determine the vanadium concentration using redox titrations.8,24–26 In addition, and contrary to ICP, these redox titrations also allow quantification of the concentrations of individual vanadium oxidation states.8 For the determination of sulfate concentration in vanadium electrolyte, the traditional pH titration with a strong base cannot be used because trivalent and tetravalent vanadium precipitates with increasing pH.26 Instead, the most common methods for sulfate determination appear to be based on precipitation of sulfate with BaCl2.7

\[
\text{BaCl}_2(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{Cl}^- (\text{aq}) \quad [1]
\]

Different methods have been developed: (1) Turbidimetric method, involving the formation of BaSO4 suspension under controlled conditions and measuring of the resulting turbidity by a nephelometer, filter photometer or spectrophotometer.27,28 (2) Thermometric titration, due to the strong exothermic reaction arising from the formation of the BaSO4 precipitate,29 and (3) Gravimetric analysis, consisting on the filtering, washing, drying and weighting of the precipitated BaSO4.30,31 However, all these methods suffer from a number of shortcomings. The turbidimetric method requires a very high dilution factor, and it is a method which presents low accuracy. Thermometric titration requires relatively costly equipment, and the gravimetric analysis involves a tedious and lengthy process, with procedures that are prone to errors.

Therefore, for research involving vanadium electrolyte production, monitoring of crossover in VRFBs, or degradation studies there is a need of a method that allows accurate determination of the sulfate concentration in vanadium electrolyte in a simple and inexpensive way.

Concept and Theoretical Description

As for the gravimetric method, the approach for sulfate determination reported in this study is based on precipitation of sulfate with BaCl2 (Eq. 1). Here, a solution of BaCl2 with known volume and concentration is added to a solution with known volume but unknown sulfate concentration. However, unlike the gravimetric analysis, which involves the direct measurement of the precipitate, it is possible to obtain the sulfate concentration by measuring the mass densities of the three solutions involved. The overall procedure is shown in Fig. 1, where a BaCl2 solution with volume VB and density \( \rho_{B} \) is mixed with a vanadium solution with volume VB and density \( \rho_{B} \). Here, the subscript B refers to before mixing of the solutions. After BaSO4 precipitation, the volume (\( V_A \)) and density (\( \rho_A \)) of the supernatant is referred to with the subscript A (after), while \( V_{\text{BaSO}_4} \) and \( \rho_{\text{BaSO}_4} \) refers to the volume and density of the precipitated BaSO4, respectively. It is noted that the molar amount of BaCl2
are the mass and molar mass of precipitated V, as well as the known volumes of the solutions before mixing V ions, respectively. The negative sign in Eq. 6 is a term out of the solution. The term becomes negative in the present case because the ions are precipitated from the solution. By inserting Eq. 6 into Eq. 5 the amount of sulfate ions can be found from Eq. 7 it can be seen that, given the known values of $M_{BaSO_4}$ and $\rho_{BaSO_4}$, as well as the known volumes of the solutions before mixing ($V_{B1}$ and $V_{B2}$), the sulfate content can be determined by the measurement of the density of the solutions before ($\rho_{B1}$ and $\rho_{B2}$) and after ($\rho_A$) mixing. The only unknown in the equation is $\Delta V$, which will be treated as a calibration variable, as shown later in the experimental section.

**Experimental**

**Density measurement and pipetting.**—All density measurements were made with a 30PX/30GQ densimeter (Mettler Toledo, USA). The minimum volume for a measurement in this device is 4.5 ml.

Volumes of reactants were transferred with Finnpipette F2 pipettes 1–10 ml (Thermo Fisher, USA) and Finnpipette F2 100–1000 μl micropipette (Thermo Fisher, USA) using 10 ml and 1 ml pipette tips, for $V_{B1}$ and $V_{B2}$, respectively. The error of the pipettes was measured, by weighing water from the pipettes, to be around 0.2% and 0.4% for the 10 ml and 1 ml pipette, respectively.

**Solutions.**—0.5 M BaCl$_2$ solution was prepared from BaCl$_2$ (Sigma Aldrich, USA, >99% purity) with MilliQ water (Direct-Q3 UV, Merck, USA) and magnetically stirred for 10 min before use.

A row of vanadium solutions with sulfate concentrations between 2.5 M and 5.5 M were prepared from a pristine vanadium electrolyte solution (GfE, Germany). In all cases, the solutions were magnetically stirred for 10 min and their densities were measured in triplicate afterwards. According to the GfE datasheet, the electrolyte presented a vanadium concentration of 5.98 ± 0.01 wt% (1.59 M), a sulfate concentration of 27.86 ± 0.01 wt% (3.93 M) and phosphate concentration of 0.3 ± 0.01 wt% (0.04 M) (Table SI).

17 vanadium solutions, 50 ml each, with sulfate concentrations in the approximate interval 4 M to 5.5 M, were prepared by addition of sulfuric acid (Sigma Aldrich, USA, ~98% purity) to the pristine vanadium solution (Table SIII).
2.5 M to 3.9 M were prepared by dilution with MilliQ water (Table SV).

Also, three vanadium solutions, 50 ml each, with different phosphate concentrations in the approximate interval 0.06 M to 0.10 M were prepared by addition of H₃PO₄ (Sigma Aldrich, USA, 85 wt%) to the pristine vanadium solution. The final theoretical SO₄²⁻ and PO₄³⁻ concentrations of each solution can be found in Table SVII. Higher H₃PO₄ concentrations were not attempted as VPO₄₂ precipitation is observed, whenever the concentration of phosphate exceeds 0.1 M in presence of vanadium.³⁰

Finally, four solutions, 20 ml each, with the same sulfate concentration but different vanadium concentration (1.46 M to 1.56 M) were prepared by diluting the pristine vanadium solution with a 3.95 M H₂SO₄ solution. The final theoretical SO₄²⁻ and vanadium concentrations in each solution can be found in Table SIX.

In all dilutions and up-concentrations of sulfate the experimental error is estimated to be approximately 0.01 M and is based on the precision/error of the pipettes.

Experimental procedure.—The concentration and volumes of BaCl₂ and vanadium solutions were chosen based on error minimization and experimental feasibility, and it is further discussed in Results and Discussion. Nonetheless, 1.75 ml of vanadium solution was added to 19.5 ml of 0.5 M BaCl₂. The samples were left at rest for 2 d until the precipitate was compacted at the bottom of the container. This step can be accelerated by centrifugation of the samples for 10 min at 6500 rpm (CompactStar CS4, VWR, USA). In all cases experiments were performed in triplicate. After this time, the supernatant density was measured, also in triplicate (all density measurements can be seen in Tables SII, SIV, SVI, SVIII and SX).

Results and Discussion

Figure 2 shows the density of the vanadium solutions (ρᵥᵥ), before mixing with the 0.5 M BaCl₂ and after mixing/precipitation of BaSO₄ (ρₐ) as a function of the sulfate concentration. The density of the BaCl₂ solution is 1.75 g ml⁻¹. It is seen that the density of the vanadium solutions before mixing has two distinct slopes below and above 3.95 M. This difference is a consequence of the dilution of the pristine vanadium solution with MilliQ water in the below concentrations, while above it has been spiked with concentrated sulfuric acid. The density after mixing (supernatant, ρₐ) with 0.5 M BaCl₂ is in general much lower, because of the higher volume and lower density of the 0.5 M BaCl₂ (19.5 ml) compared the volume of the vanadium solution (1.75 ml). Also, for the supernatant there is small change in the slope of the density below and above 3.95 M.

Figure 3. Parity plot of the method. The blue dotted line is a simple 1:1 plot and serves as a guide to the eye. The blue circles (left axis) show the experimental concentration obtained from the density measurements and calibration equation (ΔV = 21.5 ml mol⁻¹, Eq. 7). The orange crosses (right y-axis) show the deviation between the intrinsic and the experimental value. The inset (bottom right corner) shows the uncalibrated plot (ΔV = 0).

Experimental error of the SO₄²⁻ dilution/up-concentration (x-axis) is estimated to be 0.01 M and is smaller than the diameter of the datapoints.

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From the data shown in Fig. 2, a calibration/parity plot for the method was obtained and is shown in Fig. 3, plotting the calibrated sulfate concentration from the density measurement as function of the intrinsic one.

The experimental fitted concentration was obtained by applying Eq. 7, where υᵥᵥ, υᵥᵥ, ρᵥᵥ, ρᵥᵥ, ρᵥᵥ are measured values. Mᵥᵥ and ρᵥᵥ are constants, with a fixed value in all cases of 233.38 g mol⁻¹ and 4.5 g cm⁻³, respectively. ΔV is the only calibration parameter, referring to the change in molar partial volume of the solution, due to precipitation of BaSO₄. With a linear fit to the data in the whole concentration range a value of ΔV = 21.5 ml mol⁻¹ is found. With a positive value of ΔV it means that the volume of the supernatant has decreased compared to the sum of the two volumes before mixing. Millero and Marcus collect in their respective studies the value of the partial molar volume of different ions in pure water; here it is noted that there is a significant difference in the molar volumes of HSO₄⁻ and SO₄²⁻. In the present case, all solutions have pH < 0, so the speciation of sulfate is almost entirely on the HSO₄⁻ form. Hereby, the formal precipitation reaction becomes Ba⁴⁺(aq) + HSO₄⁻(aq) → BaSO₄(s) + H⁺(aq). According to the molar volumes of Millero and Marcus this gives ΔV ~ 15–20 ml mol⁻¹, depending on the molar volume of H⁺, see discussion in Marcus.³³ This agrees well with the fitted value of ΔV = 21.5 ml mol⁻¹. Also, in Eq. 6 it was assumed that ΔV(Ba⁺,X⁺,C⁷⁻) = 0. This may not be the case and this term could correlate with ΔV, and add error to the fitted ΔV value. Nonetheless, the main point is that the calibration results in a value of ΔV which has the correct sign and a value close to the literature.

As can be seen from Fig. 3, the method presents an absolute error in the range up to 0.036 M corresponding to 0.663%. The area shaded in grey in Fig. 3, shows the theoretical error (0.032 M) based on a propagation of error calculation. Details can be found in Supporting Information—Section S6, but the main conclusion is that the largest contributions to the error stem from two sources. The first is the error associated to the density measurement. Although the used densimeter already presents a relatively high accuracy (0.0004 g ml⁻¹), a device with even better accuracy and higher number of significant digits will reduce the error. The second is related to the magnitude of the volume of the BaCl₂ solution (υᵥᵥ) and the consequent smaller variation of the density after mixing (ρᵥᵥ, see Fig. 2). This error can be minimized by increasing the BaCl₂...
concentrations based on precipitation with BaCl$_2$ and density eye.

Theoretical equations as function of the intrinsic/theoretical sulfate concentration. Where it has been reported that Ba$_2^+$ is very similar to the one described in this study, but being the mass of added BaCl$_2$ the parameter going inside the system is very similar to the one described in this study, but being the mass of added BaCl$_2$ the parameter going inside the equations, instead of the density of the prepared BaCl$_2$ solution. The main reason for not choosing this approach was that it would require larger sample (vanadium) volumes, as the minimum volume for the density measurements (minimum 4.5 ml), and to not waste large amounts of vanadium electrolyte due to a very large number of samples. However, other combinations of volumes/concentration leading to a lower error, might be used according to the specific applications.

It should be noted that other variants of the method, where solid BaCl$_2$ is added directly to the sulfate ion solution, are also feasible. For this case, the theoretical description (mass and volume balances to the system) is very similar to the one described in this study, but being the mass of added BaCl$_2$ the parameter going inside the equations, instead of the density of the prepared BaCl$_2$ solution. The main reason for not choosing this approach was that it would require larger sample (vanadium) volumes, as the minimum volume for the density measurement was 4.5 ml.

**Influence of phosphate and vanadium concentration on sulfate determination.**—Figure 4 shows the results of the sulfate determination for samples with varying phosphate and vanadium concentrations as function of the intrinsic/theoretical sulfate concentration. The blue dotted line is a simple 1:1 plot and serves as a guide to the eye.

For all samples with both varying vanadium and H$_3$PO$_4$ concentration, it is seen that the absolute error is in the range up to 0.014 M, corresponding to 0.35%. Although it appears that the measured concentration of samples with additional PO$_4^{3-}$ is systematically overestimated, all samples, both with varying vanadium and PO$_4^{3-}$ concentration, have errors within the experimental/calculated error of 0.03 M (Fig. 3). This is also in agreement with the literature, where it has been reported that Ba$^{2+}$ ions will not precipitate PO$_4^{3-}$ ions in acidic solutions. Thus, it can be concluded that, within the precision of the method, there are no significant errors/interferences from phosphates or vanadium on the sulfate concentration determination.

**Conclusions**

In this paper, a method for the determination of high sulfate concentrations based on precipitation with BaCl$_2$ and density measurements is proposed. The suggested approach was studied for sulfate concentrations between 2.5 M and 5.5 M in pristine vanadium electrolyte and a maximum experimental deviation of 0.036 M (0.7%) was obtained, in good agreement with a propagation of error analysis (±0.032 M). Errors can be reduced by the use of a densimeter with higher precision and the use of higher concentration BaCl$_2$ solutions. Additionally, the method is insensitive to interferents, having been tested for vanadium and phosphates.

The method overcomes the disadvantages of previously used methodologies in the literature for high sulfate concentration determination. It is anticipated that the method optimizes the overall performance of existing methods in terms of precision, accuracy, labor intensity and cost.

Also, the method has some general aspects, as it can be used for determination of any type of ions that can be precipitated out. This could e.g. be metal ion concentration determination by precipitation with hydroxide.

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**Author Contributions**

Conceptualization, A.B.; funding acquisition, A.B.; methodology, S.N.O., P.B. and A.B.; experimental, S.N.O.; supervision, A.B.; validation, S.N.O.; visualization, S.N.O., writing—initial draft, S.N.O., review and edition, S.N.O, P.B. and A.B.

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