

Kinetic study of niobium and tantalum and their substituted ions by capillary electrophoresis in alkaline media

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Abstract

In this work capillary electrophoresis (CE) is used for the kinetic study of the substitution of hexameric forms of two strategic metals, tantalum and niobium in an alkaline medium. Recently proposed processes for production and separation of tantalum and niobium are based on the use of highly alkaline media. It is already known that in these media, tantalum and niobium exist as $H_xTa_6O_{19}^{X-8}$ and $H_xNb_6O_{19}^{X-8}$ hexameric forms and can be analysed in CE with an alkaline electrolyte and a direct UV detection. However, by using this method a minor species that should correspond to a substituted Ta_1Nb_5 form was observed in an industrial sample. This is why a kinetic study was performed and the occurrence of the substituted ions, $Ta_{6-x}Nb_x$, from mixtures of both hexameric forms. To accomplish this task a new CE method allowing the separation of all the substituted ions was developed. It consisted in an adaptation of a CE method previously developed with an Agilent set-up for the ultra-fast detection of Ta_6 and Nb_6 and it was done first with a Beckman instrument. The total capillary length, the applied voltage, the injection volumes, the rinsing steps and the internal standard were adjusted to improve the separation. During the kinetic study a sample containing hexameric forms of tantalum and niobium in a 1:1 molar ratio was heated at 60°C and analysed every hour. The substitutions of both hexameric forms into five different sub forms were observed for the first time. The process was fully completed after 21 hours. The developed CE method was next transferred to an Agilent instrument and the kinetic study repeated. The results confirm the earlier findings thus providing a validation of the kinetic study, and give evidence of the methods transferability.

1. Introduction

In this study a short-end capillary electrophoresis (CE) method is used for the separation of two strategic metals, being the hexameric forms of Niobium (Nb) and Tantalum (Ta). A kinetic study in alkaline medium was performed in order to follow the formation of different substituted ions of a sample initially containing hexameric forms of Ta and Nb, $H_xTa_6O_{19}^{x-8}$ and $H_xNb_6O_{19}^{x-8}$ respectively, further denoted as Ta_6 and Nb_6 . These hexameric polyoxometalate ions dominate the chemistry of Nb and Ta at pH higher than ~ 9 and will catch growing attention in the industry as processes containing these ions are currently under development. The substitution process was followed by CE, a separation technique based on differences in electrophoretic mobilities and existing in different formats, such as capillary zone electrophoresis, capillary gel electrophoresis, capillary isoelectric focussing electrophoresis, etc. Electrophoretic mobilities of the analytes are determined by the ratio of the charge over the hydrated radius of the analyte [1]. CE either or not coupled with a mass spectrometry detector, is gaining an increased interest nowadays in the analysis and characterisation of biopharmaceuticals [2, 3]. It is an alternative and complementary separation technique to the more frequently applied high performance liquid chromatography. Advantages of CE are fast analyses, high separation efficiency, small sample sizes and the fact that it is a green and economical technique [4].

A particular case of CE applications are Short-end CE methods, often used in kinetic studies, enzymatic reactions, clinical analyses and high-throughput screening studies in the pharmaceutical industries to reduce analysis times [5]. Short-end injections use a default effective length, being the distance between injection end and detection window of the capillary, of 8.5 or 10 cm, for an Agilent or a Beckman CE instrument respectively [6]. The minimally required effective length when performing a regular injection method is 25 – 30 cm. The short effective length not only reduces the analysis time, it potentially leads to stacking effects and thus an increased efficiency and higher sensitivity. Furthermore due to the reduced analysis time, lower voltages can be applied when facing a joule heating

effect. Prerequisite for a short-end injection is a highly efficient method to compensate the loss of resolution due to the reduced migration length [7-10].

In the kinetic study performed in this paper a short-end injection method to separate Nb₆ and Ta₆ developed earlier by Deblonde et al. [9], was adapted. Ta and Nb are two group V metals essential in various industries, such as the aerospace, gas, oil, electronic and nuclear sectors. Both metals are found in the same natural source and due to their almost identical physicochemical features, their separation is challenging and is the subject of many research projects [11-15]. Earlier research on their production and separation processes mainly focused on complexation of both compounds in acidic fluoride-based media and many different techniques, such as HPLC, Nuclear Magnetic Resonance, Raman Spectroscopy, Inductively Coupled Plasma, and potentiometry were used as analytical tools [12-15]. Deblonde et al. [11] suggested the application of a faster and greener capillary electrophoretic separation in an alkaline background electrolyte (BGE). It was found earlier that Ta and Nb exist in hexameric forms in alkaline media, i.e. at pH-values above 9. The hexameric forms of Ta and Nb possess absorption characteristics in the UV-spectral region in contrast to the monomeric chelates found in acidic and complexing aqueous solutions [16]. This UV visibility facilitates the use of CE as an analytical method and avoids the use of prior complexation techniques for detection purposes. Although the molar mass of Ta₆ is higher than that of Nb₆ they both possess a rather identical hydrated radius. This similar radius also complicated the analytical separation of both compounds in previously tested techniques [11, 12, 15]. As stated above the physicochemistry of Tantalum and Niobium was studied earlier and it was proven that in addition to their UV visibility the hexaniobate and hexatantalate ions, which are naturally formed at pH above 9, possess different electrophoretic mobilities and can thus be separated by means of capillary electrophoresis [9, 2]. A difference in electrophoretic mobility is determined by a difference in the charge on the hydrated radius ratio of an ion, and since their hydrated radius was rather identical, the effective charges of both hexameric forms need to be different to allow a separation by means of CE. The difference in charge of the hexameric forms, and thus in

electrophoretic mobilities, is occurring due to different protonation and ion pair formation with alkaline cations of both compounds in alkaline media. The analysis of an industrial sample (figure 1) containing Nb₆ and Ta₆ showed also a small peak of what is expected to be a substituted ion, namely Ta₁Nb₅. Therefore a kinetic study was performed to verify whether Ta₁Nb₅ is formed during the synthesis of Nb₆ and Ta₆ from their respective starting materials (oxides, monomeric complexes, etc) or if it is the result of a spontaneous substitution when combining the polyoxoanions Nb₆ and Ta₆ in alkaline medium. In a first part of our study the earlier developed separation method [9] was, due to the unavailability of the earlier used Agilent instrument, transferred to a Beckman instrument in the same laboratory. During this inter-instrumental transfer the earlier defined guidelines by De Cock et al [17,18] were applied. Subsequently, in order to be able to separate all the substituted ions that can appear between the Ta₆ and Nb₆ peaks, the CE method was adapted to get peaks that are baseline separated and the repeatability was improved, by adjusting the total capillary length, the applied voltage, the injection volume, the rinsing steps and the internal standard (IS). In a third and final part the new CE short-end injection method was transferred to an Agilent instrument and the kinetic study was repeated to confirm the earlier observed results.

2. Material and instruments

2.1 Chemicals

Dimethylformamide, used as electroosmotic flow (EOF) marker, and 2-naphtalene sulfonic acid, used as internal standard, both in a 0.1 % m/v aqueous solution were purchased from Sigma-Aldrich (Steinheim, Germany). The ultra-pure water was made in house by a Direct-Q3 UV system (Millipore, Molsheim, France) and used for the preparation of all stock solutions and the BGE. LiOH.H₂O and LiCH₃COO.2H₂O were purchased from Alfa Aesar (ThermoFisher Scientific, Waltham, Massachusetts, USA). The BGE, at a pH of 12.0, consisted of 35 mM LiCH₃COO.2H₂O and 10 mM LiOH.2H₂O and was, because of the high pH, prepared daily by dissolving the appropriate amounts of LiOH.H₂O and LiCH₃COO.2H₂O in ultra-pure water. The hexameric forms, Na₇HNb₆O₁₉.15H₂O and Na₈Ta₆O₁₉.24.5H₂O,

were synthesised as reported earlier [19] and stored at 4 °C. Stock solutions were freshly prepared every week by dissolving $\text{Na}_7\text{HfNb}_6\text{O}_{19}\cdot 15\text{H}_2\text{O}$ (2 g/L) and $\text{Na}_8\text{Ta}_6\text{O}_{19}\cdot 24.5\text{H}_2\text{O}$ (4 g/L) in ultra-pure water while stirring during 2 hours and were stored at 4 °C. The BGE and all stock solutions were filtered through a 0.25 μm syringe filter (Minisart® RC25, Sartorius, Goettingen, Germany) and placed during 10 min in an ultra-sonic bath prior to CE experiments.

2.2 Instrumental set-up

The first kinetic study was performed on a P/ACE Capillary Electrophoresis system from Beckman Coulter (Fullerton, California, USA) equipped with a diode array detector (DAD). A fused silica capillary (Photonlines, Marly-le-Roi, France) with an internal diameter of 50 μm , an effective length of 10 cm (short end injection) and a total length of 60 cm was installed in the capillary cartridge. The detection wavelength was set at 211 nm \pm 6 nm bandwidth, the reference wavelength was put at 325 nm \pm 50 nm bandwidth and a data acquisition rate of 4 Hz was applied. The capillary temperature was kept at 31.0 °C by liquid cooling and the electropherograms were processed with the 32 Karat™ software version 5.0 (Beckman Coulter, Fullerton, California, USA). The applied electrical field was -22.0 kV which generated a current of approximately -49.0 μA . Capillary preconditioning was performed by rinsing the capillary with consecutively 1.0 M and 0.1 M $\text{LiOH}\cdot\text{H}_2\text{O}$; ultra-pure water and BGE at a pressure of 60 PSI / 4.13 bar during 10 min each, corresponding to 81.16 μL [20]. Between runs, the capillary was rinsed during 2 min with BGE at 60 PSI / 4.13 bar, corresponding to a rinse volume of 16.14 μL [20]. The samples were hydrodynamically injected at 0.1 PSI / 6.9 mbar during 9.0 s at the anodic end, equal to an injection volume of 2.03 nL [20].

The Agilent G1600A instrument (Agilent Technologies, Santa Clara, California, USA), used during the second kinetic study, was likewise equipped with a DAD module and following detection parameters; the wavelength was set at 211 nm \pm 6 nm and the reference wavelength was kept at 325 nm \pm 50 nm. The data acquisition rate was adapted to 3.33 Hz, instead of 4.00 Hz on the Beckman instrument. A fused silica capillary from the same

batch (Photonlines, Marly-le-Roi, France) with an internal diameter of 50 μm , an effective length of 9.5 cm and a total length of 60 cm was installed in the capillary cartridge. The applied voltage was lowered, because of joule heating, to -21.0 kV which generated a current of approximately -42.5 μA . The capillary temperature was also here kept at 31°C, by means of a high-speed forced-air cooler, while the electropherograms were processed by means of the 3D-CE chemstation software (Agilent Technologies, Santa Clara, California, USA). Capillary preconditioning and rinsing steps were performed with identical volumes and parameters as on the Beckman instrument which were calculated with CE expert lite tool (Sciex, Framingham, Massachusetts, USA) [20]. An identical injection volume was obtained by applying an injection pressure of 0.1 PSI / 6.9 mbar during 8.5 s.

3. Results and Discussion

3.1 Quantitative method

Initially the short-end injection method of Deblonde et al [9] was used during the kinetic study. In this study a sample containing the hexameric forms of Ta and Nb in a 1:1 molar ratio was heated at 60 °C and analysed hourly to evaluate the possibility of a spontaneous transition of Ta₆ and Nb₆ into different substituted ions. The initial method [11] was found inadequate because of the high variation in and shift of migration times (Mt) and areas under the curve (AUC) of the peaks, as RSD values higher than 10 % occurred for both the Mt and AUC. The use of mobilities and relative AUC were insufficient to overcome the problem. The high variability was initially accepted since the developed method was purely meant to identify and separate Nb₆ and Ta₆. On the other hand a highly repeatable method with baseline separation is needed to quantitatively evaluate the different substituted ions observed during the kinetic study. Therefore several parameters of the initial method were adapted as shown in Table 1. In a first step, the total capillary length was increased from 30 to 60 cm while keeping an effective length of 10 cm, therefore the advantages of the ultra-fast short end injection remained. The longer total capillary length leads to a higher electrical resistance as illustrated in [Equation 1].

$$R = \frac{L}{k * A} \quad \text{Equation 1}$$

with L the total capillary length, k the electrical conductivity and A the cross-sectional area of the capillary.

The increased electrical resistance while applying an identical constant voltage leads to a lower current as depicted in [Equation 2].

$$V = I * R \quad \text{Equation 2}$$

with I the current, V the voltage and R the electrical resistance.

The use of a longer capillary did further allow the application of a higher voltage while generating a lower current, 49 μA as compared to 70 μA during the initial method on the Agilent instrument. Both the longer capillary and the lower current decrease the heat generation inside the capillary as shown in [Equation 3].

$$\frac{dH}{dt} = \frac{I * V}{L * A} \quad \text{Equation 3}$$

with $\frac{dH}{dt}$ the increase of heat inside the capillary as a function of the analysis time, I the amount of current generated, V the applied voltage, L the total capillary length and A the cross-sectional area of the capillary. (already defined)

The lower heat generation (due to joule heating) leads lower temperature and thus improves the precision and separation efficiency of a capillary electrophoretic method [21, 22]. The amount of voltage per column length decreased from 16 kV / 30 cm total capillary length to 22 kV / 60 cm total capillary length. The lower electrical field combined with the longer effective length, due to the instrumental different capillary cartridge (10 cm instead of 8.5 cm), did lead to a longer analysis time as shown on Figure 1B but also to an improved separation of Ta₆, Nb₆ and the substituted ions.

The longer capillary length did furthermore allowed a longer injection time, or higher injection pressure, to generate an equal injection volume as the initial method, as illustrated by [Equation 4].

$$V_{inj} = \frac{\Delta p d^4 \pi t}{128 \eta L} \quad \text{Equation 4}$$

with v_{inj} the injection volume, Δp the applied pressure difference, d the capillary internal diameter, π the constant pi, η the viscosity inside the capillary-

The initial injection volume of 1.96 nL by application of 0.14 psi / 9.6 mbar during 3.0 s was replaced by an injection step of 9 s with a pressure of 0.1 psi / 6.9 mbar leading to an injection volume of 2.02 nL [20]. A longer injection time allows the injection pump to have more time to generate a given and constant pressure and thus more repeatable injection volumes [21, 23].

Some detection parameters needed to be adapted according to the guidelines defined in De Cock et al. [18]. Due to instrumental limitations the bandwidth of 5 nm could not be selected, therefore 6 nm was opted. A difference of 1 nm in bandwidth was not found statistically significant and would therefore not cause a significant variation in AUC or peak height. The required acquisition rate of 3.33 Hz was instrumentally impeded on the Beckman instrument. An acquisition rate of 4.00 Hz was set since it was the closest available option to the original parameter value. As shown in De Cock et al [18], the non-significant interval of the data acquisition rate is rather small when inter-instrumentally transferring a CE method. Therefore variations of the signal-to-noise ratio and efficiency were eventually to be expected but in practice did not influence the study.

The initial voltage of 16 kV was increased after implementation of a longer total capillary length and a consequentially lower current. After application of a Joule test, where the linear increase of the current versus the applied voltage is investigated, 22 kV was selected as maximum separation voltage. A higher voltage leads to increased separation efficiencies as illustrated by [Equation 5].

$$N = \frac{\mu_{ep} V l}{2 D_m L} \quad \text{Equation 5}$$

with N the efficiency, μ_{ep} the electrophoretic mobility of the compound, V the applied voltage, D_m the diffusion coefficient of the solute, l the effective capillary length and L the total capillary length (already defined).

The goal of the initial method [9] was an ultra fast identification of Nb_6 and Ta_6 . However the ultra fast aspect of this method was impeded by a rinse step of ten min. Therefore a reduction of this rinse step without loss of precision was evaluated. A 2 min rinse step at 60 psi / 4.13 bar with BGE resulted in similar RSD of the migration times (approximately 0.7 %) and relative AUC (approximately 4.5 %) compared to the 10 min rinse at 14.5 psi / 1 bar and was thus included in the adapted method. The naphthalene 1.5 disulphonate was selected as IS during the method development by Deblonde et al. [11], as it migrates between Ta_6 and Nb_6 and does not lengthen the analysis time. Nevertheless, it is not adapted to the study of the substituted ions as it could co-migrate with Ta_1Nb_5 . 2-naphthalenesulfonic acid was selected as an IS because it is less negatively charged and thus migrates faster and does not interfere with Nb_6 , Ta_6 or any of the substituted ions as shown in Figure 2. All above discussed adaptations lead to a more precise quantitative method, *i.e.* with all compounds baseline separated, as described in Section 2. This method was used during the following kinetic study on the Beckman instrument.

3.2 Kinetic study on the Beckman instrument

A first kinetic study was carried out on the Beckman instrument, since the quantitative method was developed on this instrument. A sample containing 0.05 mM of $Na_7HNb_6O_{19} \cdot 15H_2O$ and $Na_8Ta_6O_{19} \cdot 24.5H_2O$ both dissolved in the basic BGE was prepared. The samples were then heated at 60 °C and analysed every hour during 24 h. In Figure 2, an overview of the appearance of different substituted ions, after a given period of time, is shown. After 2 h a first substituted form appeared with an electrophoretic mobility/migration time situated between Nb_6 and Ta_6 but very close to Nb_6 , and it was

defined as Ta_1Nb_5 . This minor species was already noticed in the industrial samples earlier analysed (Figure 1). Furthermore the apparition of a second substituted ion, situated between Nb_6 and Ta_6 but very close to Ta_6 , occurred after 3 h and should correspond to Ta_5Nb_1 . Ta_5Nb_1 was, unlike Ta_1Nb_5 , not observed in either of the industrial samples. The industrial sample analysed on the Beckman instrument, containing a 1:1 molar ratio of Ta_6 and Nb_6 , only showed one substituted ion, being Ta_1Nb_5 , and thus Ta_5Nb_1 was absent. Considering Figure 1B showing the industrial sample analysed on the Agilent instrument, containing a 1:25 molar ratio of Ta_6 and Nb_6 , the presence of two substituted ions is seen, but not that of Ta_5Nb_1 . The absence is potentially linked to the very low concentration of Ta in this industrial sample.

Subsequently during the kinetic study more substituted forms appeared, such as Ta_2Nb_4 after 7 h, Ta_4Nb_2 showed up after 10 h and as last Ta_3Nb_3 was formed after 11 h in the oven. After 24 h the five different substituted ions of Ta_6 and Nb_6 in basic medium are clearly seen (Figure 2). The identification of the substitutions is based on their electrophoretic mobilities and UV absorbance spectra. Further confirmation by means of inductively coupled plasma (ICP) or X-ray diffraction (XRD) should be performed.

The substitutions occur in a logical sequence, one Nb or Ta atom at-a-time is exchanged from the corresponding hexameric forms and the corresponding electrophoretic mobilities of the substitution consequently is situated in between Ta_6 and Nb_6 . The substitution of an Nb atom by a Ta atom always occurred before the substitution of a Ta atom by an Nb atom as shown in Figure 2. In Figure 3 the rather linear AUC variations as a function of time of each Nb or Ta hexameric form and the resulting substituted ions are illustrated. The % AUC decrease of Ta_6 is larger than that of the Nb_6 % AUC reduction, potentially explaining the faster Nb to Ta substitution since more Ta is thus available for substitution. This kinetic study was repeated once on the Beckman instrument and similar results were found suggesting that a mixture of the hexameric forms of both Nb and Ta spontaneously substitute in basic medium. This also indicates that the minor species found in the industrial sample are substituted ions and are not degradation or side products. The results also

emphasize that the formation of the substituted Nb-Ta ions, which depends on the process conditions (temperature, residence time, etc.), has to be taken into account when developing Nb-Ta industrial processes in alkaline media, and more generally, for industrial methods dealing with polyoxometalates. The analytical procedures developed in this study could therefore be helpful in the development of such industrial projects.

3.3 Kinetic study on the Agilent instrument

For the initial transferred confirmatory kinetic study on the Agilent instrument the baseline separation between Ta_6 and Ta_5Nb_1 was lost and thus the qualitative analysis hampered [6]. When applying the interinstrumental method transfer of this short end injection method, an instrumental difference, being the capillary cartridge construction, caused a difference in effective length. The total capillary length remained constant but the lower effective length, *i.e.* 10 cm on the Beckman instrument versus 8.5 cm on the Agilent system, did lead to the initial loss of baseline separation. This instrumental difference was overcome by lowering the injector lift, by means of the lift offset parameter on the Agilent system, from 4 mm (= default value) to 14 mm as described in De Cock et al. [6]. The increase of the effective capillary length, from 8.0 to 9.5 cm, on the Agilent system led to a successful interinstrumental method transfer, with restoration of the baseline separation.

A new kinetic study was next performed and afforded confirmation of the earlier results obtained on the Beckman instrument. As seen in Figure 4, an identical trend considering the apparition of the different substituted ions was observed as during the first kinetic study accomplished on the Beckman system. It should be noted that, because of a larger noise, the signal-to-noise ratios obtained on the Agilent instrument are lower than those obtained on the Beckman instrument although the detector and data collection settings were kept as identical as possible [18]. Reasons are potentially a difference in lamp hours, lamp instability or inherent at the Agilent instrument data-handling. After 2 h the formation of the first substitution, Ta_1Nb_5 , was observed. Exactly as in the first kinetic study Ta_5Nb_1 and Ta_2Nb_4 appeared after 3 and 7 h respectively, although the apparition of Ta_2Nb_4 is less evident due to the increased noise. Ta_4Nb_2 was observed slightly later than during the

earlier performed kinetic study, namely after 11 instead of 10 h (probably also due to the increased noise level). Ta_3Nb_3 was, identical to the first study, the finally formed substituted ion. Although the appearance of Ta_3Nb_3 , after 15 h, was seen later during the second study, the global pattern and time schedule of the substituted forms confirmed the observations made on the Beckman instrument. The time difference in the observations might be due to the increased noise level and lower signals that were seen on the Agilent system. Finally as shown in Figure 4, after 24 h, the substitution from Nb_6 and Ta_6 into Ta_5Nb_1 , Ta_4Nb_2 , Ta_3Nb_3 , Ta_2Nb_4 and Ta_1Nb_5 clearly occurred reducing largely the amounts of Ta_6 and Nb_6 initially present in the sample, as was also illustrated in Figure 3.

4. Conclusions

In a preliminary study it was found that a Ta_6 and Nb_6 industrial sample, extracted from a natural source by use of a basic medium, contained one or more minor species. To investigate the origin of these impurities a first kinetic study was carried out on a Beckman instrument. In the kinetic study a sample containing a 1:1 molar ratio of Nb_6 and Ta_6 dissolved in a basic medium, heated at 60 °C, and analysed hourly. For the purpose of this study, the earlier developed CE method by Deblonde et al. [11] was modified to allow the separation of all the substituted ions (Ta_xNb_{6-x} ; $1 \leq x \leq 5$). Our study illustrates, for the first time, the spontaneous formation in basic media of five substituted ions when starting from non-substituted hexameric forms of Ta_6 and Nb_6 . The substitutions noticed were, in order of appearance: Ta_1Nb_5 , Ta_5Nb_1 , Ta_2Nb_4 , Ta_4Nb_2 and Ta_3Nb_3 . The proposed substitution sequence and the experimental electrophoretic mobilities well correlate ~~corresponding~~ to the expected substitutions pattern. Furthermore it was shown that the substitution of an Nb atom by a Ta atom always occurred prior to the exchange of a Ta atom for an Nb atom. In a follow-up study after a successful interinstrumental transfer, including the lowering of the lift offset, the kinetic study was repeated on an Agilent instrument. The results confirmed the earlier observed trend and thus it can be concluded that a basic medium potentially induces the substitution between both pure hexameric forms. The implications of these results not only concern the on-going development of Nb-

Ta processes operated in alkaline media but it is also of interest for other processes and analytical methods dealing with polyoxometalates.

5. References

- [1] Altria K. D., Trends in Analytical Chemistry, 1998, 17, 204-214.
- [2] Kašička V., Electrophoresis, 2001, 22, 4139-4162.
- [3] Tamizi E., Jouyban A., Electrophoresis, 2015, 36, 831-858.
- [4] Haselberg R., De Jong G. J., Somsen G. W., Journal of Chromatography A, 2007, 1159, 81-109.
- [5] Kelly M.A., Altria K.D., Clark B.J., Journal of Chromatography A, 1997, 768, 73-80.
- [6] De Cock B., Oliver J. D., Delaunay N., Deblonde G., Mangelings D., Vander Heyden Y., Interinstrumental method transfer of an ultra-fast short-end injection capillary electrophoretic separation of Niobium, Tantalum and their substituted ions, submitted for publication.
- [7] Altria K. D., Kelly M. A., Clark B. J., Chromatographia, 1996, 43, (3), 153-158.
- [8] Perrin C., Vander Heyden Y., Maftouh M., Massart D. L., Electrophoresis, 2001, 22, 3203-3215.
- [9] Deblonde G., Chagnes A., Cote G., Vial J., Rivals I., Delaunay N., Journal of Chromatography A, 2016, 1437, 210-218.
- [10] Glatz Z., Electrophoresis, 2013, 34, 631-642.
- [11] Deblonde G., Delaunay N., Lee D., Chagnes A., Cote G., Gareil P, RSC Adv, 2015, 5, 64119-64124.

- [12] Li D. L., Hu X. Y., Wang H. Z., *Talanta*, 63, 2004, 233-237.
- [13] Nete M. Purcell W., Nel J., *The journal of the Minerals, Metals and Materials Society*, 2016, 2, 556-566.
- [14] Kabangy M., Crousse P., *Hydrometallurgy*, 2012, 129-130, 151-155.
- [15] Ayanda O., Adekola F., *Journal of Minerals and Materials Characterization and Engineering*, 2011, 10, 245-256.
- [16] Deblonde G., Moncomble A., Cote G., Bélair S., Chagnes A., *RSC Advances*, 2015, 5, 7619-7627.
- [17] De Cock B., Dejaegher B., Stiens J., Mangelings D., Vander Heyden Y., *J Chromatogr A*, 2014, 1353, 148-159.
- [18] De Cock B., Hamza N., Mangelings D., Vander Heyden Y., interinstrumental transfer of a chiral capillary electrophoretic method: The use of robustness test information to overcome differences in detector and data-handling specifications, unpublished results.
- [19] Deblonde G., Moncomble A., Cote G., Bélair S., Chagnes A., *RSC Advances*, 2015, 5, 7619-7627.
- [20] CE expert tool, Beckman Coulter, Fullerton, USA, <http://sciex.com/ce-features-and-benefits/ce-expert-lite> accessed on 09/08/2016.
- [21] Mayer B.X., *Journal of Chromatography A*, 2001, 907, 21-37.
- [22] Xuan X., Li D., *Journal of Micromechanics and Microengineering*, 2004, 14, 1171-1180.
- [23] Altria K., Fabre H., *Chromatographia*, 1995, 40, 5/6, 313-320.

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Figure 1: A) Electropherogram of an industrial sample of Ta₆ and Nb₆ 1:1 (M/M) ratio, spiked with Ta₆ for identification reasons, and sodium naphthalene 1,5 disulfonate as internal standard, with the initial short-end injection method developed by Deblonde et al [9], 45 mM LiOH/LiCH₃COO BGE at pH 12, 31°C, -16 kV and a total capillary length of 30 cm, obtained on the Agilent instrument. Reproduced from [9] with permission. B)

Electropherogram of an industrial sample containing purified Nb₆ and Ta₆ (25:1 ratio), with the final short-end injection method, 45 mM LiOH/LiCH₃COO BGE at pH 12, 31°C, -21 kV and a total capillary length of 60 cm obtained on the Agilent instrument.

Figure 2: Overview of the apparition of the different substituted ions during the kinetic study performed on the Beckman instrument.

Figure 3: Hourly overview of the change in area under the curves of Ta, Nb and the occurring substitutions.

Figure 4: Overview of the apparition of the different substituted ions during the kinetic study performed on the Agilent instrument.