# Lawrence Berkeley National Laboratory
## Chemical Sciences

**Title**

Kinetic study of niobium and tantalum hexameric forms and their substituted ions by capillary electrophoresis in alkaline medium

**Permalink**

https://escholarship.org/uc/item/9dj8r3mv

**Authors**

De Cock, Bart
Delaunay, Nathalie
Deblonde, Gauthier
<u>et al.</u>

**Publication Date**

2017-12-01

**DOI**

10.1016/j.talanta.2017.07.025

Peer reviewed

# Kinetic study of niobium and tantalum hexameric forms and their substituted ions by capillary electrophoresis in alkaline medium

Bart De Cock[a], Nathalie Delaunay[b,c], Gauthier Deblonde[b], Valentina Bosi[d], Luisa Pasti[d], Debby Mangelings[a], Yvan Vander Heyden[a,*]

[a] Department of Analytical Chemistry and Pharmaceutical Technology, Center for Pharmaceutical Research, Vrije Universiteit Brussel (VUB), Laarbeeklaan 103, B-1090 Brussels, Belgium
[b] Laboratoire Sciences Analytiques, Bioanalytiques et Miniaturisation (LSABM), UMR CBI 8231, ESPCI Paris, PSL Research University, 10 Rue Vauquelin, F-75005 Paris, France
[c] CNRS, UMR CBI 8231 Paris, France
[d] Department of Chemistry and Pharmaceutical Sciences, University of Ferrara, 9 Via Savonarola, 44121 FE, Ferrara, Italy

## ARTICLE INFO

## ABSTRACT

In this work a capillary electrophoretic (CE) method is used for the kinetic study of the intermetallic substitutions in hexameric ions of two strategic metals, tantalum and niobium in an alkaline medium. Recently proposed processes for the production and analytical separation of tantalum and niobium that are faster, more economical and environmental friendly are based on the use of highly alkaline media. It was previously established that in these media, tantalum and niobium exist as hexameric species, $H_xTa_6O_{19}^{X-8}$ ($Ta_6$) and $H_xNb_6O_{19}^{X-8}$ ($Nb_6$), which can be analysed with a CE method using an alkaline electrolyte and UV detection. However, when using the above method on an industrial sample a minor species that should correspond to the substituted $Ta_1Nb_5$ form was observed. The purpose of the present study is to probe, by means of CE, the kinetic of the formation of substituted niobate-tantalate ions, $Ta_{6-x}Nb_x$ ($1 \leq x \leq 5$), starting from mixtures of pure hexaniobate and hexatantalate ions. This study required the development of a new CE method allowing the separation of all the five substituted ions and their two non-substituted hexameric parent ions in less than seven minutes. In details, a previously developed separation method was transferred to a Beckman instrument and the separation improved by adjusting the total length, the applied voltage, the injection volume, the rinsing steps and the internal standard. The kinetic study shows that samples initially containing non-substituted hexameric forms of tantalum and niobium in a 1:1 M ratio naturally form the five possible substituted species $Ta_{6-x}Nb_x$ ($1 \leq x \leq 5$) after only a few hours which may represent an issue for future Nb-Ta separation processes operated in alkaline media. The developed method was also transferred to an Agilent instrument and the kinetic study repeated. Results obtained with the Agilent instrument corroborate those obtained with the Beckman instrument. The proposed electrophoretic separation method lays the ground for new analytical techniques that could help assessing the presence of substituted species that can be deleterious for Nb-Ta purification processes.

## 1. Introduction

Tantalum (Ta) and Niobium (Nb) are two group V metals and are essential to various industries, such as aerospace, gas, oil, electronic and nuclear sectors. Both metals are found in the same natural source and, because of their almost identical physicochemical features, their separation is challenging and is the subject of many on-going research projects. Multiple techniques, such as High Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance, Raman Spectroscopy, Inductively Coupled Plasma (ICP), and potentiometry were used as analytical tools for these elements [1–4]. Earlier research on their production processes mainly focused on complexation of both compounds in acidic fluoride-based media [5]. Recently proposed processes for production or analytical separation of tantalum and niobium that are faster, more economical and environmental friendly are based on the use of highly alkaline media. Hexameric polyoxometalates, $H_xTa_6O_{19}^{X-8}$ and $H_xNb_6O_{19}^{X-8}$ with $0 \leq x \leq 3$ (hereafter named $Ta_6$ and $Nb_6$, respectively), dominate the chemistry of Ta and Nb at a

pH above ~9 [6,7]. The hexatantalate ions crystalize without protons (only with alkali counter-ions and $H_2O$), protonation can on the other hand occur during dissolution. Hexaniobate is furthermore more prone to protonation than hexatantalate [8].

Deblonde et al. [9] proposed the application of a faster and greener capillary electrophoretic (CE) separation in an alkaline background electrolyte (BGE) for the separation of $Ta_6$ and $Nb_6$. CE is a separation technique based on differences in electrophoretic mobilities of the analytes [10]. Occasionally coupled to a mass spectrometry detector, CE is currently gaining an increasing interest in the analysis and characterisation of biopharmaceuticals [11,12]. It is an alternative and complementary separation technique to the more frequently applied HPLC. Advantages of CE are fast analyses, high separation efficiency, small sample volumes and the fact that it is a green and economical technique [13].

The above mentioned hexameric forms exhibit absorption characteristics in the UV-spectral region in contrast to the monomeric chelates found in acidic and complexing aqueous solutions [14]. This spectroscopic feature facilitates the use of CE as an analytical tool and avoids the pre-separation complexation steps usually required for detection of the compounds of interest. Although the molar mass of $Ta_6$ is about twice higher that than of $Nb_6$, they both exhibit a rather identical hydrated radius. This similar radius also complicated the analytical separation of both compounds in previously tested techniques [1,2,4]. As stated above, the physicochemistry of tantalum and niobium was studied earlier and it was proven that, in addition to their UV absorption, the hexaniobate and hexatantalate ions, which are naturally formed at pH above 9, have readily different electrophoretic mobilities and can thus be separated by means of CE methods [9,15]. A difference in electrophoretic mobility is determined by a difference in the charge on the hydrated radius ratio of an ion. Since the ionic radius of both metals is rather identical, the effective charges of both hexameric forms need to be different to allow a CE separation. Indeed, the charge difference of the hexameric forms occurs due to different protonation and ion pair formation of both compounds with cations in alkaline media [7].

The analysis of an industrial sample containing $Nb_6$ and $Ta_6$ (Fig. 1A) showed an unexpected minor peak of what is expected to be a substituted ion, namely $Ta_1Nb_5$. The presence of such mixed Nb-Ta species may represent an issue for separation processes operated in alkaline media since the complete separation of $Nb_6$ and $Ta_6$ can potentially be compromised. Therefore a kinetic study was performed to verify whether substituted species are formed during the synthesis of $Nb_6$ and $Ta_6$ from their respective starting materials (oxides, monomeric complexes, etc.) or is the result of a spontaneous substitution when combining the non-substituted polyoxoanions $Nb_6$ and $Ta_6$ in alkaline media. The potential substitution process was followed by CE, with a short-end injection method adapted to the one developed earlier by Deblonde et al. used to separate only $Nb_6$ and $Ta_6$ [9]. Indeed, a particular case within 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 [16]. Short-end injections use a default effective length, being the distance between the capillary injection end and the detection window of the capillary, being 8.5 or 10 cm, for an Agilent or a Beckman CE instrument respectively [17]. The minimally required effective length when performing a long-end injection method is 20–30 cm. A short effective length not only reduces the analysis time, it potentially leads to additional stacking effects and thus an increased efficiency and higher sensitivity. Furthermore because of 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 [15,18–20].

7In a first part of the actual study the earlier developed method for the separation of $Ta_6$ and $Nb_6$ [15] was transferred to a Beckman instrument in the same laboratory and evaluated for the separation of all substituted ions. During this inter-instrumental transfer the earlier defined guidelines by De Cock et al. [21,22] were applied. Subsequently, in order to be able to separate all substituted ions that can appear between the $Ta_6$ and $Nb_6$ peaks, the originally more explorative qualitative method was adapted to allow an increased separation efficiency and repeatability. A first kinetic study was performed with the adapted method on the Beckman instrument. In a third and final part the CE short-end injection method was transferred to an Agilent instrument and the kinetic study was repeated to confirm the earlier observed results.
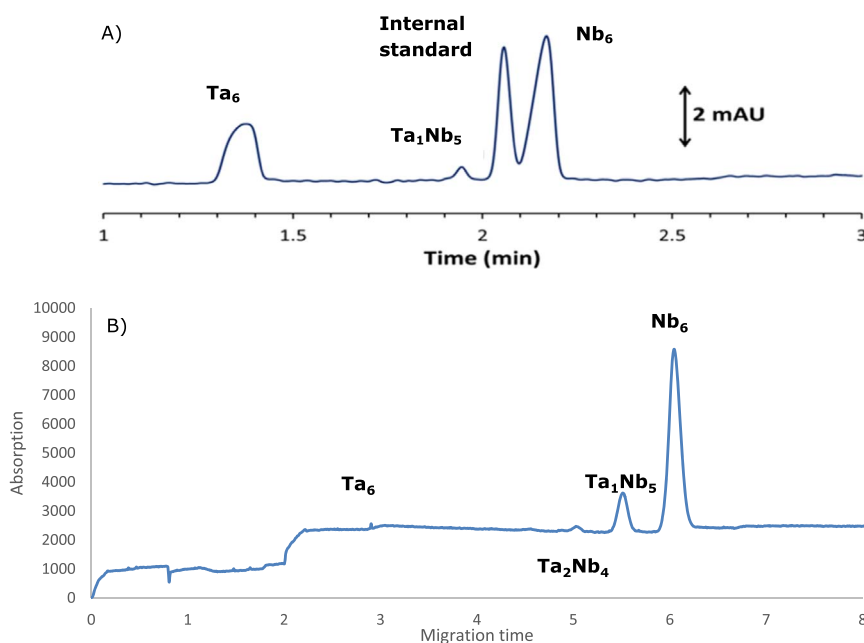


**Fig. 1.** A) Electropherogram of an industrial sample of $Ta_6$ and $Nb_6$ 1:1 (M/M) ratio, spiked with $Ta_6$ for identification reasons, and sodium naphthalene-1,5-disulfonate as IS, with the initial short-end injection method developed by Deblonde et al. [14], 45 mM LiOH/LiCH3COO BGE at pH 12, 31 °C, −16 kV and a total capillary length of 30 cm, obtained on the Agilent instrument. Reproduced from [14] with permission. B) Electropherogram of another industrial sample containing purified $Nb_6$ and $Ta_6$ (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 but now obtained on the Beckman instrument.

## 2. Material and instruments

### 2.1. Chemicals

Dimethylformamide, used as electroosmotic flow (EOF) marker, and 2-naphtalene sulfonic acid, used as internal standard (IS), both used 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. $LiOH \cdot H_2O$ and $LiCH_3COO \cdot 2H_2O$ were purchased from Alfa Aesar (ThermoFisher Scientic, Waltham, Massachusetts, USA). The BGE consisted of 35 mM $LiCH_3COO$ and 10 mM LiOH dissolved at a pH of 12.0. The BGE was, because of the high pH and the fact that it is not buffering, prepared daily by dissolving the appropriate amounts of $LiOH \cdot H_2O$ and $LiCH_3COO \cdot 2H_2O$ in ultra-pure water. The pH in both inlet and outlet vials was measured daily and no buffer depletion effect was noticed. The hexameric forms, $Na_7HNb_6O_{19} \cdot 15H_2O$ and $Na_8Ta_6O_{19}.24 \cdot 5H_2O$, were synthesised as reported earlier [14] and stored at 4 ºC. Stock solutions were freshly prepared weekly by dissolving $Na_7HNb_6O_{19} \cdot 15H_2O$ (2 g/L) and $Na_8Ta_6O_{19}.24.5H_2O$ (4 g/L) in ultra-pure water while stirring during 2 h and were stored at 4 ºC. 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 ± 6 nm, the reference wavelength at 325 nm ± 50 nm and a data acquisition rate of 4 Hz was applied. The capillary temperature was kept at 31.0 ºC by liquid cooling and the electropherograms were processed with the 32 Karat™ software version 5.0 (Beckman Coulter, Fullerton, California, USA). The applied voltage was −22.0 kV which generated a current of approximately −49.0 µA. Capillary preconditioning was performed prior to the first use by rinsing the capillary with consecutively 1.0 M and 0.1 M LiOH; ultra-pure water and BGE at a pressure of 60 psi / 4.13 bar during 10 min each, corresponding to 81.16 µL used solvent per rinsing step [23]. 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 [23]. The samples were injected hydrodynamically at 0.1 psi / 6.9 mbar during 9.0 s at the anodic end, leading to an injection volume of 2.03 nL [23].

The Agilent G1600A instrument (Agilent Technologies, Santa Clara, California, USA), used during the second kinetic study, was equipped with a DAD module and following detection parameters were set; the wavelength at 211 nm ± 6 nm and the reference wavelength at 325 nm ± 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 reduced, because of joule heating, to −21.0 kV which generated a current of approximately −42.5 µA. The capillary temperature was kept at 31 ºC 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, for which they were calculated with CE expert lite tool (Sciex,

Framingham, Massachusetts, USA) [23]. 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. Development of a CE method allowing the analysis of $Ta_6$, $Nb_6$ and their substituted ions

Deblonde et al. [15] optimized a short-end injection CE method to separate $Ta_6$ and $Nb_6$ ions on an Agilent 7100 instrument. Due to the unavailability of the earlier used Agilent instrument, this method was first transferred to a Beckman instrument. The transferred method was found inadequate because of the high variation and shift in migration times (Mt) and peak areas under the curve (AUC) resulting in RSD values above 10% for both parameters. 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 only $Nb_6$ and $Ta_6$. However, a highly repeatable method with baseline separations is needed to quantitatively evaluate the formation of different substituted ions during a kinetic study. Therefore several parameters of the initial method were adapted during the transfer from the Agilent to Beckman system as shown in Table 1. In a first step, the total capillary length was increased from 30 to 60 cm while, due to instrumental differences, the effective length increased from 8.5 to 10 cm. A longer total capillary length leads to a higher electrical resistance as illustrated by (Eq. (1)).

$$R = \frac{L}{kA} \tag{1}$$

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 expressed in (Eq. (2)).

$$V = I*R \tag{2}$$

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

The use of a longer capillary hence allowed 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. The longer capillary and the lower current both decreased the heat generation inside the capillary as shown in (Eq. (3)).

$$\frac{dH}{dt} = \frac{I*V}{L*A} \tag{3}$$

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

The reduced heat generation leads to less Joule heating and thus improves the precision and separation efficiency of a capillary electrophoretic method [24,25]. The amount of voltage per cm total capillary length decreased from 0.53 kV/cm to 0.37 kV/cm. The lower electrical field combined with the longer effective length due to the different capillary cartridge designs between instruments (10 cm instead of 8.5 cm), led to a longer analysis time as shown on Fig. 1B but also to an improved separation of $Ta_6$, $Nb_6$ and the substituted ions, compared with the original method (Fig. 1A). The longer capillary length furthermore allowed a longer injection time, or higher injection pressure, to result in an equal injection volume as the initial method, as illustrated by (Eq. (4)).

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

with $V_{inj}$ the injection volume, $\Delta p$ the applied pressure difference, d the capillary internal diameter, $\varpi$ the constant pi, $\eta$ the viscosity inside the capillary and L the total capillary length.

**Table 1**
Method parameters used during the analysis of the hexameric forms of Niobium and Tantalum in basic medium by Deblonde et al. [9] on the Agilent 7100 CE system and by the adapted method on the Beckman P/ACE MDQ instrument respectively. Parameters in bold have been adapted.

| Equipment | Agilent 7100 CE system | Beckman P/ACE MDQ |
|---|---|---|
| Focus | **Identification of Ta$_6$ and Nb$_6$** | **Separation of substituted ions** |
| Capillary | 50 μm ID, effective length of **8.5 cm** and total length **30 cm** | 50 μm ID, effective length of **10 cm** and total length **60 cm** |
| Detection parameters | Wavelength: 211 nm ± **5 nm** Reference wavelength: 325 nm ± 50 nm Acquisition rate: **3.33 Hz** | Wavelength: 211 nm ± **6 nm** Reference wavelength: 325 nm ± 50 nm Acquisition rate: **4 Hz** |
| Temperature | 31.0 °C | 31.0 °C |
| Voltage | **16.0 kV** at reversed polarity (± −70 μA) | **22.5 kV** at reversed polarity (± −49 μA) |
| Injection | Short end: **3 s at 0.14 psi** | Short end: **9 s at 0.1 psi** |
| Rinse steps | **10 min BGE at 1 bar** | **2 min BGE at 14.5 bar** |
| Internal standard | **Naphtalene 1,5 disulphonate** | **2-naphtalene sulfonic acid** |

The initial injection volume of 1.96 nL obtained 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 [23]. A longer injection time allows the injection pump to have more time to generate a given and constant pressure and results in more repeatable injection volumes [24,26].

Some detection parameters of the original method, developed on an Agilent instrument, needed to be adapted according to the guidelines defined in De Cock et al. [22]. Due to instrumental limitations the bandwidth of 5 nm could not be selected, therefore 6 nm was chosen. 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 [22]. The required acquisition rate of 3.33 Hz was instrumentally impeded on the Beckman instrument. An acquisition rate of 4.00 Hz was selected since it was the closest available option to the original parameter value. As shown in De Cock et al. [22], the robust interval of the data acquisition rate, calculated after performing a robustness test, is rather small. Therefore, variations of the signal-to-noise ratio and efficiency were eventually to be expected when transferring a CE method between instruments 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 heating test, where the linear increase in 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 (Eq. (5)) and improved the separation of Ta$_6$, Nb$_6$ and the substituted ions.

$$N = \frac{\mu_{ep} V l}{2 D_m L} \tag{5}$$

with N the efficiency, $\mu_{ep}$ 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.

The goal of the initial method [15] was an ultra-fast identification of Nb$_6$ and Ta$_6$. However, the ultra-fast aspect of this method was impeded by a non-optimized rinse step of 10 min. Therefore, a reduction of the rinse time while increasing the applied pressure was evaluated, as it is possible to reach higher pressure with the Beckman CE system than with the Agilent instrument without adding an external gas bottle. A 2 min rinse step at 60 psi / 4.13 bar was included in the adapted method. Naphthalene-1,5-disulphonate was selected as IS during the method development by Deblonde et al. [9], as it migrates between Ta$_6$ and Nb$_6$ and does not increase the analysis time. Nevertheless, it is not used in the study of the substituted ions as it could interfere with Ta$_1$Nb$_5$ as illustrated in Fig. 1A. Therefore 2-naphtalenesulfonic acid was selected as IS here because it is less negatively charged and thus migrates faster in a counter-electroosmotic flow and does not interfere with Nb$_6$, Ta$_6$ or any of the substituted ions as shown in Fig. 2. All above discussed adaptations led to a more quantitative method, *i.e.* with all compounds baseline separated and RSD values below 1% for the MT and 2% for the AUC. This adapted method was used for the subsequent 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 method was developed on this instrument. Prior to the study, samples containing 0.05 mM of both Na$_7$HNb$_6$O$_{19}$·15H$_2$O and Na$_8$Ta$_6$O$_{19}$.24·5H$_2$O dissolved in the BGE were prepared. The samples were then heated at 60 °C and analysed every hour during 24 h. The samples were heated to speed up the substitution process since it was too slow at room temperature. The use of a temperature higher than 25 °C was also thought to be more a realistic comparison with
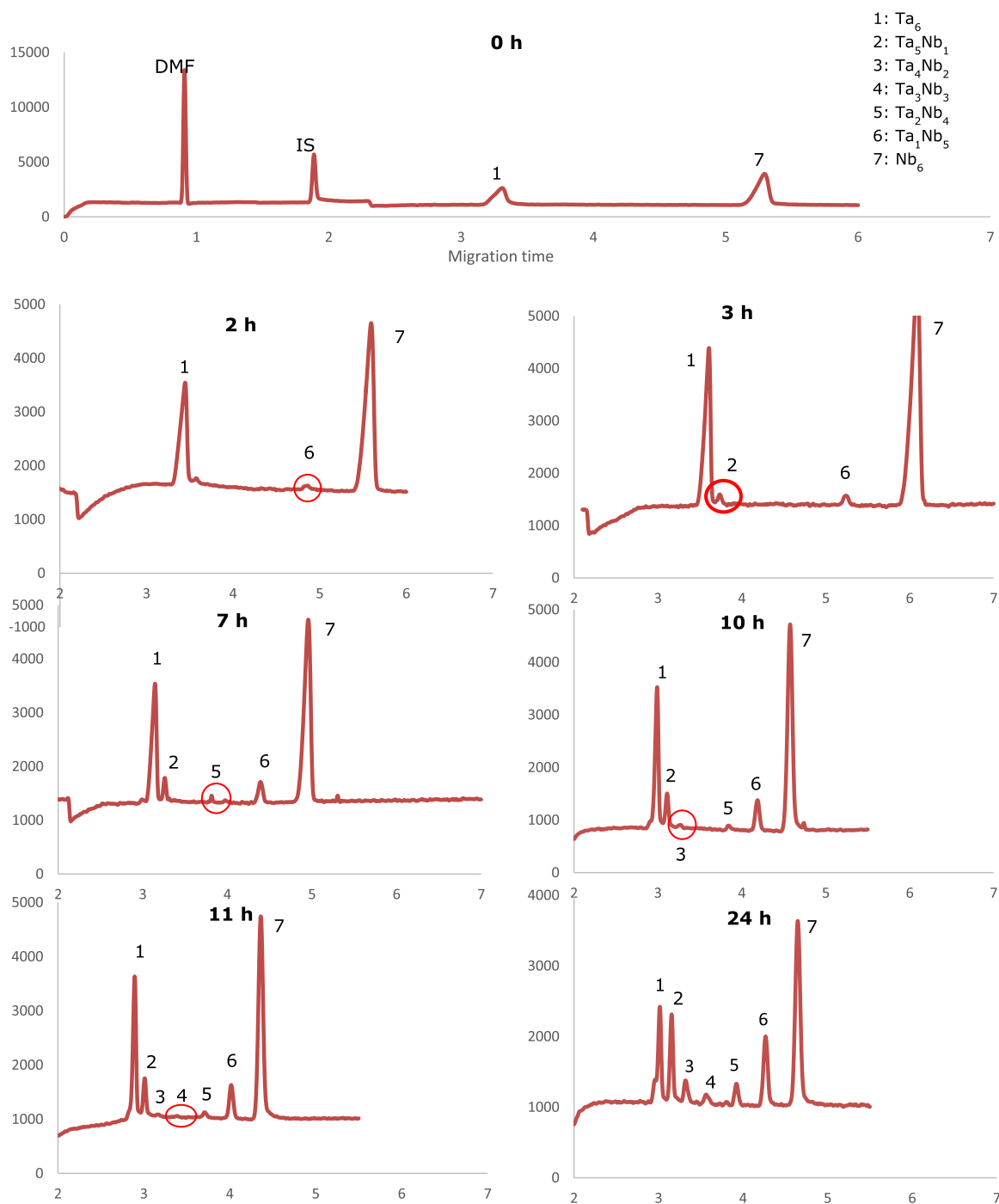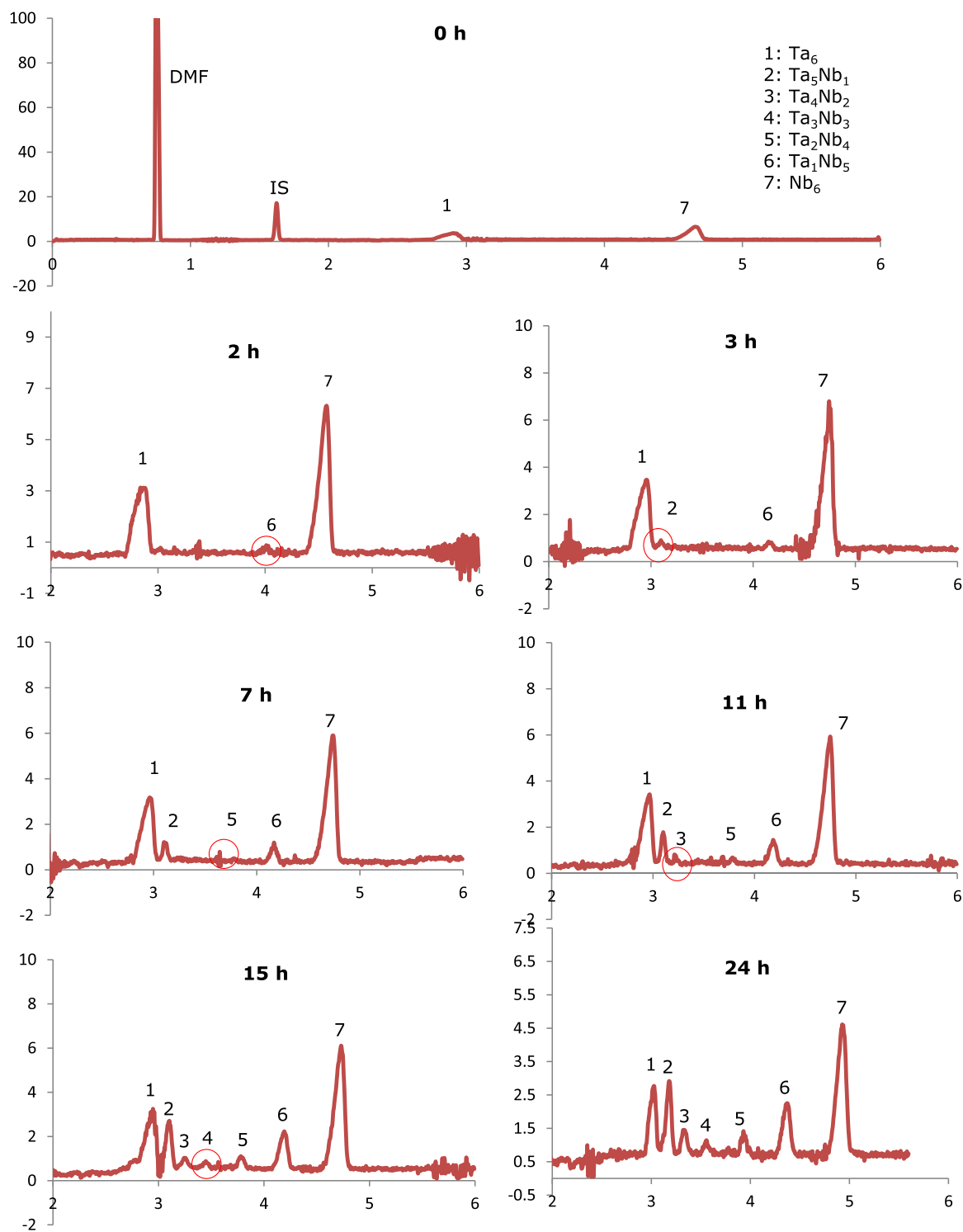
Electrophoretic conditions: BGE: 35 mM LiCH₃COO.2H₂O and 10 mM LiOH.2H₂O at a pH of 12.0, short-end injection 0.1 psi during 9.0 s, applied voltage – 22.0 kV, capillary temperature 31.0°C.

**Fig. 2.** Overview of the appearance of the different substituted ions during the kinetic study performed on the Beckman instrument. With IS: internal standard = 2-naphtalene sulfonic acid. Electrophoretic conditions: BGE: 35 mM LiCH₃COO·2H₂O and 10 mM LiOH·2H₂O at a pH of 12.0, short-end injection 0.1 psi during 9.0 s, applied voltage – 22.0 kV, capillary temperature 31.0 °C.

industrial Nb-Ta separation processes which are rarely operated at room temperature. The syntheses of hexaniobate and hexatantalate salts are also performed at near-boiling point temperatures [27]. In Fig. 2, an overview of the appearance of different substituted ions, at certain time points, is shown. After 2 h, a first substituted form appeared with an electrophoretic mobility situated between those of Nb₆ and Ta₆ but close to that of Nb₆, which was defined as Ta₁Nb₅. Indeed, the intermetallic substitutions in Nb₆ and Ta₆ can only lead to

five different mixed ions Ta₆₋ₓNbₓ (1 ≤ x ≤ 5). The minor species Ta₁Nb₅ was previously observed in industrial niobium samples containing a low content of tantalum (Fig. 1). In our synthetic samples, a second substituted ion, situated between Nb₆ and Ta₆ but close to Ta₆, appeared after 3 h and should correspond to Ta₅Nb₁. Ta₅Nb₁ was, unlike Ta₁Nb₅, not observed in any of the industrial samples, although the study of such mixed species has been, so far, largely overlooked. The industrial sample analysed on the Agilent instrument (Fig. 1A),

Electrophoretic conditions: BGE: 35 mM LiCH$_3$COO.2H$_2$O and 10 mM LiOH.2H$_2$O at a pH of 12.0, short-end injection 0.1 psi during 9.0 s, applied voltage − 22.0 kV, capillary temperature 31.0°C.

**Fig. 3.** Overview of the appearance of the different substituted ions during the kinetic study performed on the Agilent instrument. With IS: internal standard = 2-naphtalene sulfonic acid. Electrophoretic conditions: BGE: 35 mM LiCH$_3$COO·2H$_2$O and 10 mM LiOH·2H$_2$O at a pH of 12.0, short-end injection 0.1 psi during 9.0 s, applied voltage − 22.0 kV, capillary temperature 31.0 °C.

containing a 1:1 M ratio of Ta$_6$ and Nb$_6$, only showed one substituted ion, being Ta$_1$Nb$_5$. Considering the industrial sample analysed on the Beckman instrument (Fig. 1B), containing a 1:25 M ratio of Ta$_6$ and Nb$_6$, the presence of two substituted ions is seen, but not that of Ta$_5$Nb$_1$. Its absence may be linked to the very low concentration of Ta$_6$ in this industrial sample.

During the kinetic study, more substituted forms appeared over-time and were identified, based on their migration time, as Ta$_2$Nb$_4$ after 7 h, Ta$_4$Nb$_2$ after 10 h and as last Ta$_3$Nb$_3$ was formed after 11 h at 60 °C. After 24 h the five different substituted ions of Ta$_6$ and Nb$_6$ in basic medium are clearly seen (Fig. 2). The identification of the substitutions is based on their electrophoretic mobilities and UV

absorbance spectra but further confirmation by means of ICP or mass spectrometry is a possibility. The rather large difference in UV absorbance between $Ta_6$ and $Nb_6$ combined with the fact that only hexameric forms possess UV–visible properties, as stated in [14], lead for example to a slightly increased maximum of the peaks at 250 nm of $Ta_5Nb_1$ compared to $Ta_6$. Although, as mentioned above, the intermetallic substitutions starting from $Nb_6$ and $Ta_6$ can only lead to a finite number of substituted species and, as expected for the five $Ta_{6-x}Nb_x$ ions, no more than five intermediate peaks appeared. The Nb-Ta substitutions occurred also in a logical sequence, one Nb or Ta atom at-a-time is exchanged from the corresponding hexameric forms and the corresponding electrophoretic mobility of the substitution consequently is situated in between $Ta_6$ and $Nb_6$. The Nb or Ta atom exchange happens simultaneously since stable Nb and Ta monomer ions do not exist in basic media at the concentrations used in the present study [5]. The results clearly indicate that the substituted species can be formed spontaneously starting from a mixture of pure niobate and tantalate species which suggests that the mixed niobium-tantalum hexametalate ions are thermodynamically favoured compared to their pure hexaniobate and hexatantalate forms. Consequently, the mixed species are most likely to be found in the industrial processes or solution-state studies where both elements are present. The analytical procedures developed in this study could therefore be helpful in the development of Nb- and Ta-related industrial projects. The results also emphasize that the formation and level of the substituted Nb-Ta ions in solution depends on the process conditions (temperature, residence time, etc.). The presence of an excess of one element compared to the other will also result in the complete disappearance of the pure hexameric ions of the limiting element, as previously observed in hexaniobate industrial samples containing a low content of Ta where $Nb_5Ta$ was detected but not $Ta_6$ [15]. Although the separation of $Nb_6$ ions from $Ta_6$ already represents a scientific challenge, the separation of the mixed $Ta_{6-x}Nb_x$ ions from $Nb_6$ or $Ta_6$ ions seems rather difficult using classical and large-scale industrial techniques such as liquid-liquid extraction or other hydrometallurgical methods. The proposed CE method could be extended to other polyoxometalates such as vanadates, tungstates, molybdates and their mixed species formed with niobates and tantalates [7].

### 3.3. Kinetic study on the Agilent instrument

During the initial transfer to the Agilent instrument, the baseline separation between $Ta_6$ and $Ta_5Nb_1$ was lost and thus the qualitative analysis hampered [17]. At the interinstrumental method transfer of this short-end injection method, an instrumental difference, being the capillary cartridge construction, caused a difference in effective capillary length. The total capillary length remained constant but the different effective lengths, *i.e.* 10 cm on the Beckman instrument versus 8.5 cm on the Agilent system, lead to the initial loss of the 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. [17]. The increase in effective capillary length, in addition to the earlier performed adaptations, led to a successful interinstrumental method transfer, with restauration of the baseline separation.

A new kinetic study was performed and confirmed the results obtained earlier on the Beckman instrument (Fig. 3). An identical trend considering the appearance of the different substituted ions was observed as in the first kinetic study. It should be noticed that, because of a larger baseline noise, the signal-to-noise ratios obtained on the Agilent instrument were lower than those on the Beckman instrument although the detector and data collection settings were kept as identical as possible [22]. Potential reasons are a difference in lamp age, lamp instability, inherent at the Agilent instrument data-handling software, the larger capillary window and the decreased dip of the electrodes in

the BGE [17]. After 2 h, the formation of the first substituted ion, $Ta_1Nb_5$, was observed. 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 hardly observed due to the increased noise. $Ta_4Nb_2$ was seen slightly later than in the earlier performed study, i.e. after 11 instead of 10 h, probably also due to the increased noise level. $Ta_3Nb_3$ was, similarly to the first study, the last formed substituted ion. Although the appearance of $Ta_3Nb_3$, after 15 h, was also seen later in this 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 both to the increased noise level and the lower signals that were observed on the Agilent system. Finally after 24 h, as shown in Fig. 3, the partial 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 initially present amounts of $Ta6$ and $Nb_6$ in the sample.

## 4. Conclusions

In a preliminary study, it was observed that a $Ta_6$ and $Nb_6$ containing industrial sample, extracted from a natural source in a basic medium, contained one or two minor species. To investigate the origin of these impurities a kinetic study of synthetic samples containing a 1:1 M ratio of $Nb_6$ and $Ta_6$ dissolved in a basic medium, heated at 60 ºC, and analysed hourly was carried out on a Beckman CE instrument. For the purpose of this kinetic study, an earlier CE method developed by Deblonde et al. [15] was modified and afforded the baseline separation of all substituted ions ($Ta_xNb_{6-x}$; $1 \leq x \leq 5$) and pure ions ($Nb_6$ and $Ta_6$). Our study illustrates, for the first time, the spontaneous formation in basic medium of five substituted ions starting from the non-substituted hexameric forms: $Ta_6$ and $Nb_6$. The observed substitutions were, in order of appearance: $Ta_1Nb_5$, $Ta_5Nb_1$, $Ta_2Nb_4$, $Ta_4Nb_2$ and $Ta_3Nb_3$. The substitution sequence and the experimental electrophoretic mobilities correlate well to the expected substitutions pattern. In a second instance, the kinetic results were confirmed on an Agilent instrument after a successful interinstrumental transfer, including the lowering of the lift offset parameter. The results corroborated the earlier observed trend of substitution and thus it can be concluded that a basic medium naturally induces the substitution between pure hexameric forms of niobium and tantalum. These results not only concern the on-going development of Nb-Ta processes operated in alkaline media but are also of potential interest for the speciation of Nb and Ta in alkaline environments, and for analytical methods dealing with polyoxometalates.

## Conflict of interest statement

The authors declare no conflict of interest.

## References

[1] D.L. Li, X.Y. HU, H.Z. Wang, Separation and simultaneous determination of niobium and tantalum in steel by reversed-phase high-performance liquid chromatography using 2-(2-pyridylazo)–5-diethylamino phenol as a pre-column derivatizing reagent, Talanta 63 (2004) 233–237.

[2] M. Nete, W. Purcell, J. Nel, Hydrometallurgical separation of Niobium and Tantalum: a fundamental approach, J. Miner. 2 (2016) 556–566.

[3] M. Kabangy, P. Crousse, Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction, Hydrometallurgy 129–130 (2012) 151–155.

[4] O. Ayanda, F. Adekola, A review of niobium-tantalum separation in hydrometallurgy, J. Miner. Mater. Charact. Eng. 10 (2011) 245–256.

[5] A. Agulyanski, The Chemistry of Tantalum and Niobium Fluoride Compounds, 1st ed., Elsevier, Amsterdam, Boston, 2004.

[6] M. Nyman, Polyoxoniobate chemistry in the 21st century, Dalton Trans. 40 (2011) 8049–8058.

[7] J.D. Sures, S.A. Serapian, K. Kozma, P.I. Molina, C. Bo, M. Nyman, Electronic and

relativistic contributions to ion-pairing in polyoxometalates model systems, Phys. Chem. Chem. Phys. 13 (2017) 8715–8725.

[8] G.J.-p. Deblonde, C. Coelho-Diogo, A. Chagnes, G. Cote, M.E. Smith, J.V. Hanna, D. Luga, C. Bonhomme, Multinuclear solid-state NMR investigation of hexaniobate and hexatantalate compounds, Inorg. Chem. 55 (2016) 5946–5956.

[9] G. Deblonde, N. Delaunay, D. Lee, A. Chagnes, G. Cote, P. Gareil, First investigation of polyoxoniobate and polyoxotantalate aqueous speciation by capillary zone electrophoresis, RSC Adv. 5 (2015) 64119–64124.

[10] K.D. Altria, Current applications in the analysis of pharmaceuticals by capillary electrophoresis, Trends Anal. Chem. 17 (1998) 204–214.

[11] V. Kašička, Recent advances in capillary electrophoresis of peptides, Electrophoresis 22 (2001) 4139–4162.

[12] E. Tamizi, A. Jouyban, The potential of the capillary electrophoresis techniques for quality control of biopharmaceuticals a review, Electrophoresis 36 (2015) 831–858.

[13] R. Haselberg, G.J. De Jong, G.W. Somsen, Capillary electrophoresis-mass spectrometry for the analysis of intact proteins, J. Chromatogr. A 1159 (2007) 81–109.

[14] G. Deblonde, A. Moncomble, G. Cote, S. Bélair, A. Chagnes, Experimental and computational exploration of the UV–visible properties of hexaniobate and hexatantalate ions, RSC Adv. 5 (2015) 7619–7627.

[15] G. Deblonde, A. Changes, G. Cote, J. Vial, I. Rivals, N. Delaunay, Development of a capillary electrophoresis method for the analysis in alkaline media as polyoxoanions of two strategic metals: niobium and tantalum, J. Chromatogr. A 1437 (2016) 210–218.

[16] M.A. Kelly, K.D. Altria, B.J. Clark, Approaches used in the reduction of buffer electrolysis effects for routine capillary electrophoresis procedures in pharmaceutical analysis, J. Chromatogr. A 768 (1997) 73–80.

[17] B. De Cock, J.D. Oliver, N. Delaunay, G. Deblonde, D. Mangelings, Y. Vander Heyden, Interinstrumental method transfer of an ultra-fast short-end injection

capillary electrophoretic separation of niobium, tantalum and their substituted ions, submitted for publication (10.1002/elps.201700094).

[18] K.D. Altria, M.A. Kelly, B.J. Clark, The use of a short-end injection procedure to achieve improved performance in capillary electrophoresis, Chromatographia 43 (3) (1996) 153–158.

[19] C. Perrin, Y. Vander Heyden, M. Maftouh, D.L. Massart, Rapid screening for chiral separations by short-end injection capillary electrophoresis using highly sulfated cyclodextrins as chiral selectors, Electrophoresis 22 (2001) 3203–3215.

[20] Z. Glatz, Electrophoresis 34 (2013) 631–642.

[21] B. De Cock, B. Dejaegher, J. Stiens, D. Mangelings, Y. Vander Heyden, Inter-instrumental method transfer of chiral capillary electrophoretic methods using robustness test information, J. Chromatogr. A 1353 (2014) 148–159.

[22] B. De Cock, N. Hamza, D. Mangelings, Y. Vander Heyden, 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.

[23] CE expert tool, Beckman Coulter, Fullerton, USA, ⟨http://sciex.com/ce-features-and-benefits/ce-expert-lite⟩ accessed on 06/04/2017.

[24] B.X. Mayer, How to increase precision in capillary electrophoresis, J. Chromatogr. A 907 (2001) 21–37.

[25] X. Xuan, D. Li, Joule heating effects on peak broadening in capillary zone electrophoresis, J. Micromech. Microeng. 14 (2004) 1171–1180.

[26] K.D. Altria, H. Fabre, Approaches to optimisation of precision in capillary electrophoresis, Chromatographia 40 (5/6) (1995) 313–320.

[27] G. Deblonde, V. Weigel, Q. Belier, R. Houdard, F. Delvallée, S. Bélair, D. Beltrami, Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process, Sep. Purif. Technol. 162 (2016) 180–187.