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# Precise measurement of mobility from the length of isotachophoretic zones

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**Abstract**

A new method for the precise estimation of the ionic mobilities was described. The procedure issues from the measurement of the time of moving boundary between leading and terminating electrolyte in the geometrically and thermometrically well-defined device for capillary isotachophoresis. An indirect method for the determination of mobilities of low movable ionic species was also derived. The ionic mobilities of some anionic pesticides and cationic drugs were measured. The procedure can be used for estimation of transference numbers and also their temperature coefficient. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Ionic mobilities are important physical constants and their precise values enable the optimization of separation conditions in all electromigration techniques. The precise mobility values of single ions were measured by classical methods—conductometry, measurement of transference numbers—many years ago [1].

Mobilities for many new prepared important ionic compounds, such as drugs and ionic pesticides, are not known or only approximately measured. When uncertain values of mobilities are used for the simulated computations of separation parameters [2,3], agreement with the experimental values is often problematic.

Mostly, the mobility values are deduced from the migration times of capillary zone electrophoresis or from the relative zone heights of capillary isotachophoresis (ITP).

The first named procedure gives results with lower reproducibility because it is affected by the electroosmotic flow, injection manner and composition of buffer, the second one is noted for a higher R.S.D. in connection with the drift of the detector response from measurement to measurement.

The response of the universal ITP detector, i.e., potential gradient [4–6], conductivity measured as electrical resistance [7] or high frequency signal [8] and temperature [5], is in the reciprocal relation to the mobility value:

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$$\frac{u_x}{u_s} = \frac{E_x}{E_s} = \frac{R_x}{R_s} = \frac{T_x}{T_s} \quad (1)$$

where $u$ represents mobilities, $E$ potential gradients, $R$ electrical resistances and $T$ temperatures. The indices $x$ and $s$ denote measured and standard ions, respectively.

The main trouble in using a contact detector is caused by contamination of its electrodes measuring potential gradient or conductivity. The response of a contactless high-frequency detector is not linear in relation to the resistance (reciprocal mobility) and it is very sensitive to the geometry and temperature changes. A thermometric detector is not suitable because of its thermal inertia and non-linear signal profile.

From the practical experience of ITP, it is well known that the migration times of the boundary between leading and terminating ions are reproducible, with the relative deviation near to one-tenth of a percent regardless of thermostating of the capillary. This precision is allowed by the measurement of migration velocity of a sole ion in the long own zone. There are only two works in the literature [9,10] in this connection. The first procedure [9] was based on the measurement of the terminating ion migration time through the capillary using a constant potential. The thermometric detector was used for the detection, which was not suitable for the mentioned thermal inertia, and there were also problems with the determination of the end point of the measurement. The main problem of the mentioned method was that the instantaneous velocity and Joule's heat were not constant during the experiment. The second paper [10] served only for effective mobility measurements, particularly in the nonaqueous solvents. The migration time of the leading ion was measured at a constant driving current. But the knowledge of the precise length of the capillary was necessary here, and the applied voltage was considered to be the same as the potential drop through the capillary. Thus the results did not correspond to the accuracy demands.

The aim of the present work was to develop an isotachophoretic technique for the precise measurement of ionic mobility and to use it for obtaining the mobility values of some important ions with metrological level precision.

Here, two procedures were applied. In both the migration times of ions forming leading electrolyte were measured in a geometrically and thermometrically well-defined ITP system.

For the first procedure (direct method), the migration time of anion (chloride was applied as the primary standard ion) was measured, the capillary was filled with the same leading electrolyte, the polarity was changed and the migration time of cation was recorded. From the obtained values the transference numbers (Eq. (3)) or mobilities (Eq. (4)) can be derived. This procedure requires a terminating electrolyte with less movable ions than the leading ones.

The second procedure (indirect method) was applied to the electrolytes, where one of the ions is less movable than the ion with the same charge in the terminator. For the indirect method, the migration time of one of the ions in the standard electrolyte, e.g., sodium ion in sodium chloride, was measured, the capillary was filled with the electrolyte containing the common ion, e.g., sodium phenoxyacetate, and the migration time of the sodium ion was recorded. The mobility of the less movable ion was calculated from Eq. (11). Two conditions must be fulfilled for obtaining precise values of limiting ionic mobilities: a well thermostated space from the boundary between the measured (leading) and terminating electrolyte to the detector and purity of both, particularly the terminating electrolytes.

## 2. Theoretical part

For the migration time of leading ion (migration time of boundary between leading and terminating electrolyte) in ITP the Eq. (2) holds:

$$t = \frac{lSF(u_L + u_P)c_L}{1000Iu_L} \quad (2)$$

where $l$ represents the length of the capillary, $S$ is its cross-section, $F$ is the Faraday constant, $u_L$ and $u_P$ are the mobilities of the leading ion and the counter ion, $c_L$ is the concentration of the leading uni-univalent electrolyte and $I$ is the value of the constant current (SI units).

This migration time is independent on the ter-

minating electrolyte (ion). If the terminating electrolyte contains both less movable cation and anion we can obtain the ratio of mobilities and corresponding transference number from the measurement of migration times in anionic and cationic mode as follows:

$$\frac{u_+}{u_-} = \frac{t_-}{t_+}; \; T_+ = \frac{t_-}{t_+ + t_-} \tag{3}$$

where $u$ represents the mobility, $t$ is the migration time, $T$ is the transference number and the symbols + and − denote cation or anion, respectively.

The transference number or the charge, which is passed by cation or anion, depends on the temperature. That is why the temperature must be carefully kept at precise mobility measurement. If the leading or counter ion is changed in the measured (leading) electrolyte then migration times for each of them are in reciprocal relation to their mobilities regardless to their charges. For example for the change of counter ion holds:

$$\frac{t_1}{t_2} = \frac{u_{C1}}{u_L} \text{ and } \frac{u_{C2}}{u_L} = \frac{t_3}{t_4}, \text{ hence } \frac{u_{C2}}{u_{C1}} = \frac{t_2 \cdot t_3}{t_1 \cdot t_4} \tag{4}$$

These equations can be used for the determination of mobility values of ionic components in electrolytes where both leading and counter ion are more mobile than corresponding ions in the terminating electrolyte.

If one of the ions in the measured electrolyte is less movable than corresponding ion in the terminator the indirect method must be used. The indirect method can be explained as follows.

If the measurement is carried out in two electrolyte systems with the same standard ion (an ion with a very well-known mobility) under constant driving current, the electric charge passing through both systems in the time unit is constant:

$$I = \frac{Q_1}{t_1} = \frac{Q_2}{t_2} = \text{constant} \tag{5}$$

By expressing of constant current density condition in the form:

$$c_L u_L E_1 + c_{C1} u_{C1} E_1 = c_L u_L E_2 + c_{C2} u_{C2} E_2 \tag{6}$$

we obtain:

$$\frac{(c_L u_L + c_{C1} u_{C1})}{(c_L u_L + c_{C2} u_{C2})} = \frac{E_2}{E_1} \tag{7}$$

where $Q_1$ and $Q_2$ are passed electric charges in both measurements, $c_L$, $c_{C1}$ and $c_{C2}$ are concentrations of the shared standard ion and its counter ions in both electrolyte systems, $u_L$, $u_{C1}$ and $u_{C2}$ are corresponding mobilities and $E_1$, $E_2$ are corresponding potential gradients in leading electrolyte zones.

If $c_L = c_{C1} = c_{C2}$, the equation will be simpler:

$$\frac{(u_L + u_{C1})}{(u_L + u_{C2})} = \frac{E_2}{E_1} \tag{8}$$

For the migration velocities the following equations can be written:

$$v_{L1} = u_L E_1 = \frac{l}{t_1} \text{ and } v_{L2} = u_L E_2 = \frac{l}{t_2} \tag{9}$$

where $l$ represents the length of the capillary.

It can be seen from previous text that the ratio of migration times is proportional to the ratio of the sum of leading ion and counter ion mobilities in both systems:

$$\frac{(u_L + u_{C1})}{(u_L + u_{C2})} = \frac{t_1}{t_2} \tag{10}$$

In the case of precise determination of the ratio of migration times of the leading ion in both electrolyte systems and knowledge of mobility of leading ion and one of counter ions, the mobility of second counter ion can be obtained from the following equation:

$$u_{C2} = (u_L + u_{C1}) \cdot \frac{t_2}{t_1} - u_L \tag{11}$$

where $t_1$ is the migration time of the leading ion in the electrolyte system with the standard counter ion (an ion with well-known ionic mobility) and $t_2$ is the migration time of the leading ion in the system with the studied counter ion.

## 3. Experimental

### 3.1. Equipment

The equipment used was developed in Research

laboratories and workshops of Palacký University Olomouc. It comprised a capillary system T 422-1, a constant current source Z 426-1, a microprocessor unit Z 426-1 with a converter. A personal computer was used for data collection and handling.

The constant current source had the reproducibility of the driving current, 0.01%.

The capillary system had no inlet for the sample electrolyte between the leading and terminating electrolyte, so a sharp boundary existed between both electrolyte systems from the start of experiment.

The material of the capillary system is Teflon, which is advantageous because of its inertness. The capillary length was 31.27 cm and the capillary bore was 0.4 mm. The capillary was separated from the leading electrolyte vessel using a rigid cross cellophane membrane, so the electroosmotic flow was negligible.

Platinum wires were used for the electrodes of the driving system.

The conductivity detector was used in all experiments. The detector response value was not used for the mobility determination; it only indicated the entering of the zone boundary into the detector cell. Detection electrodes were created by the alloy of platinum and rhodium (10% Rh).

For temperature control, an ultrathermostat Höppler NBE (Dresden, Germany) was used. Silicone oil was used as thermostating medium. The geometry of the tube in which the capillary was placed was chosen in order that the biggest part of the capillary system was thermostated (Fig. 1). The achieved accuracy of the thermostating was $\pm 0.05$°C in the temperature range 20–50°C.

Both accuracy and reproducibility could be also influenced by the ions, which are generated on the driving electrodes. If these ions ($H_3O^+$ and $OH^-$) enter into the capillary, they increase the charge necessary for migration of the leading electrolyte into the detector and increase the migration time in the electrolyte system without a buffer. This possible problem was solved by changing the leading and the terminating electrolytes in the electrolyte vessels. From the geometry of the electrolyte vessel of the terminating electrolyte and the location of electrodes, the critical time for entering the generated ions into the capillary was calculated. The time under the conditions used (driving current, 100 μA; concentration of electrolytes, 0.01 mol $l^{-1}$) was estimated as 80 min (diffusion supposed to be negligible). If the maximal time of the measurement was 15 min, it was possible to carry out five safe measurements. The leading electrolyte vessel was bigger, so the critical time could be longer. The terminating electrolyte was changed after three measurements, and the leading electrolyte after five measurements. For illustration, the migration times representing results of direct and indirect methods, respectively, are given in Tables 1 and 4.

### *3.2. Chemicals*

For all experiments the following basic chemicals were used: potassium chloride, annealed (400°C), sodium chloride, sodium hydroxide, acetic acid, sodium salicylate, sodium benzoate, 3,5-dinitrobenzoic acid, benzene (all analytical-reagent grade from Lachema, Brno, Czech Republic), lithium carbonate, tetrabutylammonium hydroxide, water solution (20%, w/w) (both analytical-reagent grade from E. Merck, Darmstadt, Germany).

The following phenoxyalkanoic acids with pesticide effects were used for measurements: phenoxyacetic acid, 4-chlorophenoxyacetic acid, 4-chloro-3-methylphenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, 2-phenoxypropionic acid, 2-(4-chlorophenoxy)propionic acid, 2-(4-chloro-3-methylphenoxy)propionic acid, 2-(2,4-dichlorophenoxy)propionic acid, 2-(2,4,5-trichlorophenoxy)propionic acid. All these compounds were prepared in our laboratory in the highest possible purity. 2,4-Dichlorophenoxyacetic acid was a laboratory product from Lachema (Brno, Czech Republic). Solutions of sodium salts (0.01 *M*) were prepared by means of alkalimetric titration of saturated solutions using 0.02 *M* NaOH and phenolphthalein as indicator. The solution of NaOH was prepared by dilution of 50% (w/w) NaOH with carbonateless water.

The following local anesthetics (as hydrochlorides) were measured: amylocaine, β-eucaine, procaine (novocaine), mesocaine (trimecaine), tropacocaine.

All these local anesthetics were obtained from the Department of Physiological Pathology, Faculty of Medicine.

Lithium acetate buffer and tetrabutylammonium

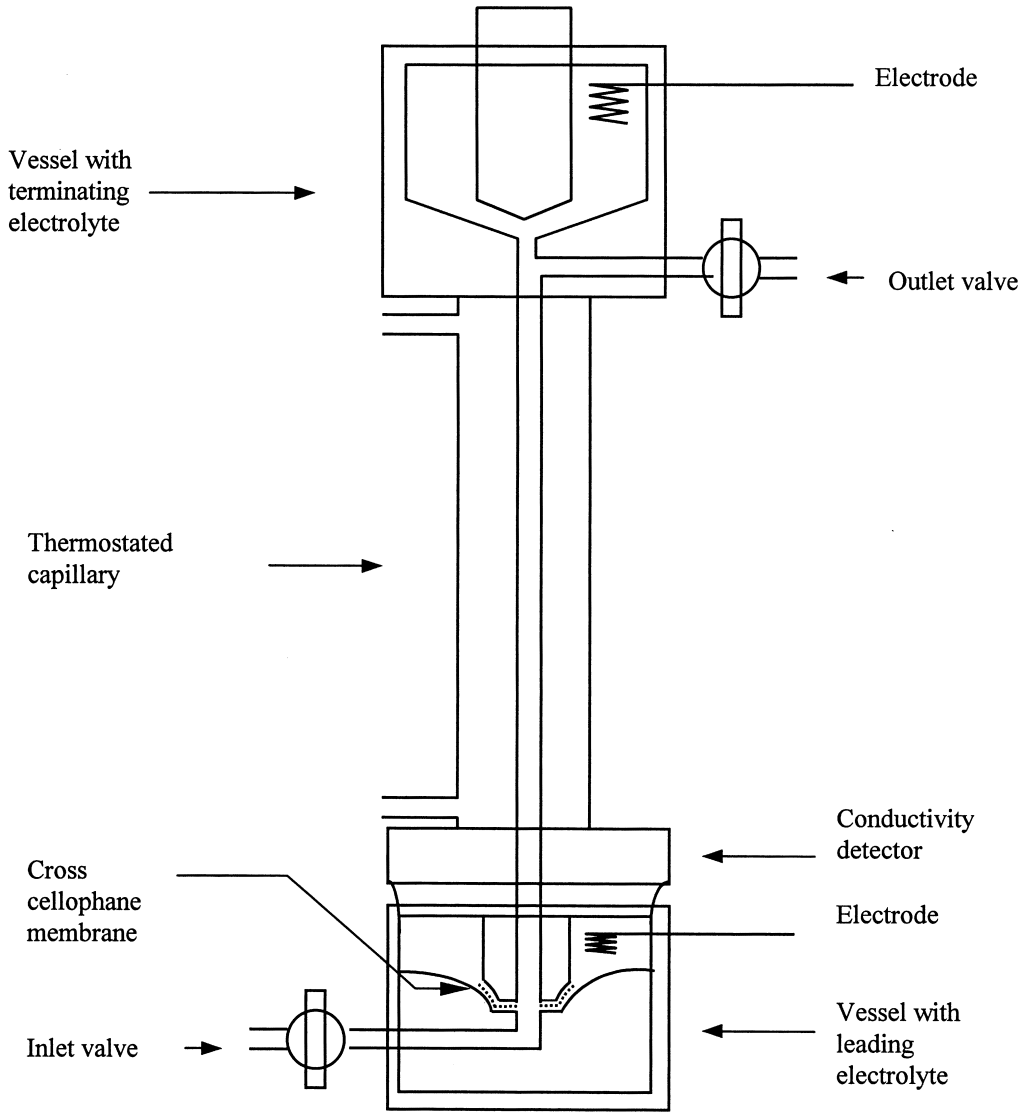


Fig. 1. Scheme of capillary system used.

3,5-dinitrobenzoate were used as terminating electrolytes. The acetate buffer, which contains $Li^+$ ions in a concentration of 0.01 mol $l^{-1}$, was prepared by dissolving 73.887 mg of lithium carbonate in 2 ml of acetic acid ($c=1$ mol $l^{-1}$), and 100 ml of deionized water were added. The pH value was adjusted to 5.4 by acetic acid and the solution was refilled to 200 ml.

The concentration of all the leading (measured) and terminating electrolytes was strictly 0.01 mol $l^{-1}$. The values of actual mobilities obtained for this concentration level were corrected along Eq. (12) as presented in Tables 1,3–5.

For the preparation of tetrabutylammonium 3,5-dinitrobenzoate, the least mobile terminator, we had to find a sufficient procedure: 8.1 g of 3,5-dinitrobenzoic acid were dissolved in 50 ml of a 20% (w/w) water solution of tetrabutylammonium hydroxide. The prepared solution was evaporated and dried out in a desiccator with $P_2O_5$. The dried product was

crushed and dissolved in hot benzene (10.5 g of dried product in 40 ml of hot benzene). The insoluble part was separated out from benzene solution after a while. This insoluble part was filtered out and the filtrate was left for crystallization in the icebox. The compound crystallized slowly. The obtained compound was purified by washing, using cold benzene, and air dried. The defined solution was prepared from the purified product by dissolution in deionized water.

The purity of all compounds was controlled by elementary analysis and melting points, and good agreements were observed with theoretical values [11,12]. All prepared solutions were also controlled for ITP purity in both cationic and anionic modes. No ballast zones were found.

## 4. Results and discussion

The proposed method of determination of ionic mobilities was tested by the measurement of values of standard electrolytes (potassium and sodium chlorides), in the temperature range of 20–50°C (Table 1). The results for potassium and sodium ions were obtained by the direct method of measurement (Eq. (4)). A value of $79.08\times10^{-9}$ $m^2$ $V^{-1}$ $s^{-1}$ at 25°C was used for the chloride ion as a mobility standard, and a value of 0.0216 $K^{-1}$ as a thermal mobility coefficient, were chosen for this ion from the literature [13].

The correction of the ionic strength was carried out according to the Debye–Hückel–Onsager equation [13]:

$$u^{akt} = u^0 - (Bu^0 + A)\cdot\frac{\sqrt{I}}{1+\sqrt{I}} \quad (12)$$

where $I$ is ionic strength, $A$ and $B$ are coefficients dependent on the viscosity of solvent $\eta$, relative permittivity $\epsilon_r$ and thermodynamic temperature $T$ according to following expressions:

$$A = \frac{0.42698\times10^{-12}}{\eta\sqrt{\epsilon_r T}} \quad (m^2\ V^{-1}\ s^{-1}) \quad (13)$$

$$B = \frac{8.4961}{(\epsilon_r T)^{3/2}} \quad (14)$$

Very good agreement can be seen with published data [13,14]. Relative differences between measured and published values are in the range 0.29–1.07% for potassium and 1.23–1.87% for sodium ions. Transference numbers (Eq. (3)) obtained by these measurements are shown in Table 2, and they can be compared (for 25°C) with literature values 0.4902 for potassium ions and 0.3918 for sodium ions, which were obtained by the moving boundary meth-

Table 1
Limiting mobility of potassium and sodium ions in relation to temperature[a,b]

| $T$ (°C) | Potassium | | | | Sodium | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_1$ (s)[c] | $t_2$ (s)[d] | $u^e_{meas}$ | $u_{lit}$ [13] | $t_1$ (s)[c] | $t_2$ (s)[d] | $u^c_{meas}$ | $u_{lit}$ [13] |
| 20 | 743.39 | 764.56 | 70.49±0.08 | 69.86 | 628.22 | 970.06 | 46.60±0.04 | 47.28 |
| 25 | 743.20 | 764.62 | 76.95±0.08 | 77.44 | 632.84 | 970.12 | 52.40±0.18 | 53.05 |
| 30 | 743.39 | 770.92 | 84.61±0.33 | 85.02 | 630.05 | 976.00 | 57.72±0.19 | 58.82 |
| 40 | 741.32 | 773.81 | 100.47±0.37 | 100.18 | 630.93 | 967.20 | 69.70±0.32 | 70.36 |
| 50 | 739.53 | 774.19 | 116.57±0.64 | 115.34 | 636.53 | 956.87 | 82.64±0.30 | 81.90 |
| | $u^0_K = 1.55048t + 38.65053$[f] | | | | $u^0_{Na} = 1.19759t + 22.2893$[f] | | | |
| | $R = 0.99900$[g] | | | | $R = 0.99896$[g] | | | |

Direct method, 0.01 mol $l^{-1}$ solution of lithium acetate was used as terminating electrolyte.
[a]Mean of 10 measurements in solution of potassium chloride and sodium chloride, respectively.
[b]Mobility values are given in $10^9$ $m^2$ $V^{-1}$ $s^{-1}$.
[c]Mean of migration times in anionic mode (chloride as leading ion, potassium and sodium, respectively, as counter ion).
[d]Mean of migration times in cationic mode (potassium and sodium, respectively, as leading ion and chloride as counter ion).
[e]Measured mobility values are given using confidence interval ($\alpha = 0.05$).
[f]Regression equations of relationships between ionic mobility and temperature (°C).
[g]Correlation coefficient.

Table 2
Transference number values for potassium and sodium ions

| $T$ (°C) | Potassium | Sodium |
|---|---|---|
| 20 | 0.4930 | 0.3931 |
| 25 | 0.4929/0.4904[a] | 0.3947 |
| 30 | 0.4909 | 0.3923 |
| 40 | 0.4893 | 0.3948 |
| 50 | 0.4886 | 0.3995 |

[a]These values were obtained at the start and the end of the experimental period.

od [15]. To verify the long time reproducibility, two parallel series of measurements at 25°C were carried out at the start of the work and 2 years later. The values of limiting ionic mobility or transference number at the start of experiment were $76.95\times10^{-9}$ $m^2\ V^{-1}\ s^{-1}$ or 0.4929, respectively, while at the end of measurement values $76.27\times10^{-9}$ $m^2\ V^{-1}\ s^{-1}$ or 0.4909 were found. This corresponds to a relative standard deviation of 0.63 or 0.51%.

Table 3
Limiting mobility of benzoate and salicylate ion ($T=25$°C)[a]

| Ion | $u_{meas}$ [b] | $u_{lit}$ |
|---|---|---|
| Benzoate | −32.16±0.87 | −32.9 [2]; −31.9 [9] |
| Salicylate | −34.14±0.63 | −35.4 [14]; −33.9 [9] |

Indirect method, 0.01 mol $l^{-1}$ solution of tetrabutylammonium 3,5-dinitrobenzoate was used as terminating electrolyte.
[a]Mobility values are given in $10^9$ $m^2\ V^{-1}\ s^{-1}$.
[b]Measured mobility values are given using confidence interval ($\alpha=0.05$).

The accuracy and the reproducibility of indirect method (Eq. (11)) were tested by the mobility measurement of benzoate and salicylate ions, which can be measured both by direct (Eq. (4)) and indirect (Eq. (11)) methods. The migration times of sodium ion in the 0.01 $M$ solutions of sodium chloride and sodium benzoate or sodium salicylate were measured at 25°C. Table 3 shows the results of indirect measurement with tetrabutylammonium 3,5-dinitrobenzoate as a new terminating electrolyte. There is a good agreement with published data [2,9,14]. The relative difference between measured data and the average of the published data was 0.74% for benzoate and 1.49% for salicylate, respectively. This shows that the method is suitable for the relatively precise mobility measurement of large organic ions.

The indirect method was used for the determination of mobilities of some practically important anions (anionic pesticides) and cations (cationic drugs). Pesticide acids are relatively strong so they can be easily converted into sodium salts. The sodium salts are fully dissociated in neutral (water) solution and the sodium ion was used for the indirect method. The results are presented in Table 4.

Local anesthetics are usually used in the form of hydrochlorides in medicine. This fact can be useful for the measurement by the indirect method. So we

Table 4
Limiting mobility of pesticide acid anions ($T=25$°C)[a,b]

| Anion of pesticide acid | $t_1$ (s)[c] | $t_2$ (s)[d] | $u_{meas}$ | $u_{lit}$ |
|---|---|---|---|---|
| Phenoxyacetic | 957.66 | 595.23 | −32.73±0.49 | −36 [7]; −27.8 [2] |
| 4-Chlorophenoxyacetic | 956.96 | 598.25 | −32.17±0.46 | −34.1 [7] |
| 2,4-Dichlorophenoxyacetic | 951.02 | 568.13 | −28.01±0.33 | −32 [7]; −25 [2] |
| 4-Chloro-3-methylphenoxyacetic | 956.38 | 588.34 | −30.91±0.28 | −32.4 [7] |
| 2,4,5-Trichloropheoxyacetic | 956.38 | 580.78 | −29.91±0.19 | −30.2 [7] |
| 2-Phenoxypropionic | 959.49 | 584.74 | −30.18±0.29 | −33.6 [7] |
| 2-(4-Chlorophenoxy)propionic | 959.49 | 583.31 | −30.01±0.29 | −31.4 [7] |
| 2-(4-Chloro-3-methylphenoxy)propionic | 959.49 | 574.80 | −28.90±0.28 | −29.9 [7] |
| 2-(2,4-Dichlorophenoxy)propionic | 956.96 | 570.50 | −28.53±0.16 | $x$ |
| 2-(2,4,5-Trichlorophenoxy)propionic | 958.95 | 589.92 | −30.46±0.45 | −28.1 [7] |

Indirect method, 0.01 mol $l^{-1}$ solution of tetrabutylammonium 3,5-dinitrobenzoate was used as terminating electrolyte.
$x$, the value has not been published yet.
[a]Mobility values are given in $10^9$ $m^2\ V^{-1}\ s^{-1}$.
[b]Measured mobility values are given using confidence interval ($\alpha=0.05$).
[c]Mean of migration times of sodium ion (cationic mode) in standard salt–sodium chloride (the first experiment).
[d]Mean of migration times of sodium ion (cationic mode) in sodium salt of pesticide acid (the second experiment).

Table 5
Limiting mobility of local anesthetic cations ($T=25°C$)[a]

| Local anesthetic cation | $u^{b}_{meas}$ | $u_{lit}$ [8] |
|---|---|---|
| Amylocaine | 27.84±0.53 | 25.5 |
| β-Eucaine | 24.54±1.02 | 23.2 |
| Procaine | 25.84±0.43 | 25.7 |
| Mesocaine | 22.68±1.54 | 22.4 |
| Tropacocaine | 26.89±0.24 | 26.0 |

Indirect method, 0.01 mol $l^{-1}$ solution of tetrabutylammonium 3,5-dinitrobenzoate was used as terminating electrolyte, migration time of chloride was measured.
[a]Mobility values are given in $10^{9}$ $m^{2}$ $V^{-1}$ $s^{-1}$.
[b]Mobility values are given using confidence interval ($\alpha=0.05$).

measured migration times of chloride (anionic mode) in hydrochlorides of local anesthetics and in potassium chloride (Table 5).

There were bigger relative differences between measured and published (or the average of published) mobility data. They were 0.96–10.18% in the case of anions of pesticide acids and 0.54–9.1% in case of cations of local anesthetics. The data published so far have been obtained in ITP experiments using measurement of the detector response so there can be problems with uncertainty, noted in Section 1, and the pH adaptation in the sample zone. In our measurement we avoided the contamination of unbuffered leading zone by maintaining the pH in the reservoir of the terminator at a safe ITP region, by changing the terminator electrolyte, as described in Section 3; also, the electrode in the terminating reservoir was placed in the top of the compartment, the protons or hydroxylic ions produced on the electrodes could not penetrate into the capillary.

All the modifications of the method are only slightly affected by the Joule heat, because the whole capillary was well thermostated, and the effect of the temperature profile across the capillary was substantially depressed due to the fact that all the results are calculated as the ratio of two measurements obtained under very similar conditions, including the dissipation of the heat.

## 5. Conclusion

The proposed method for the precise measurement of ionic mobilities, which is based on the measurement of migration times of ions forming the leading electrolyte, gives accurate and reproducible results. It is applicable for strong electrolytes in the safe ITP region. The procedure can be used for the determination of the mobilities of biologically and pharmaceutically important ions.

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