Trace analysis of acids and bases by conductometric titration with multiparametric non-linear regression

Lúcia H.G. Coelho, Ivano G.R. Gutz *

Departmento de Química Fundamental, Instituto de Química, Universidade de São Paulo,
Av. Prof. Lineu Prestes 748, 05508-000 São Paulo, SP, Brazil

Abstract

A chemometric method for analysis of conductometric titration data was introduced to extend its applicability to lower concentrations and more complex acid–base systems. Auxiliary pH measurements were made during the titration to assist the calculation of the distribution of protonable species on base of known or guessed equilibrium constants. Conductivity values of each ionized or ionizable species possibly present in the sample were introduced in a general equation where the only unknown parameters were the total concentrations of (conjugated) bases and of strong electrolytes not involved in acid–base equilibria. All these concentrations were adjusted by a multiparametric nonlinear regression (NLR) method, based on the Levenberg–Marquardt algorithm. This first conductometric titration method with NLR analysis (CT-NLR) was successfully applied to simulated conductometric titration data and to synthetic samples with multiple components at concentrations as low as those found in rainwater ($\sim 10 \,\mu mol \, L^{-1}$). It was possible to resolve and quantify mixtures containing a strong acid, formic acid, acetic acid, ammonium ion, bicarbonate and inert electrolyte with accuracy of 5% or better.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Acid–base; Conductometric titration; Multiparametric nonlinear regression; Levenberg–Marquardt; Synthetic rainwater; Acid rain

1. Introduction

The application of conductivity measurements for analytical purposes was first suggested in the beginning of last century by Küster and Grüters [1], the inventors of conductometric titrimetry. Their experimental work on the study of conductivity of sodium salts from organic acids led them to the conclusion that end-points of acids titrated with bases and vice versa were indicated by a minimum in the conductivity, located at the intercept of two linear segments. They had also correctly identified the parameters that govern the shape of conductometric titration curves.

Measurement of solution's conductance, commonly applied in laboratories, could disclose information about the ionic content of a sample [2–6]. However, direct conductometric analysis had limited application [7] due to the non-selective character of the technique [8,9].

Conductometric titrations (CT) have a more selective character when acid–base [10], complexometric [11,12] or precipitation [13,14] reactions are explored, thus widening the range of analytical applications. As mentioned, in favorable situations, the stoichiometric point of conductometric titrations is indicated by the intersection between two straight-line segments. CT has been widely used as an auxiliary tool in the study of polyelectrolytic compounds [15] including humic substances [16–18], due to the possibility of studying association phenomena and the analysis of charged groups nature and behaviour [19–21]. Additionally, CT has been used as a complement to potentiometric measurements for characterization of complexes and determination of their stability constants [22,23].

Nowadays, besides monitoring the efficiency of ion exchange columns of water purification systems, direct conductometry has a few other practical applications in the laboratory, such as the evaluation of ionic strength of solutions or studies of charge association phenomena. It is, however, widely used in universal detectors, mainly in ion chromatography equipment [24] but more recently, also in capillary electrophoresis [25]. For this purpose, the oscillometric mode is particularly advantageous

---

* Corresponding author. Tel.: +55 11 3091 2150; fax: +55 11 3091 2150.
E-mail address: gutz@iq.usp.br (I.G.R. Gutz).

and effective, as demonstrated in various applications [26–29], because no direct contact with the electrodes is needed; it is also amenable for miniaturization permitting the construction of capillary electrophoresis equipment on a chip [30].

The aim of this work is to revisit conductometric titrations and introduce modern chemometric resources to extend its applicability to more dilute and complex samples. It is well known that in very diluted solutions or when non-quantitative reactions are involved, linearity deviations are observed during CT, especially near the stoichiometric points. For binary mixtures of acids, the end-points of CT are easily determined by graphical methods only when the stronger acid is almost completely dissociated and the weaker one is rather undissociated in the sample. In the worst cases, no linear regions are observed at all along the titration curve, rendering them untreatable by graphical analysis.

Under similarly unfavorable situations, potentiometric titrations had been solved by using modern chemometric methods, such as multiparametric nonlinear regression, in order to fit the concentrations of the analytes and to refine their equilibrium constants [31]. Unexpectedly, nonlinear regression methods had not yet been applied to CT for analytical purposes. However, linear regression had been used to assist the analysis of CT when there were linear segments [32]. With help of "direction lines" nonlinear regions of the titrations had been solved for mixtures of a strong acid with a partially dissociated one in the sample or of a partially dissociated acid and an undissociated one [33–35]. This approach did not suffice to resolve relatively simple and common mixtures of weak acids such as acetic and formic acids, with dissociation constants differing by no more than one order of magnitude ($\Delta pK_d \approx 1$).

It is demonstrated here that not only very diluted mixtures of formic and acetic acids but much more complex systems can be solved by defining complete mass and charge balance equations of the involved equilibria and applying multiparametric nonlinear regression (NLR) to the CT data, a method shortened as CT-NLR now on. The robust and efficient Levenberg–Marquardt algorithm was elected for the least squares regression, but other algorithms could be used instead. Besides conductance measurements, auxiliary pH data was collected simultaneously during the titrations and fed into the NLR model to simplify and speed-up calculations. CT-NLR was investigated and validated with simulated and synthetic acid–base multi-component systems, aiming the application to real samples of rainwater with low concentrations of acids and bases.

2. Experimental

The CT-NLR method was implemented in the commercial computer program Origin® 5.0 from Microcal that incorporates satisfactory spreadsheet facilities and excellent graphical and regression resources, including NLR by the Levenberg–Marquardt algorithm.

2.1. Fundaments of the method

The net conductivity measured during a titration encompasses the contribution of all ionic species in the titration cell after each titrant addition. For a generic titration of a weak monoprotic acid HA with a strong base BOH, at the beginning, only some free (hydrated) H^+ and A^- (from the dissociation of HA) and minute amounts of OH^- (from dissociation of water) are present in the cell. As the titration proceeds, new species, like B^+, are gradually added to the system and contribute to the conductance; meanwhile, the dissociation of more acid is promoted by the reaction of H^+ with OH^-, until the stoichiometric point is reached. Afterwards, an excess of OH^- builds up, with proportional increase in the conductance, defining a straight line after correction of the dilution effect. The (nonlinear) shape of the first half of the curve is dependent of the dissociation constant and the concentration of HA, but as a rule, a precise intercept of the lines near the stoichiometric point is obtained even for diluted solutions and very weak acids ($pK_{HA} > 9$, $[HA] \approx 10^{-5}\,mol\,L^{-1}$), where conventional potentiometric titration fails. It is well known that the CT of a mixture of a strong and a weak acid with a strong base is straightforward, presenting two intercepts.

However, when more acids or bases of different dissociation constants coexist in the sample solution, there are no clear intercepts anymore and the graphical analysis of the curve becomes cumbersome or useless. Under such unfavorable conditions, good results can still be obtained by multiparametric NLR, as will be shown, by describing the system with a generic set equations for acid–base equilibria and effective parameter estimation for the fitting of the calculated curve to the experimental one by minimizing the sum of the squares of the residuals. The Levenberg–Marquardt method (LM) was chosen for this purpose due to its speed and robustness.

The LM method combines, in a controlled form, two other NLR methods: the steepest descent (based on first derivatives and known not to converge well near a flat minimum) and the Gauss–Newton one (quite efficient when the contribution of second-order terms is minimal) [36]. Thus, the parameter that controls the magnitude and the search direction of the LM algorithm gives higher weight to the search direction indicated by the steepest descent method in steep regions and gradually transfers control to the Gauss–Newton method in flatter areas, usually closer to the minimum (of the sum of the least squares of the residuals).

The general equations, used to describe the chemical composition of the system in the equilibrium state established after each titrant addition are based on the contribution of all ionic species to the net conductivity. To calculate the contribution of each ion in solution involved in acid–base equilibria, its molar fraction α_i must be determined. This task becomes difficult when only conductometric measurements are available but could be elegantly solved here by using auxiliary pH data, collected simultaneously during the titration to provide estimates of $[H^+]$ at each point. Dissociation constants (K_d) of the acids or the inverse of their values (to simplify equations and use the same nomenclature of complexation reactions), known as the protonation constants ($K_{p,i}$, where i is the number of protons) of the conjugated bases can be taken from the literature to calculate the molar fractions α_0 of the anionic specie A^- and α_1 of the protonated

(and uncharged) specie HA:

$$K_{p,1} = \frac{[HA]}{[H^+][A^-]} \quad \alpha_0 = \frac{1}{K_{p,1}[H^+] + 1} \quad \alpha_1 = \frac{K_{p,1}[H^+]}{K_{p,1}[H^+] + 1}$$

For a polyprotic acid, the following general equation applies:

$$\alpha_i = \frac{\sum_{i=0}^{n} i\beta_i[H^+]^i}{\sum_{i=0}^{n} \beta_i[H^+]^i} \quad \text{where} \quad \beta_i = \prod_{i=0}^{n} K_{p,i}$$

As defined in the literature [37], the ionic conductance Λ_i (in S cm^2 mol^{-1}) of a dissociated ion i involved in acid–base equilibria could be calculated for any value of the molar fractions α_i from the ionic conductance at infinite dilution Λ_i^0:

$$\Lambda_i = \alpha_i \times \Lambda_i^0$$

The net conductivity κ takes into account the sum of the product of ionic conductivity (Λ_i) and the concentration C in mol L^{-1}, for all anions and cations in solution:

$$\kappa = \sum_{i=0}^{n} \Lambda_i C_i$$

In this work, devoted to the CT of diluted samples ($\leq 10^{-3}$ mol L^{-1}), the effect of the ionic strength (I) on equilibria and conductivity was disregarded (deviations of 2–3% for monovalent ions and 3–5% for divalent ones are expected). At higher values of I, corrections could be introduced, for example, by using the Davies equation [38].

During titration of an initial volume V_i of generic monoprotic acid HA, the total volume v of added base BOH was increased stepwise. Conductivity data was calculated based on equilibria established after each base addition. The estimated values must be multiplied by a dilution factor f:

$$f = \frac{V_i + v}{V_i}$$

2.2. Simulating conductometric titration curves

Conductometric titration curves were simulated in order to evaluate the applicability of CT-NLR. The computational program CURTIPOT (freeware), downloaded from the Internet, was used to generate potentiometric titration curves for the parameter set chosen in each simulation (protonation constants, concentration of acids and bases in the "sample", initial volume in the titration cell, constant increments of volume or pH during titration). Additionally, data with dispersion was produced with CURTIPOT, simulating experimental errors with normal distribution in the volume additions or pH measurements.

Generated pH data as a function of added volume of titrant was copied to a spreadsheet of the Origin® program, in which all calculations were performed to simulate CT data and to analyze it afterwards. New columns were added as needed to perform calculations like molar fraction α_i and the number of mols of OH$^-$ and B$^+$ added during the titration. The net conductivity was estimated as the sum of all Λ_i. Fig. 1 shows the potentiometric and conductometric titration curves of a 10.0 μmol L^{-1} solution
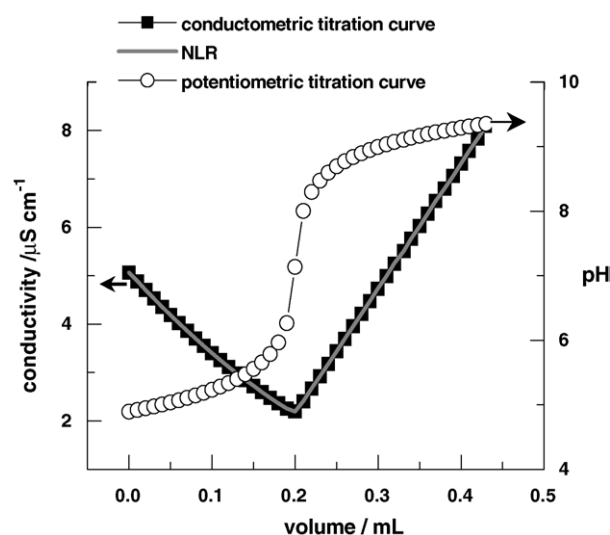

Fig. 1. Simultaneous potentiometric (□) and conductometric (●) titration curves for 20.0 mL of 10.0 μmol L^{-1} of a generic monoprotic acid HA (p$K = 4.7$) titrated with BOH 1.00 mmol L^{-1}. NLR (▬) applied to conductometric titration data.

of the generic monoprotic acid HA (p$K = 4.7$) titrated with BOH 1.00 mmol L^{-1}.

To initialize the NLR method in the Origin® program, it was necessary to consider the net conductivity κ as an independent variable and all parameters such as [H$^+$], α_i and the number of mols of titrant added as dependent variables.

2.3. Conductometric and potentiometric titrations

A Micronal® model B330 conductivity meter provided with a glass cell comprising two platinized platinum electrodes was calibrated with standard KCl solution (100.0 μS) on a daily basis and used throughout the work. A 10 mL piston burette (with 5 μL divisions and 1.5 μL precision) was used for titrant addition.

Potentiometric titration data was acquired simultaneously with the conductometric one, using a Quimis® pH-meter model Q400M½ (precision of 1 mV) coupled to a combined glass electrode (model QA-338-ECV), previously calibrated with certified Sigma buffers.

All titrations were made in jacketed glass-cells with controlled temperature (25.0 ± 0.1)°C maintained with a Formatemp Bath & Flow water bath. The conductivity cell was stirred during the titrations. After each titrant addition, 30 s were allowed to achieve stability of the readings of pH and conductance.

2.4. Solutions and reagents

Ca(OH)$_2$ solution was chosen as titrant, due to the low solubility of CaCO$_3$, formed from (undesirable but inevitable) CO$_2$ absorption, thus reducing the contamination with carbonate. The analytical grade reagent was dissolved in ultrapurified water (Nanopure, Barntead) with low CO$_2$ content, and immediately stored in a glass flask (gas tight) internally covered by a polyethylene layer (OH$^-$ resistant). A cartridge with NaOH lentils was

connected to the cap of the flask, for air entrance free of CO_2. The connections of the burette with the titrant reservoir and the cell were made with silica tubing (a piece of a GC capillary column) to stop CO_2 permeation through the wall (a problem with polymeric tubing). Titrant was periodically standardized with potassium hydrogen phthalate primary standard.

Synthetic diluted samples were prepared from stock solutions of acids and bases previously standardized against a base or an acid. All solutions were prepared with water from the Nanopure system, to minimize CO_2 contamination.

3. Results and discussion

3.1. CT-NLR applied to simulated conductometric titration data

Firstly, the NLR method was applied to simulated systems containing up to four titrable components in low concentration range (10^{-6} to 10^{-5} mol L^{-1}). Fig. 1 shows simulated conductometric and potentiometric titration curves and the non-linear regression curve fitted to the conductometric data. The system is composed of 10.0 μmol L^{-1} of a generic monoprotic acid HA ($pK_d = 4.7$) titrated with BOH 1.00 mmol L^{-1}.

For single titrable component systems, the NLR method returned concentration values with standard deviations lower than 0.5%. With more complex systems, containing up to four titrable components, it was possible to evaluate the ability of the method in distinguishing different species and estimating their concentrations. Mixtures of weak acids like formic and acetic become difficult to resolve by potentiometric titration in the 10^{-6} to 10^{-5} mol L^{-1} concentration range because both acids are extensively dissociated at the initial pH. Using CT-NLR it was possible to resolve and estimate the contribution of each weak acids to the system acidity.

The CT-NLR method was applied to the difficult determination of major acids and bases in rainwater samples. Thus, the NLR equation was expanded to accommodate the following unknown concentrations: formic acid, acetic acid, ammonium, total carbonate and the residual conductance due to non-titrable electrolytes, including anions resulting from complete dissociation of strong acids. The regression model did not directly provide the contribution of the strong acids, so it was calculated by difference, subtracting from the conductance of the sample all contributions from the dissociated fraction of weak acids and of non-titrable species. Fig. 2 shows the conductometric titration curve of a simulated multiple component system titrated with $Ca(OH)_2$ 1.00 mmol L^{-1} and containing 10.0 μmol L^{-1} in HCl, 10.0 μmol L^{-1} in CH_3COOH, 20.0 μmol L^{-1} in total carbonate and 20.0 μmol L^{-1} in ionic species that do not participate on acid–base equilibrium and the NLR applied to the curve.

As will be seen in Table 1, concentrations returned by the NLR method for all simulated curves agree very well with the starting values, despite the low concentrations under consideration and the multiplicity of components. To this point, no scatter was added to the simulated curves. To improve realism, random dispersion with Gaussian distribution was added to the added titrant volumes and/or the pH and conductance
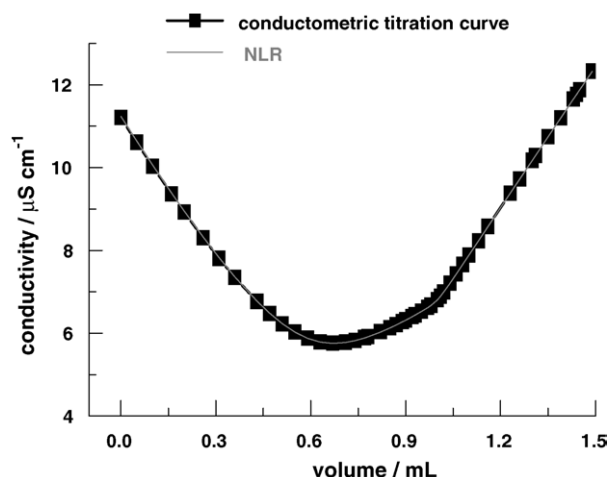

Fig. 2. NLR (▬) applied to the analysis of a simulated conductometric titration data (■) of a system containing 20.0 mL of a mixture of 10.0 μmol L^{-1} HCl, 10.0 μmol L^{-1} CH_3COOH, 20.0 μmol L^{-1} total carbonate and 20.0 μmol L^{-1} inert ionic species, titrated with 1.00 mmol L^{-1} $Ca(OH)_2$.

values. Concentration values returned by NLR analysis of such conductometric titration curves agreed with the starting values within the limits of the standard deviations estimated by the NLR program. Fig. 3 shows the NLR applied to a simulated conductometric titration curve containing dispersion of 0.002 mL in volume, 0.01 units in pH and 1% in conductivity measurements. The multiple component system contains 20.00 mL of a mixture of 10.0 μmol L^{-1} in strong acids, 10.0 μmol L^{-1} CH_3COOH, 20.0 μmol L^{-1} NH_4^+ and 25.0 μmol L^{-1} total carbonate and 50.0 μmol L^{-1} in ionic species that do not participate on acid–base equilibrium, and is titrated with 7.50 mmol L^{-1} $Ca(OH)_2$.
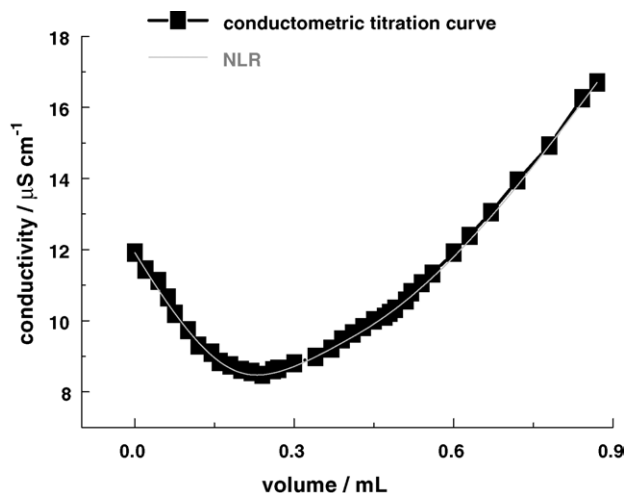

Fig. 3. NLR (▬) applied to the analysis of simulated conductometric titration data (■) of a system containing 20.0 mL of a mixture of 10.0 μmol L^{-1} in strong acids, 10.0 μmol L^{-1} CH_3COOH, 20.0 μmol L^{-1} NH_4^+, 25.0 μmol L^{-1} in total carbonate and 50.0 μmol L^{-1} in ionic species that do not participate on acid–base equilibrium titrated with 7.50 mmol L^{-1} $Ca(OH)_2$ containing approximately 70.0 μmol L^{-1} in dissolved CO_3^{2-}. Standard deviation of simulated dispersion: 0.0020 mL in volume, 0.010 units in pH and 1% in conductance measurements.

Table 1
Results obtained for CT-NLR analysis of mono and multiple component-simulated systems and for titration data of synthetic rainwater

System composition	Standard deviation of added dispersion to simulated data	Starting concentrations (μmol L^{-1})	Returned values CT-NLR (μmol L^{-1})[a]	Relative error (%)
HCl	0	20.0	(20.1 ± 0.4)	+0.5
HCl	0	10.0	(10.1 ± 0.5)	+1.0
CH$_3$COOH		10.0	(10.1 ± 0.3)	+1.0
CH$_3$COOH	0	20.0	(20.1 ± 0.1)	+0.5
HCOOH		20.0	(19.9 ± 0.3)	−0.5
HCl		10.0	(10.2 ± 1.0)	+2.0
CH$_3$COOH	pH 0.01	10.0	(9.8 ± 0.2)	−2.0
NH$_4^+$	0.002 mL volume	20.0	(20.1 ± 0.8)	+0.5
HCO$_3^-$/H$_2$CO$_3$		25.0	(24.8 ± 0.3)	−0.8
Inert ions		50.0	(50.2 ± 1.0)	+0.4
HCl		10.0	(9.7 ± 1.0)	−3.0
CH$_3$COOH	pH 0.01	10.0	(9.7 ± 1.0)	−3.0
NH$_4^+$	0.002 mL volume	20.0	(20.5 ± 0.9)	+2.5
HCO$_3^-$/H$_2$CO$_3$	1% Conductivity	25.0	(24.6 ± 0.5)	−1.6
Inert ions		50.0	(50.7 ± 1.0)	+1.4
HCl		10.0	(9.5 ± 2.0)	−5.0
HCOOH	Real titration data of synthetic rain water	10.0	(9.7 ± 1.3)	−3.0
NH$_4^+$		20.0	(20.3 ± 1.9)	+3.0
HCO$_3^-$/H$_2$CO$_3$		Unknown	(26.6 ± 1.5)	–
Inert ions		50.0	(48.7 ± 1.2)	−2.6

Dissociation constants used in the NLR method (pK_d): HCl = −6.0; CH$_3$COOH = 4.70; HCOOH = 3.70; NH$_4^+$ = 9.10; CO$_3^{2-}$/HCO$_3^-$ = 10.10; HCO$_3^-$/H$_2$CO$_3$ = 6.10.

[a] Adjusted concentration ± standard deviation calculated by the program.

The excellent quality of the results of the CT-NLR for this difficult titration can be appreciated in Table 1.

3.2. Application of CT-NLR to synthetic rain water samples

Synthetic samples were prepared and analyzed by simultaneous conductometric and potentiometric titrimetry. The Fig. 4 shows the CT-NLR applied to a sample containing
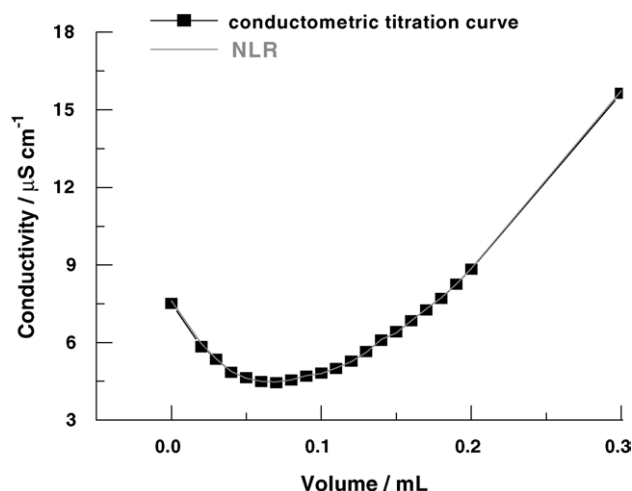

Fig. 4. NLR (▬) applied to the analysis of conductometric titration data (■) of a system containing 20.0 mL of a mixture of 10.0 μmol L^{-1} HCl, 10.0 μmol L^{-1} HCOOH, 20.0 μmol L^{-1} NH$_4^+$ and 50.0 μmol L^{-1} in inert ionic species, titrated with 7.50 mmol L^{-1} Ca(OH)$_2$ containing approximately 70 μmol L^{-1} in dissolved CO$_3^{2-}$, as obtained by NLR.

10.0 μmol L^{-1} HCl, 10.0 μmol L^{-1} HCOOH, 20.0 μmol L^{-1} NH$_4^+$ and 50.0 μmol L^{-1} of electrolytes noninvolved in acid–base equilibrium, titrated with Ca(OH)$_2$ 7.50 mmol L^{-1} containing approximately 70 μmol L^{-1} dissolved CO$_3^{2-}$.

The curve calculated with the NLR coefficients fits exactly to the experimental conductometric data. It is worthwhile to observe the low and gradual conductance changes during titration of the multiple components, defining a smooth curve that approached straight lines only at the very ends, completely impossible to evaluate by graphical methods. Despite this unfavorable situation, the relative standard deviations associated to the NLR equation parameters were less than 22% and the errors, 5% or less. When one of or more of the acids or bases considered in the regression model were absent in simulations or the synthetic sample presented in table, the correct solution was found anyway, with an uncertainty of 1 μmol L^{-1} or lower.

4. Conclusion

The goal achieved in that work was the development of a NLR method of analysis of conductometric acid–base titration curves. The new CT-NLR method allowed the analysis of very diluted systems with multiple titrable components in the presence of inert electrolytes. The innovative idea of feeding the CT-NLR with pH values from simultaneous potentiometric titration data to assist the calculation of the position of involved protonation equilibria boosted the robust and effective chemometric method for the quantification of minute amounts of acids and bases in diluted samples, such as environmental samples like

rainwater ones. Simulations of mixtures of diluted bases titrated with strong acids conducted to similarly good results. It can be envisioned that CT-NLR would be advantageously used also for simpler systems or at higher concentrations, due to its increased accuracy, evaluation of the precision, easier automation and independence of subjectivity of the analyst, in comparison with ordinary graphical or linear regression methods.

Acknowledgements

References

[1] F.W. Küster, M. Grüters, Z. Anorg. Chem. 35 (1903) 454.
[2] E. Prenesti, S. Toso, P.G. Daniele, V. Zelano, M. Ginepro, Anal. Chim. Acta 507 (2004) 263.
[3] A.J. Ranalli, Water Air Soil Poll. 104 (1998) 423.
[4] S. Licht, K. Longo, D. Peramunage, F. Forouzan, J. Electroanal. Chem. 318 (1991) 111.
[5] B. Sesta, M.L. Berardel, Electrochim. Acta 17 (1972) 915.
[6] R.E. Reeves, J.R. Jung, J. Am. Chem. Soc. 71 (1949) 209.
[7] D.C. Harris, Quantitative Chemical Analysis, 4th edn., W. H. Freeman Company, New York, 1995, 379.
[8] F. Szabadváry, R.A. Chalmers, Talanta 30 (1983) 997.
[9] B.E. Pape, J. Anal. Toxicol. 1 (1977) 46.
[10] M. Crocker, R.H.M. Herold, M.H.W. Sonnemans, C.A. Emeis, A.E. Zelano, J.N. Vandermoolen, J. Phys. Chem. 97 (1993) 432.
[11] C. Riviere, M. Nierlich, M. Ephritikhine, C. Madic, Inorg. Chem. 40 (2001) 4428.
[12] I. Pochard, P. Couchot, A. Foissy, Colloid Polym. Sci. 276 (1998) 1088.
[13] A. Kowalczyk-Marzec, M. Kurzawa, A. Szydlowska-Czerniak, E. Szlyk, Chem. Anal. (Warsaw) 47 (2002) 613.
[14] S. Prasad, K.C. Pathak, J. Electroanal. Chem. 12 (1966) 360.
[15] B.C. Bonekamp, J. Lyklema, J. Colloid Interface Sci. 113 (1986) 67.
[16] F. Rey, A.A.S.C. Machado, F. Arce, M.A.A. Ferreira, A. Toja, Anal. Chim. Acta 304 (1995) 375.
[17] J.C. Masini, G. Abate, E.C. Lima, L.C. Hahn, M.S. Nakamura, J. Lichtig, H.R. Nagatomy, Anal. Chim. Acta 364 (1998) 223.
[18] J. Riggle, R. von Wandruszka, Talanta 62 (2004) 103.
[19] A.F.D. Namor, M. Shehab, J. Phys. Chem. A 108 (2004) 7324.
[20] H. Shehata, J. Chem. Soc. 90 (1994) 3401.
[21] M. Fukushima, S. Tanaka, M. Taga, Int. J. Environ. Anal. Chem. 56 (1994) 229.
[22] M.G.A. Wahed, S.A. Wanees, M. Gamel, S.A. Haleem, J. Mater. Sci. Technol. 21 (2005) 140.
[23] C.I. Rich, Soil Sci. Soc. Am. J. 34 (1970) 31.
[24] S. Rabin, J. Stillian, V. Barreto, K. Friedman, M. Toofan, J. Chromatogr. 640 (1993) 97.
[25] J.A.S. Fracassi, C.L. do Lago, Anal. Chem. 70 (1998) 4339.
[26] P. Kuban, P.C. Hauser, Electroanalysis 16 (2004) 2009.
[27] F.R. Rocha, J.A.S. Fracassi, C.L. do Lago, A. Fornaro, I.G.R. Gutz, Atmos. Environ. 37 (2003) 105.
[28] A. Fornaro, I.G.R. Gutz, Atmos. Environ. 37 (2003) 117.
[29] P. Kuban, P. Kuban, V. Kuban, Electrophoresis 23 (2002) 3725.
[30] C.L. do Lago, C.A. Neves, D.P. de Jesus, J.G. Brito-Neto, J.A.F. da Silva, Electrophoresis 25 (2004) 3825.
[31] G. Kateman, H.C. Smit, L. Meites, Anal. Chim. Acta 152 (1983) 61.
[32] M.C. Ortiz-Fernández, A. Herreo-Gutiérrez, Chemom. Intell. Lab. Syst. 27 (1995) 231.
[33] E. Chromiak, Z. Lukaszewski, Chem. Anal. (Warsaw) 36 (1991) 59.
[34] E. Chromiak, Z. Lukaszewski, Chem. Anal. (Warsaw) 36 (1991) 733.
[35] E. Chromiak, Analyst 120 (1995) 149.
[36] D.M. Bates, D.G. Watts, Nonlinear Regression and Its Applications, Wiley, New York, 1988.
[37] P.W. Atkins, Physical Chemistry, vol. 3, third ed., Oxford University Press, Oxford, 1986, p. 663.
[38] B. Colston, V.J. Robinson, Analyst 4122 (1997) 1451.