NUMERICAL CALCULUS AND ANALYTICAL CHEMISTRY:
An example of interdisciplinary teaching

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ABSTRACT

Analytical Chemistry is an almost unexplored source of real – life problems for Numerical Calculus courses in chemical careers (Martínez Luaces, V., 2001).

In this paper, we discuss one of these problems: the pH determination of a weak monoprotic acid aqueous solution (Labandera, F. & Martínez Luaces, V., 1994).

From the mathematical viewpoint, this problem led us to solve very difficult algebraic equations. In several cases is possible to obtain an algebraic exact solution, but in other situations the algebraic approach is not useful. So, if we wont to generalise our methods, we need a numeric approximate solution.

We analyse several algorithms form well known methods as Newton – Raphson, Regula Falsi, Bisection and others (Dahlquist, G., Bjorck, A. & Anderson, N., 1974). We also study a couple of methods, developed specially for this kind of problems.

The variety of situations, and the mathematical and chemical richness of them, suggests proposing an interdisciplinary work in research and teaching. This can be carried out by a group of both Analytical Chemistry and Numerical Calculus teachers. In the same way possible to use these problems for students project – work, with interesting advantages

We comment here, some important results, strongly related with this style of teaching ((Martínez Luaces, V. 1998) and (Gómez, A. & Martínez Luaces, V., 2001)). Finally, we suggest some recommendations for these mathematical service courses in chemical careers.

Keywords: Applied Mathematics, Numerical Calculus, Analytical Chemistry, Interdisciplinary teaching.

1. Introduction

The pH determination of an aqueous solution is a very important problem in Analytical Chemistry.

From the mathematical point of view, this chemical problem is modeled using algebraic equations. As an example we have:

$$\frac{V_b.C_b}{V_a+V_b}+\left[H^+\right]=\frac{K_w}{\left[H^+\right]}+\frac{C_a.V_a}{(V_a+V_b).\left(1+\frac{\left[H^+\right]}{K_a}\right)} \tag{1}$$

In this equation C_a and C_b are the concentrations of acid and base solutions and V_a, V_b are their volumes. The symbols K_w and K_a represent the equilibrium constants for water and acid, respectively and finally $[H^+]$ is the concentration of the hydrogen ion. All these variables are positive numbers and $[H^+]$ is the unique unknown, and then, pH is obtained as - log ($[H^+]$).

Equation (**1**) corresponds to the pH determination of a weak monoprotic acid solution (Martínez Luaces, V., 2001). Obviously, this formula can be easily converted in a polynomial equation of third order.

If we consider now another situation, like the dilution of a phosphoric salt (for example Na_2HPO_4), then, the resulting problem is much more difficult. In fact, in this case (Martínez Luaces, V. & Martínez, F.,submitted), we have:

$$\left[H^+\right]+2.C_s=\frac{K_w}{\left[H^+\right]}+\frac{C_s.\left(3+\frac{2.\left[H^+\right]}{K_3}+\frac{\left[H^+\right]}{K_2.K_3}\right)}{1+\frac{\left[H^+\right]}{K_3}+\frac{\left[H^+\right]^2}{K_2.K_3}+\frac{\left[H^+\right]^3}{K_1.K_2.K_3}} \tag{2}$$

As in the other case, C_s is the concentration of the salt solution, K_w, K_1, K_2, K_3 are equilibrium constants and $[H^+]$ is the concentration of the hydrogen ion. In this equation, as in (**1**), all these variables are positive numbers and $[H^+]$ is the unknown. Finally, the pH value is obtained using the equation pH = - log ($[H^+]$)

As in the other case, equation (**2**) can be converted in a polynomial one of fifth order.

It is well known, as a result of Galois theory (Grillet, P., 1999), that there are no formulas based on Nth-roots, useful to solve general polynomial equations with a degree greater or equal than five.

Then, we need a numerical approach to solve this chemical and mathematical problem.

In this paper, we will analyze several numerical methods and all of them will be studied from the Mathematical Education view point. It is important to remark that this methods and their applications to the chemical problem already mentioned, provide a source of interdisciplinary work in research and teaching. Moreover, the variety of situations and the mathematical and chemical richness of them, suggest to use these examples to propose project-work for the students, with interesting possibilities.

Finally, we will comment some important results obtained in the last years in our department of Mathematics. Taking into account these results, we will propose several conclusions and recommendations for service courses in chemical careers.

2. The numerical approach.

In this section, we will analyze the applicability of several numerical methods: Functional Iteration, Newton-Raphson, Bisection, Secant and Regula Falsi (Martínez Luaces, V. 1998). All these methods are very common and well known by students.

As a complement, we will mention a couple of methods developed specially for these problems.

- Functional Iteration:

A first easy option is to put equations 1 and/or 2 in the form:

$$[H^+] = g([H^+]) \tag{3}$$

Then, it is possible to find the solution using a fixed point iteration method (Martínez Luaces, V. 1998). In this case, if $V_a = 10$ ml, $V_b = 3$ ml, $C_a = 0.1$ M, $C_b = 0.1$ M and $K_a = 10^{-3}$ (K_w is a constant, and its value is 10^{-14}), then, the correct pH will be 2.69. Unfortunately, if we start the iterative method with a pH of 3 (that is, the best entire approximation), next iterant will be 1.81, and the next one does not exist! (pH is a positive number and in this third iteration we obtain the log of a negative number, and that situation has no chemical sense).

It is possible to show that the same situation takes place for almost all the reasonable values of pH in this case (Martínez Luaces, V. & Martínez, F., 2002), so we cannot recommend this method. It is impossible to use it for this problem.

- Newton-Raphson.

The speed of convergence for this method depends strongly of the initial approximation and the precision required.

For chemical reasons (Kolthoff, I. & Sandell, E., 1943), pH is given with only two significative numbers, so, the maximum precision needed will be 0.01.

The speed of convergence can be measured considering "n", that is the number of iterations to reach the pH value with a given precision "ε".

Taking into account all this facts, we can plot the variable "n" against "pH_0" (the initial approximation) and "ε". We decided to make the plot in ! ^{2} putting "pH_0" in the "x" axis and "ε" in the "y" one, and the value of "n" can be visualized with different tones of blue. In this plot we put a dark blue color (almost black) for a fast convergence point (that is a small "n" value), a blue color for a moderately fast one, and sky blue for slow convergence points (which correspond to big "n" values). Finally, the white color is for very slow convergence, or for points where the iterative method does not converge at all.

All this facts can be visualized in the following figure:

Newton Raphson
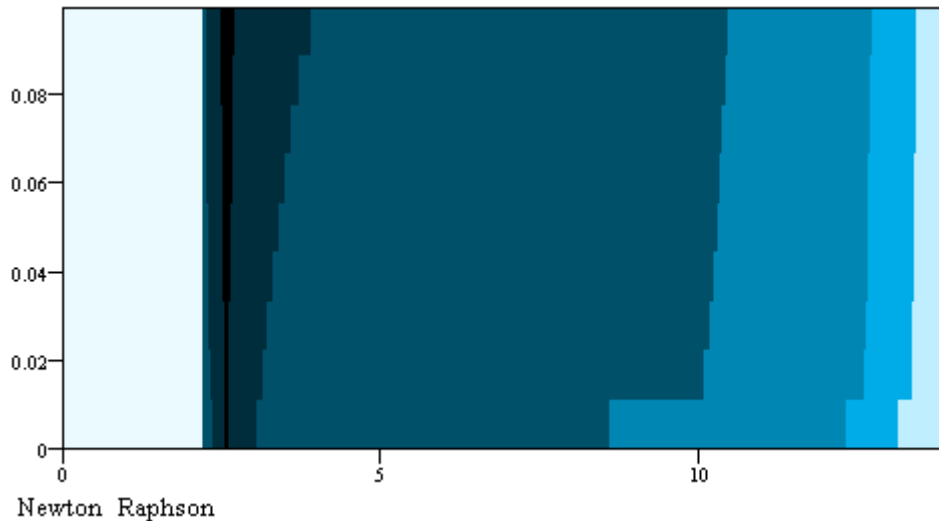
A first observation is that if we increase the "ε" value, then zones with a deep blue color predominate. This is really obvious taking into account that if we accept a big error for this method, then we need less iterations.

The second, and not so obvious observation, is that for "pH_0" values greater than 2.69 (the correct pH value, in this case), the iterative method converges, but for several initial values (pH_0 less than 2.30) iteration does not converge or is very slow for practical purposes. So, students must be very careful with the initial value, if they decide to use this method.

- Methods with two initial approximations.

These methods (Bisection, Secant and Regula Falsi) need two initial values "pH_1" and "pH_2" in order to start the iterative process (Martínez Luaces, V. 1998).

As a consequence of this fact, we decided to put "pH_1" in the "*x*" axis and "pH_2" in the "*y*" axis. As in the other case, we represent the "***n***" value with different tones of gray (for Bisection Method), bright blue (for Secant Method) and green (for Regula Falsi), to show the speed of convergence for each point $(pH_1, pH_2) \in (0,14] \times (0,14]$

The figures are (for an "ε" of 0.01):

Bisection

Secant
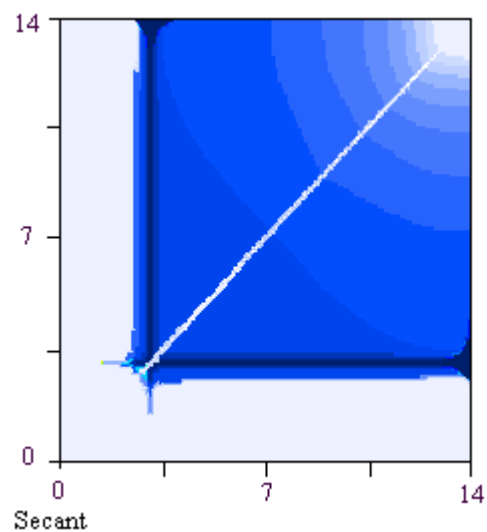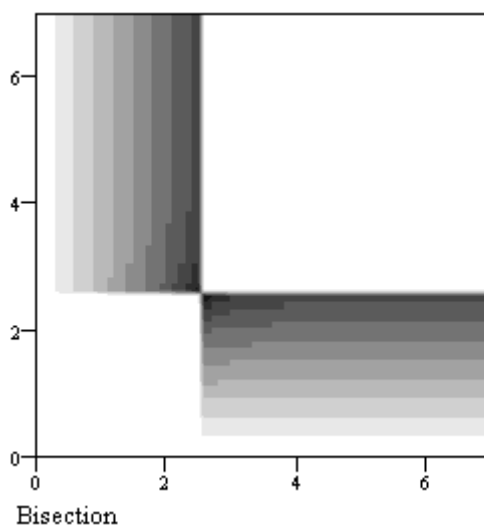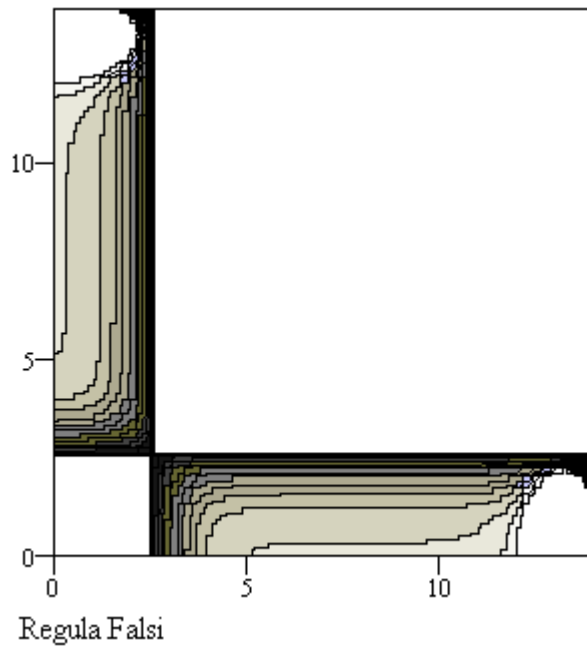
Regula Falsi

The figure of Secant Method is the most interesting. The reason is that Bisection and Regula Falsi methods, need initial values with different signs in their functional values. As a consequence of this fact, important parts of the figures (for these last methods) remain uncolored.

For this reason, we decided to present only the figure corresponding to Secant Method (in black and white), for another "ε" value (this "ε" will be 0.04):

Secant Method: error 0.04
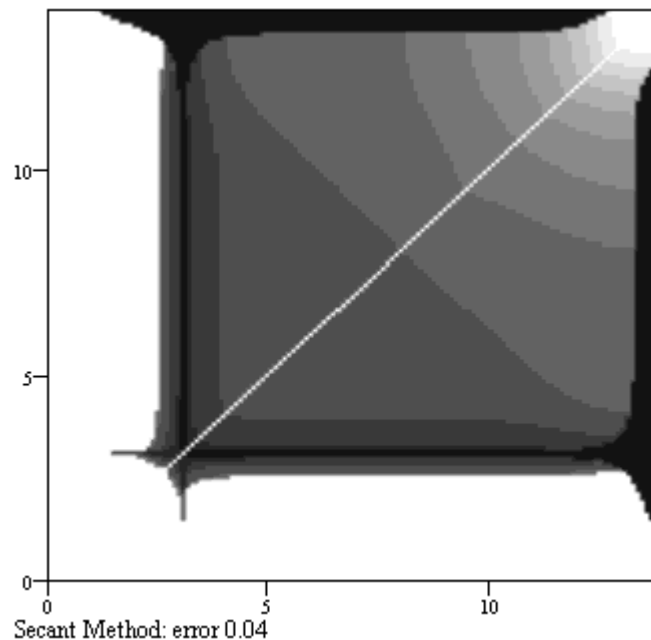
As in the other cases, dark zones become greater when "ε" is increased.

- Two special methods for this problem.

In a previous paper (Martínez Luaces, V., 2001), a couple of methods were presented in order to determine the pH value for certain aqueous solutions.

One of them consists in an approximate equation based only in several chemical considerations (Day Jr., R. & Underwood, A., 1980). With this formula, very poor results are obtained for certain weak acids, so it is not the best option.

For this reason, another method was developed specially for this problem (Martínez Luaces, V., 2001). This last one uses the chemical idea of electro - neutrality (Day Jr., R. & Underwood, A., 1980) in aqueous solutions, and the corresponding algorithm seems like a modification of Bisection Method. It is a very particular iterative method, useful for an analytical chemist, but not very interesting for mathematicians. So, in this paper, this algorithm was used only to confirm the results of the other methods.

3. The Mathematical Education viewpoint:

Typical courses of Numerical Calculus propose to the students pure mathematical exercises, which are not the best way to motivate the group.

In chemical careers, the situation is even more difficult for teachers (in order to motivate students), at least if we compare with Engineering, Informatics, etc. In fact, it is not easy to find real problems, related with other subjects that can be useful for Numerical Calculus courses.

Determination of pH in solutions of weak acids, or aqueous solutions of salts, are exactly what we need for this purpose. As we have seen before, they are real-life problems, with important connections with other subjects (as Analytical Chemistry), and they represent an important source of interesting Numerical Calculus problems.

As can be easily observed, there is no optimal method for this kind of problems. Besides this, results showed a very strong dependence with the initial approximations and with the precision required. Then, students realize that not always real-life problems can be solved in a routinary form. Moreover, in several cases, it is necessary to find a more creative solution.

These problems, among others, were studied and developed by interdisciplinary groups, integrated with both Analytical Chemistry and Mathematics teachers.

In this first stage, three courses (Numerical Calculus, Statistics and Differential Equations), were based on real problems, strongly related with other disciplines. The other three courses offered by the Mathematics Department (Calculus I, Calculus II and Linear Algebra), remained traditional, at least in this first experiment. So, at present time, all second year courses of our department are in connection with other disciplines, while first year ones will be changed probably next year (this will be the second part of this experiment).

There are other important differences between first and second year courses. For example, in second year courses, real problems represent more than fifty percent of final examinations. Moreover, in several cases, these final examinations can be substituted by project-work, where students try to solve this kind of problems with help of computers or electronic calculators (and, of course, with orientation of teachers).

4. Results and conclusions.

In a previous paper, an expert group was consulted, and almost all the experts remarked the importance of teaching significative concepts and procedures in service courses ((Martínez Luaces, V. & Casella, S., 1996) and (Martínez Luaces, V., 1998)).

From a different point of view, Chemistry students showed an important preference for teachers who make the effort of presenting real-life problems, related with their own careers (Day Jr., R. & Underwood, A., 1980).

Finally, Cluster Analysis and other Multivariate Statistical methods showed a very similar situation (Gómez, A. & Martínez Luaces, V., to appear). More precisely, in our group of mathematical teachers (that is, twelve teachers of the Mathematics Department at the Chemistry Faculty in Montevideo), the Cluster Analysis of "Applications", separate a group of them as the better ones (this variable "Applications" consists of an $!^2$ vector with the average results of two questions: one of them related with real-life problems and the other one about the connection with other disciplines). This group of five teachers was integrated almost exclusively with teachers of second year courses (Numerical Calculus, Statistics and Differential Equations) and almost all of them participated in interdisciplinary work with teachers and researchers of other departments and laboratories. Moreover, two teachers of this group are researchers in Applied Mathematics.

From these comments and results, it is obvious that real applications produce positive reactions in Chemistry students, in concordance with experts´ opinion (Martínez Luaces, V., 1998).

In an important paper of ICMI (ICMI, 1986), this style of teaching, where Mathematics is applied to other disciplines, was considered as "the ideal situation" for mathematical service courses.

Other aspect, very important to be considered is assessment. The evaluative process must not be dissociated from the style of teaching. So, if we try to teach through problem-solving of real-life situations, in context with other subjects, assessment must be carried out in the same way. This purpose can be put into practice through project-work, where students (with orientation of an interdisciplinary team of teachers) try to solve real problems of their careers, in order to approve their mathematical courses.

It is important to remark that Analytical Chemistry is an excellent source for this kind of problems. In most cases, they remain almost unexplored in their mathematical richness. Also, this branch of Chemistry provides a good opportunity for interdisciplinary work in research and teaching.

Finally, as it was mentioned before, these problems represent an interesting challenge for applied mathematicians and Mathematical Education researchers.

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