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Towards a Mexican School of General Analytical Chemistry

Alberto Rojas-Hernández*, María Teresa Ramírez-Silva, Annia Galano

UAM-Iztapalapa. Departamento de Química. Av. Ferrocarril San Rafael Atlixco 186, Col. Leyes de Reforma 1era Sección, Iztapalapa, C.P. 09310, CDMX, México.

***Corresponding author:** Alberto Rojas-Hernández, email: suemi918@xanum.uam.mx

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Abstract. This year the 50th anniversary of the Metropolitan Autonomous University is celebrated. It is for this reason that the JMCS decided to publish a special issue with contributions from professors from the Department of Chemistry. We thank the Editorial Committee of the issue for the invitation to write an article about the academic work that has been done in the Analytical Chemistry Area of this Department. We hope that we have managed to give a good description of the achievements we have had since the Analytical Chemistry Area was founded in the Iztapalapa Unit of the Metropolitan Autonomous University.
Keywords: General Analytical Chemistry teaching; Generalized Species and Equilibria Method (GSEM); chemical equilibrium.

Resumen. En este año se celebra el 50 aniversario de la Universidad Autónoma Metropolitana. Es con ese motivo que el JMCS decidió publicar un número especial con contribuciones de profesores del Departamento de Química. Agradecemos al Comité Editorial del número la invitación para hacer una contribución acerca del trabajo académico que se ha hecho en el Área de Química Analítica. Esperamos que hayamos logrado dar una buena descripción de los logros que hemos tenido desde que se fundó el Área de Química Analítica en la Unidad Iztapalapa de la Universidad Autónoma Metropolitana.
Palabras clave: Enseñanza de Química Analítica General; Método de Especies y Equilibrios Generalizados (MEEG); equilibrio químico.

Introduction

In mid-2000, the creation of the most recent Academic Area of the Department of Chemistry at the Metropolitan Autonomous University, Iztapalapa Unit (UAM-Iztapalapa), was authorized: the Analytical Chemistry Area.

This concluded a work of some 22 years that María Teresa Ramírez-Silva (Tere) and I had undertaken, beginning at the Faculty of Higher Studies-Cuautitlán of the National Autonomous University of Mexico (FESC-UNAM, by its acronym in Spanish), and which continued at the UAM-Iztapalapa to since 1985, within the Electrochemistry Area.

But at the same time, when the Area of Analytical Chemistry was founded at the UAM-Iztapalapa, the path towards the establishment of a Mexican School of General Analytical Chemistry began.

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Our training within the Charlot's School of General Analytical Chemistry

Gaston Charlot conceived the teaching of General Analytical Chemistry, which aims to describe chemical reactions and other physicochemical processes in an analytical manner and then apply this knowledge in a systematic and controlled way. This allows not only to develop methods of chemical analysis, but also to transcend the explanation and development of other physicochemical procedures that occur in chemical synthesis and industrial chemistry (among other parts of chemistry), which are applied in solving problems in many sectors of society. [1]

As students at FESC-UNAM we learned this approach of General Analytical Chemistry thanks to Margarita Rosa Gómez-Moliné (Rosamar), Helmut Pitsch and Michel Cassir. [2,3]. But there we were also trained as teachers, and we were given the freedom to make innovations in the teaching of analytical chemistry [4].

When Tere and I were hired at the UAM-Iztapalapa (between 1985 and 1987) we were in charge of teaching Analytical Chemistry in the Undergraduate and Graduate Studies in Chemistry.

Approach to Analytical Chemistry at the UAM-Iztapalapa

This is how we were able to translate our approach to teaching the discipline in the study programs of the Analytical Chemistry subjects of the Bachelor's Degree. This approach is made up of four items: Chemical Analysis, Physicochemical Processes Analysis, Instrumental Analysis and Chemometric Analysis.

Of these four areas, the one that really characterizes Charlot's method is the Physicochemical Processes Analysis, since this is what makes this Analytical Chemistry transcend from typical problems of chemical analysis to other problems of application in the chemistry of materials or industrial chemistry. [5]

Today, teaching Analytical Chemistry in our undergraduate courses begins with the main tools of Charlot's method (such as reaction prediction scales, predominance-zone diagrams, parameters of force and stability of species, tables of variation of substance quantities, chemical separations for chemical analysis, among others) in Brønsted's acid-base chemistry. With this, it is possible to have a robust model to predict and interpret what happens in acid-base titrations and in the preparation and application of pH buffer solutions.

Charlot's tools developed for the study of Brønsted acid-base systems are so useful that they can be applied to other types of reactions, such as those that occur in the formation of coordination compounds and redox processes. However, in Charlot's approach this is done when it is assumed that the processes in these systems are two-components (or occur through the exchange of one particle) [6], which is actually a simplification. –somewhat crude– of the real behavior of these systems.

In the case of our teaching, after studying the topics from Brønsted acid-base to pH buffer systems and acid-base titrations, we proceed to learn the systems where coordination compounds and redox species are formed through the Generalized Species and Generalized Equilibria Method; or simpler: Generalized Species and Equilibria Method (GSEM) [7].

GSEM not only allows the study of the systems described above, but also many others, including separation processes such as selective precipitation, liquid-liquid extraction and ion exchange. This is why this topic is included in the mandatory Analytical Chemistry courses at the UAM-Iztapalapa

Finally, Analytical Chemistry curriculum in the Bachelor's Degree also considers aspects of Instrumental Analysis and Chemometrics in different courses.

In the following sections of the article, the different areas where it is thought that the greatest contributions have been made to teaching (with this approach) or to the knowledge of Analytical Chemistry will be considered.

Contributions to Analytical Electrochemistry and Supramolecular Chemistry

Perhaps the main contribution to electrochemical field has been the proposal to using carbon paste electrodes in multiple studies, modifying the electrode surface with substances such as conductive polymers, surfactants or cyclodextrins. [8-14]

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Fig. 1. shows an example of this kind of research in neurotransmission field.

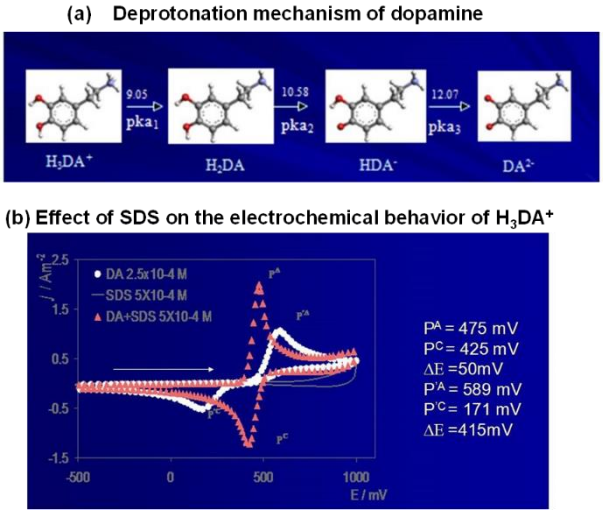

Fig 1. In 2009 Tere, with students and other professors of UAM-Azcapotzalco, received the research award of CBI Division of UAM, by the paper cited as [10], related with the effect of sodium dodecilsulfate (SDS) in the electrochemical behavior of dopamine over a carbon paste electrode.

Tere also proposed using composite graphite-epoxy electrodes to construct Flow Injection Electroanalytical systems. [15-17]

The Analytical Chemistry Area was one of the first groups in Mexico to use conductive polymers to develop highly selective ion sensors, by the collaboration of Tere with Dr. Salvador Allegret, form Barcelona. And with the aid of Dr. Manuel Palomar-Pardavé (from Materials Area of UAM-Azcapotzalco) it was possible to use theoretical current transients models (used at that time mainly to study the electrodeposition of metals) to fit the experimental data and obtain important information about the electropolymerization process, the diffusion of the ion through the polymer, and its correlation with the analytical performance. [18]

Taking about the contributions in the field of cyclodextrins and their polymers, and neurotransmitters, it is important to mention that in the comprehensive characterization of these systems, Charlot's approach was used, and all of these led to the development of important quantitative methodologies for trace determination of lead, mercury, and cadmium. [19-21]

Contributions to Brønsted's acid-base teaching and research

From an educational point of view, possibly the greatest contribution has been the development of a robust calculation algorithm to predict and interpret titration curves, as well as their first derivative, which has also led to interesting interpretations of the concept of buffer capacity. [22-25]

Nevertheless, teaching Brønsted acid-base systems with this approach requires knowledge of the acidity constants, and this led to establishing a line of research to determine these parameters. Thus, in 1990 the SQUAD program [26] was captured and compiled, as part of a master's thesis [27]. SQUAD determines acidity constants by fitting absorption spectra of systems of different chemical composition by non-linear least squares.

Acidity constants of organic substances (such as curcumin, mangiferin, and neurotransmitters, among others) have been determined, in aqueous solution and in other solvents; confirming previously reported values, but also providing unreported values in some cases (see Fig. 2). [28-33]

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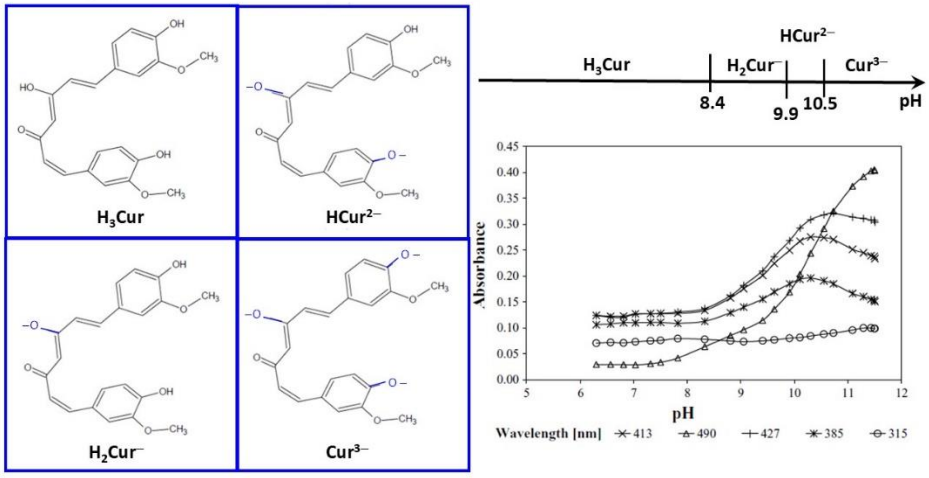

Fig. 2. This spectrophotometric study of curcumin is consistent with three pKa values, and not with two as reported until 2004. Reference [29] is one of our most cited papers. (Adapted from [29].)

As it can be seen in these works, various experimental methods (such as NMR, capillary electrophoresis, potentiometry, conductimetry, voltammetry) are frequently used to confirm the values obtained experimentally. [34,35]

Since it is sometimes not possible to do experiments to confirm the information obtained by spectrophotometry or potentiometry, in 2008 Annia Galano joined the group, with the aim of complementing the experimental studies with the help of computational chemistry and providing some relevant information, generally structural, but also kinetic (see Fig. 3). [36-42]

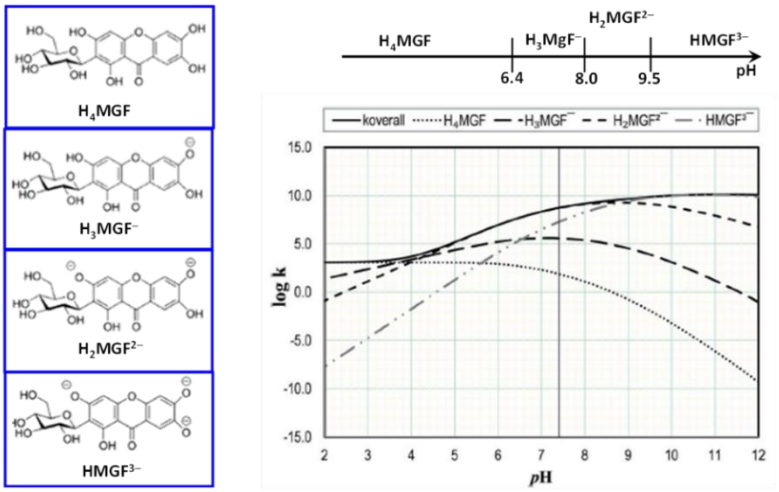

Fig. 3. Manfigerin (H_4MGF) has antioxidant activity. In reference [40] the overall rate constant was calculated by computational chemistry calculations, and pKa values were confirmed by NMR studies. The species contributing the more to this rate constant is H_2MGF^{2-} if $3.5 \leq pH \leq 9.0$, even though not always is the predominant species. This demonstrates that H_2MGF^{2-} is more labile to hydrogen abstraction than H_3MGF^{-} and H_4MGF. (Adapted from [40].)

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We were pioneers in carrying out this type of multidisciplinary theoretical-experimental studies in the same Analytical Chemistry group.

Contributions to the determination of equilibrium constants of coordination and inclusion compounds

Despite using SQUAD to refine acidity constants has been our most frequent work, formation constants of coordination and inclusion compounds have also been determined in systems with pharmacological properties and material precursors, mainly. [43-51]

Contributions to systematize Charlot's method for teaching General Analytical Chemistry

There are several innovations that we have made to Charlot's approach during these forty-five years, which we have not collected in books nor articles. But some contributions are worth mentioning regarding the use of the reaction prediction scale and to the construction of the predominance zone diagrams, giving maximum importance to the role played by the dismutation equilibria of the ampholytes in their construction (from the reaction prediction scale). [52,53]

We have also studied the validity of the approximations of representative equilibria, insisting on the advantages of Charlot's method when using only the equilibrium with the greatest physical significance in the system, and not the complete set of independent equilibria. Generally, this description can give an approximate answer, within the error margin considered acceptable [54].

It was also possible to demonstrate that Charlot's method is applicable to the study of systems in which polynuclear species are formed and, then the so-called thermodynamic mechanism of polymerization was established [55].

Finally we must highlight a work where it is demonstrated that species distribution diagrams summarize the distributions of the species of a system, as discrete variable distributions. There the variables are the stoichiometric coefficients of the components in the species, and the interpretation of an intrinsic buffer capacity is given as the variance of those distributions [56].

We think that this work may be the precursor of a statistical thermodynamics of substance quantity for particle polydonor systems and with polynuclear species.

The generalized species and equilibria method

The scheme shown in Fig. 4 describes the contributions of Brønsted's acid-base theory and Arrhenius's theory of electrolytic dissociation to the emergence of the donor/receptor/particle model proposed by Charlot in the 1940s in France.

Although in essence Charlot's method follows Brønsted's acid-base theory (when the exchanged particle is the proton), it generalizes it to the exchange of other particles [6]. This generalization can be done very well for two-components systems, but when there are more components and the simultaneous exchange of two or more particles appears, Charlot's generalization is not so good. In those cases, then, the same French professors introduce the definition of conditional constants and complexation coefficients made by Professor Anders Ringbom [57,58].

We have made some contributions to the donor/receptor/particle model to improve the understanding of Mexican students, as noted in the previous section. One of them consists of a more direct formalization within the Chemical Thermodynamics framework, closely following the approach of Professors Smith and Missen [59], especially for the definition of components and the set of independent equilibria in a system.

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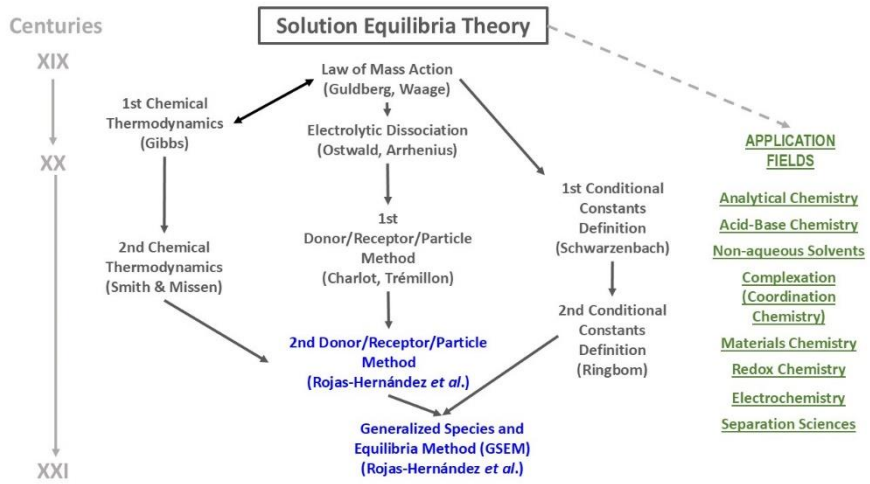

Fig. 4. Brief timeline and conceptual relationship of several methods used in Solution Chemical Equilibria Theory. This theory is applied in different Chemistry branches and is very useful in many cases.

But something that we also sought during some time was to generalize the Charlot's method to systems where there are more than two components under buffer conditions.

Charlot's method for two-components systems (M-L), which are polydonors of the L particle: $(ML_n/ML_{(n-1)}/\ldots/ML_j/\ldots/ML/M/L)$, has a complete set of n independent equilibria (containing all the chemical information of the system), which are selected from the collection of formation equilibria

$$ML_i + (j-i)L \rightleftarrows ML_j \quad with \quad K_{ML_j}^{(j-i)L} = \frac{[ML_j]}{[ML_i][L]^{(j-i)}} \;\; , \;\; i < j$$

and the set of dismutation equilibria

$$(k-i)ML_j \rightleftarrows (j-i)ML_k + (k-j)ML_i \;\; with \;\; K_{(j-i)ML_k}^{(k-i)ML_j} = \frac{[ML_k]^{(j-i)}[ML_i]^{(k-j)}}{[ML_j]^{(k-i)}} \;, i < j < k$$

From a set of n independent equilibria, Charlot's method selects the equilibrium with the greatest physical significance (given the initial conditions of the system) or representative equilibrium, as if it were the only one present in that system.

Thus, for three-components systems (M-L-X), where X is the buffered component (pX = constant), the generalization of the method leads to the proposal of a generalized species scheme that follows a model of polydonors of the L´ generalized particle: $(ML_n´/ML_{(n-1)}´/\ldots/ML_j´/\ldots/ML´/M´/L´)$, in agreement with de definitions of generalized species

$$L´ \equiv L + LX + \ldots + LX_i + \ldots + LX_o$$

$$M´ \equiv M + MX + \ldots + MX_i + \ldots + MX_p$$

…

$$ML_j´ \equiv ML_j + ML_jX + \ldots + ML_jX_i + \ldots + ML_jX_q$$

…

$$ML_n´ \equiv ML_n + ML_nX + \ldots + ML_nX_i + \ldots + ML_nX_r$$

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with molarities

$$[L´] = [L] + [LX] + \ldots + [LX_i] + \ldots + [LX_o] = [L]\alpha_{L(X)}$$

$$[M´] = [M] + [MX] + \ldots + [MX_i] + \ldots + [MX_p] = [M]\alpha_{M(X)}$$

$$\ldots$$

$$[ML_j´] = [ML_j] + [ML_jX] + \ldots + [ML_jX_i] + \ldots + [ML_jX_q] = [ML_j]\alpha_{ML_j(X)}$$

$$\ldots$$

$$[ML_n´] = [ML_n] + [ML_nX] + \ldots + [ML_nX_i] + \ldots + [ML_nX_r] = [ML_n]\alpha_{ML_n(X)}$$

where $\alpha_{L(X)},\ \alpha_{M(X)}, \alpha_{L(X)}, \ldots, \alpha_{ML_j(X)}, \ldots, \alpha_{ML_n(X)}$ are the complexation coefficients of L, M,…, ML_j, …, ML_n ,which depend of the molarity of the buffered component, [X], through polynomials (with exponents that are natural or integer numbers and coefficients that are global formation constants of the species involved in each case).

With these generalized species definitions, generalized formation equilibria can be defined

$$ML_i´ + (j-i)L´ \rightleftarrows ML_j´ \quad with \quad K_{ML_j´}^{(j-i)L´} = \frac{[ML_j´]}{[ML_i´][L´]^{(j-i)}} = K_{ML_j}^{(j-i)L} \frac{\alpha_{ML_j(X)}}{\alpha_{ML_i(X)}[\alpha_{L(X)}]^{(j-i)}}$$

as well as the generalized dismutation equilibria

$$(k-i)ML_j´ \rightleftarrows (j-i)ML_k´ + (k-j)ML_i´ \quad with \quad K_{(j-i)ML_k´}^{(k-i)ML_j´} = \frac{[ML_k´]^{(j-i)}[ML_i´]^{(k-j)}}{[ML_j´]^{(k-i)}} = K_{(j-i)ML_k}^{(k-i)ML_j} \frac{[\alpha_{ML_k(X)}]^{(j-i)}[\alpha_{ML_i(X)}]^{(k-j)}}{[\alpha_{ML_j(X)}]^{(k-i)}}$$

$K_{ML_j´}^{(j-i)L´}$ representing the conditional formation constant of the generalized species $ML_j´$ from the generalized species $ML_i´$, while $K_{(j-i)ML_k´}^{(k-i)ML_j´}$ represents the conditional dismutation constant of the generalized species ML_j' that gives rise to the generalized species ML_k' and ML_i'. Substituting subscripts i, j, k properly, all generalized equilibria of each type in the system are obtained.

From these two sets of generalized equilibria, n independent generalized equilibria are selected.

It can be shown that if the value of pX is imposed on the system, the complexation coefficients and the conditional constants are constant [60], so under these conditions everything that was done with simple chemical equilibria in the system, with Charlot´s Method, can be done with generalized equilibria, namely: diagrams of predominance zones, reaction prediction scales, tables of variation of substance quantities, reaction schemes for complexation or redox titrations, separation conditions of different chemical species, etc.

GSEM is different from the Ringbom´s method, because in the latter only one equilibrium of "primed species" is handled, which in the case of particle polydonor systems will have a conditional constant that does not depend only on the buffered pX.

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GSEM is generalizable to systems of four or more components with double or multiple buffering, since the multiconditional constants, of the second-order or higher-order generalized equilibria, only depend on the conditions imposed for the buffered components. [60]

Finally, GSEM can be handled approximately with representative equilibria, constructed with the predominant species for each generalized species. This can make it very intuitive. [61-63]. Fig. 5. shows the different approaches to the description of complexation titration of Cu(II) with EDTA at imposed pH = 5.0 with a buffer of acetic acid/acetate 0.25 M.

Although GSEM has been documented by us in a doctoral thesis [60] and different articles [64-72], where its potential is shown to make graphical representations in multi-component and multi-reacting systems (considering the formation of coordination compounds, polynuclear species, redox equilibria, condensed phases, liquid-liquid extraction or ionic exchange), its full potential has not been shown in books and articles, generalizing Charlot's method in calculations, which could make it more popular. We teach Analytical Chemistry using GSEM from 1985 to this date.

It is necessary to mention the contributions provided by Dr. Ignacio González (who agreed to direct my doctoral thesis [60]) and Dr. Jorge Ibáñez to the GSEM, established in some publications [64-70].

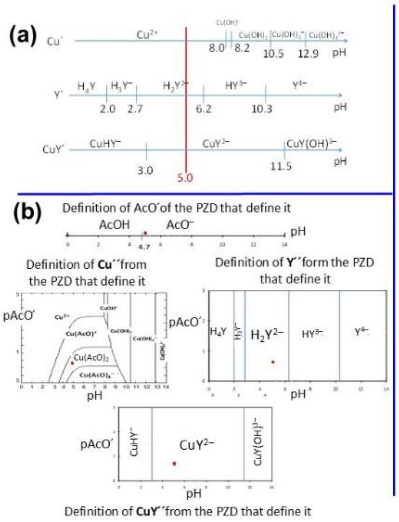

Fig. 5. Several models that could be considered to explain the complexation reaction of Cu(II) wth EDTA. **(a)** Approximated definitions of generalized species Cu´, Y´ and CuY´ at buffered pH = 5.0, without considering the effect of acetates buffer. **(b)** Approximated definitions of generalized species AcO´, Cu´´, Y´´ and CuY´´ at buffered pH = 5.0 and imposed pAcO´ = 0.6 ([AcO´ = 0.25 M). **(c)** Approximated definitions of generalized equilibria used to explain the complexation reaction. The last approach is the best. Data have been taken from [57] and HYDRA database from MEDUSA software. [73]

Conclusions

A summary of the contributions that we have made to the development of General Analytical Chemistry has been presented, both from a teaching and research point of view.

The starting point was the approach of Professor Gaston Charlot's method to Analytical Chemistry, particularly his view that individuals trained in it are expected to be creative and approach the solution of problems in a reasoned manner, involving all knowledge and experimentation that may be available.

In our approach to the study of Analytical Chemistry problems, it is always important to consider the chemical species that may be present in the system. We think that this way of approaching knowledge should not be lost, but should be enriched, along with the physicochemical processes analysis that can be present in chemical analysis, industrial chemistry, materials chemistry, etc.

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Other groups in Mexico are making other developments, but it is necessary that we communicate and join forces so that a consolidation of a Mexican School of General Analytical Chemistry can be achieved.

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