Journal of Science with Technological Applications

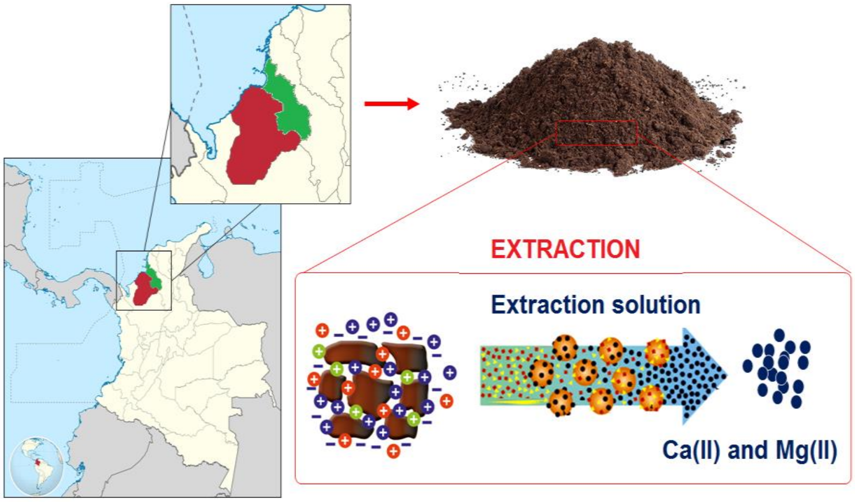
Research Article

Enrique Combatt[1*], **Jaime Mercado**[2], **Andrea Begambre**[2], **Liz Kerguelen**[2], **Katerine Borja**[3]

[1] *Department of Agricultural Engineering and Rural Development, Faculty of Agricultural Sciences, Universidad de Córdoba, Monteria - Colombia*
[2] *Research Assitant. Department of Chemistry. Universidad de Córdoba, Monteria - Colombia*
[3] *Professional in chemistry, Colombia.*

Corresponding author: ecombatt@correo.unicordoba.edu.co

Graphical abstract



Chloride solutions in the extraction of calcium and magnesium from soils with alkaline characteristics

Abstract

During soil analysis, one main problem is the selection of the method for determination of ions in the extracts. These methods must be fast, highly accurate and economical. Therefore, the objective of this work was to compare the efficiency of four calcium and magnesium extraction solutions based on chloride salts using ammonium acetate method ($AcONH_4$) as reference method. In order to do this, five cation extraction methodologies based on CH_3COONH_4, NH_4Cl, NaCl, KCl and LiCl (1N at pH 7.0) were evaluated using 14 soils from the departments of Córdoba and Sucre (Colombia) and characterized by a high content of carbonate. The results obtained were analyzed by statistical analysis using

Keywords
Chloride solution
Extraction solution
Exchange bases
Chemical extraction
Carbonate-rich soil

the software SAS; thus, tests of means, correlations, and the Test of Leite and Oliveira were performed for each fraction. According to the results obtained, the methods that extract a higher Ca and Mg contents were $AcONH_4$ (52.4 $cmol^+ kg^{-1}$) and NH_4Cl (7.2 $cmol^+ kg^{-1}$), respectively.

Soluciones de cloro en la extracción de calcio y magnesio en suelos con caractéristicas alcalinas

Resumen

Durante el análisis de suelos, un problema principal es la selección del método para la determinación de iones en los extractos. Estos métodos deben ser rápidos, altamente precisos y economicos. Por lo tanto, el objetivo de este trabajo fue comparar la eficiencia de cuatro soluciones extractoras de calcio y magnesio basadas en sales de cloro usando como referencia el método de acetato de amonio ($AcONH_4$). Con el fin de llevar a cabo lo anterior, cinco metodolgías de extracción de cationes basadas en CH_3COONH_4, NH_4Cl, NaCl, KCl y LiCl (1N a pH 7.0) se evaluaron usando 14 suelos de los departamentos de Córdoba y Sucre (Colombia) y caracterizados por presentar un alto contenido de cabonatos. Los resultados obtenidos se analizaron mediante análisis estadistico usando el sofware SAS; de este modo, pruebas de medias, correlaciones y el Test de Leite y Olivieira se realizaron a cada fracción. Según los resultados obtenidos, los métodos que extraen mayores contenidos de Ca y Mg fueron $AcONH_4$ (52.4 $cmol^+ kg^{-1}$) and NH_4Cl (7.2 $cmol^+ kg^{-1}$), respectivamente.

Palabras claves
Soluciones de cloruro
Solución de extracción
Bases intercambiables
Extracción química
Suelos ricos en Carbonatos

Recived: 05-03-2017
Accepted: 20-04-2017
Publishing date: 15 – May – 2017
Revision Code: 20170305-AAAA [Pag. 4-12]

Corresponding author:
ecombatt@correo.unicordoba.edu.co

Journal of Science with Technological Applications

Research Article

Chloride solutions in the extraction of calcium and magnesium from soils with alkaline characteristics

Enrique Combatt[1*], **Jaime Mercado**[2], **Andrea Begambre**[2], **Liz Kerguelen**[2], **Katerine Borja**[3]

[1] *Department of Agricultural Engineering and Rural Development, Faculty of Agricultural Sciences, Universidad de Córdoba, Monteria - Colombia*
[2] *Research Assitant. Department of Chemistry. Universidad de Córdoba, Monteria - Colombia*
[3] *Professional in chemistry, Colombia.*

Corresponding author: ecombatt@correo.unicordoba.edu.co

Abstract

During soil analysis, one main problem is the selection of the method for determination of ions in the extracts. These methods must be fast, highly accurate and economical. Therefore, the objective of this work was to compare the efficiency of four calcium and magnesium extraction solutions based on chloride salts using ammonium acetate method ($AcONH_4$) as reference method. In order to do this, five cation extraction methodologies based on CH_3COONH_4, NH_4Cl, NaCl, KCl and LiCl (1N at pH 7.0) were evaluated using 14 soils from the departments of Córdoba and Sucre (Colombia) and characterized by a high content of carbonate. The results obtained were analyzed by statistical analysis using the software SAS; thus, tests of means, correlations and the Test of Leite and Oliveira were performed for each fraction. According to the results obtained, the methods that extract a higher Ca and Mg contents were $AcONH_4$ (52.4 $cmol^+ \, kg^{-1}$) and NH_4Cl (7.2 $cmol^+ \, kg^{-1}$), respectively.

Keywords
Chloride solution
Extraction solution
Exchange bases
Chemical extraction
Carbonate-rich soil

1. Introduction

The development of most crops can be associated with the excess or deficiency of elements such as Ca and Mg, so when deficiencies exist of this, the crops respond to doses of fertilizers containing these cations. The relationship between these elements in plant nutrition is based on the diverse chemical properties, such as ionic radius, degree of hydration and mobility, causing competition for soil adsorption sites and root absorption (Medeiros *et al*., 2008). Therefore, the correct quantification of Ca and Mg in the soil is of great importance to establish the correct fertilization practice, and thus, to avoid the nutritional imbalance of the crops.

The quantification of the exchange cations as Ca, Mg, K and Na in soil samples is a routine procedure in all soil analysis laboratories. To carry out this determination is generally used the ammonium acetate method ($AcONH_4$, 1N pH 7.0) to extract the cations, which are generally quantified using the atomic absorption spectroscopy (AAS) technique. However, in soils with high contents of calcium and magnesium bound to carbonates, the overestimation may occur during the quantification of these elements, being this overestimation mainly associated with the extraction stage. Researchers have concluded that the amounts of potassium may also change due to the dissolution of the carbonate species and the ability of the ammonium ion to extract the fixed potassium (Ciesielski and Sterckeman, 1997). Therefore, there is no general acceptance of this method because it generates unreliable results, as a result of the pH change which leads to the alteration of the results.

According to Rodrigues *et al*., (2011) and Gillman and Bell (1976) in the determation of soils cationic exchange capacity (CEC), the results obtained depend on the method used, because in soils with variable load, any change of pH or the ionic concentration of electrolytes has a direct effect on the CEC.

From these divergences, in terms of the efficiency of $AcONH_4$, the need arises to find a methodology that allows a quantification of the real content of the ions present in the soil with high carbonate contents. According to Adams (1995), ideally the method to be used to determine the CEC is one that can extract from the soils the exchange cations in an aqueous solution with the same pH, ionic strength and dielectric constant as that present the soils under field conditions because the CEC changes with these parameters.

In order to contribute to this quandary over the extraction methodologies used, a series of investigations have been carried out to determine which extraction method generates fast, reliable and reproducible results. Among these investigations, Jetro *et al*., (2013) evaluated the extraction capacity of cations in soils, comparing the $CaCl_2$ method with the ammonium acetate ethylenediamine-tetracetic acid method; they found that the former extracts twice the cation content. Bortolon *et al*., (2011) evaluated KCl 1N, Mehlich-1 and Mehlich-3 for the simultaneous extraction of Ca and Mg from soils, concluding that Mehlich-1 and KCl 1N are the most efficient methodologies. Henríquez *et al*., (2005) compared the extraction methods $AcONH_4$, CH_3COONa y NH_4Cl (1N at pH 7); they found that there is no statistically significant difference between the NH_4Cl y $AcONH_4$ methods.

Currently, the use of $AcONH_4$ 1N at pH 7 is being questioned worldwide due to the limitations presented by this methodology. However, in Colombia the majority of soil laboratories, indistinctly in soil samples, in there analyzes extract the exchange bases, without to take into account the contents of carbonates generating unreliable results. To solve the problem resulting of carbonate contents in the soil samples, Mehlich (1942) proposed to use an aqueous solution of $BaCl_2$-trietanolamina (TEA) buffered to pH 8.2 in order to saturate the exchange complexes in calcareous soils, exploring the Ba^{2+} capacity to be absorbed by $CaCO_3$ and thus minimizing its subsequent dissolution during the exchange step, because the neutral salts do not alter the conditions that can present in these soil. Gillman (1979) and Shuman and Duncan (1990) further propose other methodologies, where the exchange reaction is carried out by means of unbuffered salts, such as ammonium chloride and barium chloride.

According to the above, in order to find a methodology that allows a reliable quantification of Ca and Mg in carbonate-rich soils, the objective of this work was to evaluate the extraction capacity of four solutions based on chlorides, and to compare the results with the standard method used at national level (*i.e.*, $AcONH_4$).

2. Experimental section

This research was carried out in the Laboratory of Soils and Waters of the Faculty of Agricultural Sciences of the Universidad de Córdoba, Colombia. For this study, 14 soil samples were collected in several municipalities from departments of Córdoba and Sucre, all samples were selected to have high carbonate contents. Samples were analyzed and characterized according to the protocols established by IGAC (2006).

For the quantification of Ca and Mg, 5.0 g of each sample were dried, sieved by a 2 mm sieve and deposited in a glass vessel to which 25 mL of extraction solution were added.

2.1. Extraction of cations

Extraction of the cations from the samples was performed using four solutions: $AcONH_4$, NH_4Cl, NaCl, KCl and LiCl at a concentration of 1.0 N and at pH 7. The samples were then stirred for 30 minutes at 170 rpm and filtered. Subsequently, Ca and Mg contents were quantified in triplicate, using AAS. Results were analyzed using statistical software SAS, performing for each of the fractions tests of means, correlations and a statistical analysis applying the Test de Leite and Oliveira (2002).

Table 1. Chemical characterization of soil samples collected from the departments of Córdoba and Sucre, Colombia.

Soils	pH	MO	S	P	K	Na	Cu	Fe	Zn	Mn	B
	1:1	%	--- mgkg^{-1} ---		---cmol^{+} kg^{-1}---		------------ mg kg^{-1} ------------				
1	7.14	0.67	30.1	125.6	0.67	0.48	0.5	5.7	2.8	29.2	0.33
2	7.26	0.5	17.8	95.2	0.54	0.29	0.6	7.2	2.2	24.4	0.28
3	7.27	3.08	6.1	41.0	0.88	0.13	0.6	1.2	0.3	2.8	0.20
4	7.40	1.69	16.1	11.9	0.44	0.23	0.10	0.90	0.40	1.20	0.20
5	7.47	1.20	18.5	90.2	0.28	0.43	0.4	1.2	0.4	35.2	0.52
6	7.53	3.41	9.3	29.2	1.09	0.18	0.4	1.6	0.2	0.6	0.18
7	7.60	2.15	17.6	19.7	1.15	0.2	0.3	0.4	0.3	6.4	0.15
8	7.76	0.51	20.1	65.2	0.83	0.30	0.4	0.4	0.4	1.2	0.25
9	7.81	2.23	7.0	16.6	0.29	0.13	0.2	1.5	0.1	8.0	0.08
10	7.81	2.2	26.9	9.0	0.32	0.11	0.4	0.4	2	2.8	0.05
11	7.95	1.20	20.7	40.4	0.32	0.11	0.4	9.2	0.4	0.8	0.27
12	8.08	1.03	7.0	87.1	0.49	0.33	0.2	0.7	0.3	18.8	0.08
13	8.11	0.17	8.4	44.4	0.14	0.15	0.2	0.6	0.1	12.4	0.06
14	8.21	0.34	7.0	55.9	0.20	0.28	0.4	10.4	0.4	14.8	0.16
Minimun	7.14	0.17	6.10	9.00	0.14	0.11	0.10	0.40	0.08	0.60	0.05
Maximun	8.21	3.41	30.1	125.6	1.15	0.48	0.60	10.4	2.80	35.2	0.52
Average	7.67	1.46	15.2	52.25	0.55	0.24	0.34	3.09	0.77	12.0	0.20
Std. dev.	0.34	1.03	7.85	35.89	0.33	0.12	0.14	3.66	0.92	11.8	0.13

Std. dev: Standard deviation

3. Results and discussion

The characterization data showed that the average pH values of the analyzed samples was 7.67, and therefore, these soils can be classified as slightly alkaline. In addition, soils showed low contents of organic matter (MO) and sulfur, in contrast with high contents of phosphorus and potassium. Sodium did not cause problems because of its content in the samples is low, besides, the minor elements were seen to be deficient (Cu, Fe, Zn, Mn and B).

3.1. Contents of calcium and magnesium by different methods of extraction

As can be seen in Table 2, the methods that allowed a higher extraction of Ca were the $AcONH_4$, with mean values of 52.4 cmol^{+}kg^{-1}, followed by KCl with 44.9 cmol^{+} kg^{-1}. In addition, the methods with the lower extraction capacity were NH_4Cl, LiCl and NaCl with 21, 23.3 and 25 cmol^{+}kg^{-1}, respectively. The extraction efficiency of $AcONH_4$ can be explained as a result of the fact that acetic acid and ammonium produced by dissociation can dissolve calcium-containing compounds in their structure, overestimating the amount of calcium that is adsorbed in inorganic and organic colloidal micelles. Dohrmann (2006) indicates that, in the determination of CEC and exchange bases from samples of calcareous and gypsiferous soils, problems related to the partial dissolution of calcite and gypsum can be identified and associated with the interaction of soil particles with the electrolyte rich exchange solution. Therefore, there is an overestimation of exchange calcium and magnesium, as well as, of CEC. According to Okazaki (1963), there are numerous discrepancies in the determination of exchangeable cations in soils which can be attributed to several factors such as salt retention, hydrolysis of the exchange cation and

Table 2. Calcium and magnesium contents extracted with different extraction solutions.

pH	Ca (cmol$^+$kg $^{-1}$)					Mg (cmol$^+$kg $^{-1}$)				
	NH_4OAc	NH_4Cl	KCl	NaCl	LiCl	NH_4OAc	NH_4Cl	KCl	NaCl	LiCl
7.14	49.2	5.0	23.3	20.3	5.2	2.1	2.1	1.0	1.6	1.6
7.26	55.2	3.0	18.3	18.1	4.3	2.1	2.8	0.7	1.4	1.2
7.27	48.9	21.0	41.6	23.3	21.7	7.6	16.7	1.9	3.9	1.9
7.40	53.4	24.0	58.3	28.3	28.3	10.2	10.0	3.2	5.5	2.2
7.47	47.3	24.0	58.2	28.3	28.3	15.3	16.7	5.3	13.9	8.3
7.53	47.3	22.0	43.3	26.6	16.7	7.6	13.3	1.9	4.4	1.9
7.60	41.1	16.0	41.6	15.0	21.6	7.6	10.0	2.4	4.7	1.9
7.76	57.5	22.0	43.3	25.0	18.3	2.1	2.1	0.8	1.3	1.1
7.81	63.5	23.0	53.3	28.3	25.0	2.1	2.1	1.1	1.8	1.6
7.81	56.5	27.0	48.3	31.6	21.7	7.6	2.1	3.2	5.3	2.6
7.95	53.4	25.0	58.3	28.3	26.6	2.1	1.0	0.4	3.3	0.9
8.08	55.9	22.0	43.3	23.3	23.3	7.6	10.0	3.1	5.0	2.8
8.11	56.5	23.0	46.6	33.3	28.3	2.1	2.1	0.8	1.5	1.2
8.21	47.3	21.0	56.6	25.0	23.3	7.6	10.0	3.7	6.9	3.1
Maximun	56.5	27.0	88.2	33.3	28.3	15.3	16.7	5.3	13.9	8.3
Minimun	9.2	3.0	18.3	15.0	4.3	2.1	1.0	0.4	1.3	0.9
Average	52.9	19.8	44.9	25.3	20.9	6.0	7.2	2.1	4.3	2.3
Std. dev.	16.2	7.2	19.9	5.1	7.7	4.0	5.8	1.4	3.3	1.8

Std. dev: Standard deviation

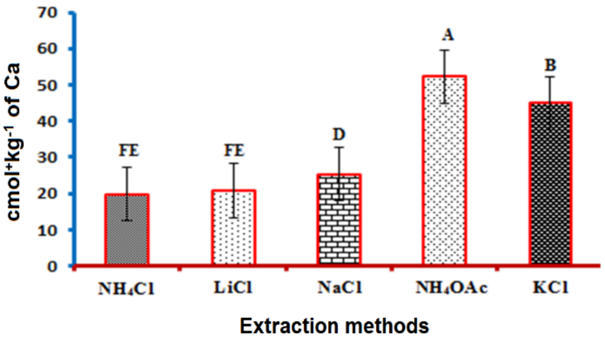


Figure 1. Test of means between extraction methods, for the evaluation of the contents of exchangeable Ca

ion adsorption in the form of insoluble compounds. On the other hand, in this research the extraction solutions NH_4Cl, NaCl and LiCl presented very similar results in relation to the extracted content of calcium, which showed that these three salts generate a very similar extraction capacity.

Rodriguez *et al*., (2011) indicated that $AcONH_4$ 1N at pH 7 is more influenced by soil pH and the presence of carbonates than the 0.2 N ammonium chloride method.

In the case of Mg, the difference between extraction capacities is lower, finding very similar results among the five methodologies. The highest extraction capacity was gotten with NH_4Cl, followed by $AcONH_4$, with values of 7.2 and 6.0 cmol$^+$kg^{-1}, respectively. Polemio and Rhodes (1977) indicated that the complications derived from the dissolution of $CaCO_3$ in the soil during the determination of bases of exchange and CEC are particularly problematic.

The efficiency of NH_4Cl is explained by the fact that the ammonium ion has a high exchange power, but Cl^- anion does not dissolve the carbonates in the soil and therefore does not overestimate the content of the exchange cations. Reeve and Sumner (1971) and Rodrigues *et al*., (2011) confirmed that NH_4Cl behaves as a neutral salt and does not modify the natural pH of the soil quantifying actual cation contents.

From the statistical analysis of data, it was found that there are no statistical differences between the methodology of NH_4Cl and LiCl, but between these and other methodologies significant differences were determined (Figure 1).

Table 3. Comparison of extraction methods for the determination of Ca and Mg contents, according to the rules of the Leite and Oliveira Test.

Y_j	Y_i	$R^{2(1)}$	$F(H_0)^2$	$t_{(e)}^3$	$R_{YjYi} \geq 1-\lvert e \rvert$	Decisión
			Ca			
NH_4OAc	NH_4Cl	0,94	$314{,}09^{*}$	$16{,}4^{*}$	Si	$Y_j \neq Y_i$
NH_4OAc	NaCl	0,52	$21{,}92^{*}$	$4{,}85^{*}$	Si	$Y_j \neq Y_i$
NH_4OAc	LiCl	0,75	$59{,}44^{*}$	$10{,}26^{*}$	Si	$Y_j \neq Y_i$
NH_4OAc	KCl	0,52	$6{,}14^{*}$	$1{,}91^{ns}$	No	$Y_j \neq Y_i$
			Mg			
NH_4OAc	NH_4Cl	0,69	$8{,}96^{*}$	$0{,}54^{ns}$	No	$Y_j \neq Y_i$
NH_4OAc	NaCl	0,85	$7{,}58^{*}$	$4{,}50^{*}$	Si	$Y_j \neq Y_i$
NH_4OAc	LiCl	0,69	$20{,}17^{*}$	$5{,}58^{ns}$	Si	$Y_j \neq Y_i$
NH_4OAc	KCl	0,88	$67{,}7^{*}$	$8{,}34^{*}$	Si	$Y_j \neq Y_i$

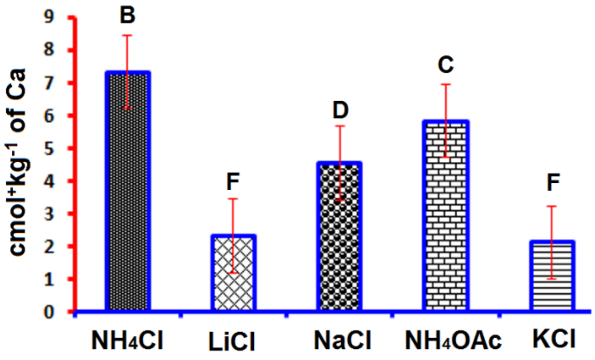


Figure 2. Test of means between extraction methods, for evaluation of the contents of exchangeable Mg

Table 4. Orthogonal contrasts between extraction methods

Methods	Ca	Mg
NH_4OAc versus NH_4Cl	25.1^{**}	-1.2^{**}
NH_4OAc versus NaCl	19.6^{**}	1.7^{**}
NH_4OAc versus LiCl	24.0^{**}	3.7^{**}
NH_4OAc versus KCl	-7.5^{**}	3.9^{**}

In addition, it is observed that the $AcONH_4$ and the KCl extract the greater amount of Ca, with respect to the other extractants. In this way, Henriquez *et al*., (2005) found that $AcONH_4$ overestimates the Ca quantification, due to the dissolution of carbonates; similarly, Cantarella *et al*., (2001) and Misopolinos and Kalovoulos (1984) pointed that the traditional method used to determine the CEC of the soil can inevitably introduce errors when it is applied to calcareous soils, since the salts of Ca and Mg in calcareous soil are easily dissolved interfering with the analysis.

With respect to the average test for the extraction of Mg, in the Figure 2 is shown that no statistical difference was found between KCl and LiCl, since there is similarity in the intrinsic characteristics of the cations. However, the methodology of higher extraction capacity was the NH_4Cl followed by the $AcONH_4$, presenting these methods significant statistical differences respect to other methodologies. Fotyma and Dobers (2008) from quantifying the Mg content in the same soil samples, by 11 laboratories on 10 countries of Central and Eastern Europe, established that the use of different methods produces different results.

By application of Leite and Oliveira test to analyze the results of the extracted Ca, by means of the test of identity of methods, it was determined that there is no equivalence between any of the methodologies evaluated; however, there is a high regression coefficient between the methodologies $AcONH_4$ and NH_4Cl with a value of 0.94, which denotes a highly significant relationship between the two methodologies for Ca extraction, by sharing the same exchange cation. According to Rhoades 1982 and Rodrígues *et al*., (2011) when the pH of the soils is greater than 6.73, there is a statistical relationship between these two extraction methodologies. The test of identity of methods for Mg contents did not determine equality between the methods, although high regression coefficients were found.

Finally, and looking for greater statistical rigor, we also used orthogonal contrasts to analyze the data obtained (Table 4). By means of this analysis it was evidenced that there are statistical differences between all Ca and Mg extraction methodologies.

However, it is widely discussed in previous research the reliability of the results found with these extraction methods.

4. Conclusions

From the methods studied, the highest Ca contents were quantified using $AcONH_4$ and KCl, which are two methodologies that generally overestimate the contents of this cation in the soil. In addition, it was determined that using the NH_4Cl method the highest Mg contents were extracted, surpassing the $AcONH_4$ method. Finally, the NH_4Cl method showed the best results for the simultaneous quantification of Ca and Mg, indicating the high effectiveness of the chloride ion and the index cation (*i.e.*, NH_4^+).

Acknowledgments

Authors thanks to Universidad de Córdoba and to the Program for Scientific Knowledge Diffusion of Mindtech s.a.s. (PSKD 2016-2020) for funds associated to the publication costs.

Conflict of interests

The authors declare no conflict of interest.

References

- Adams, M. (1995). Fundamentals of soil chemistry. Central University of Venezuela. Faculty og Agronomy. Maracay. 390 p.
- Bortolon, L., Gianello, C., Welter, S., Almeida, R., and Giasson, E. (2011). Simultaneous Extraction of Phosphorus, Potassium, Calcium and Magnesium from Soils and Potassium Recommendations for Crops in Southern Brazil. *Soil Science Society of China 21(3),* 365–372.
- Cantarella, H., Raij, B. V., Coscione, A. R., Y Andrade, J. C. (2001). Determinação de alumínio, cálcio e magnésio trocáveis em extrato de cloreto de potássio. Análise química para avaliação da fertilidade em solos tropicais. Campinas, Instituto Agronômico. 285p.
- Ciesielski, H., and Sterckeman, T. (1997). A comparison between three methods for the determination of cation exchange capacity and exchangeable cations in soils. *Agronomie 17,* 9–16.
- Dohrmann R. (2006). Cation exchange capacity metodology I: An efficient model for the detection of incorrect cation exchange capacity and exchangeable cation results. *Appl. Clay Sci. 34*, 31-37.
- Fotyma M., y Dobers E. S. (2008). Soil testing methods and fertilizer recommendations in Central-Eastern European countries. *Fertilizer and Fertilization, 30,* 6–93
- Gillman G., Bell L. (1976). Surface charge characteristics of six weathered soils from tropical north Queensland *Austr. J. Soil Res. 14*: 351-360.
- Gillman G, P. (1979). A proposed method for the measurement of exchange properties of highly weathered soils. *Aust J Soil Res 17*, 129-139.
- Henríquez, M,. Pérez, J., Gascó, J., and Rodríguez, O. (2005). Determination of the cation exchange capacity in sand and kaolin, with ammonium acetate, sodium acetate and ammonium chloride. *Bioagro 17*, 59-62.
- Instituto Geográfico Agustin Codazzi. (IGAC). 2006. Analytical methods of the soil laboratory. 6ta Ed. Bogotá, Colombia.
- Jetro N, N., George N, E., Ehabe, E., and Schnug, E. (2013). A Comparative study on the use of calcium acetate lactate, calcium chloride and acidic ammonium acetate- ethylene diaminetetra acetic acid (AAAc-EDTA) for the quantification of extractable, P, K and Mg from acidic soils. *International Research Journal of Pure & Applied Chemistry 3(1),* 22-31.
- Leite, H. G., and Oliveira, F. H. (2002). Statistical procedure to test identity between analytical methods. Commun. *Soil Sci. Plant Anal. 37 (7-8),* 1105-1118.
- Medeiros, J.C., Albuquerque, J. A., Mafra, A. L., Dalla, R. J., and Gatiboni, L. C. (2008). Relação cálcio:magnésio do corretivo da acidez do solo na nutrição e no desenvolvimento inicial de plantas de milho em um Cambissolo Húmico Álico. *Semina: Ciências Agrárias, Londrina, 29 (4),* 799-806.
- Mehlich, A. (1942). Rapid estimation of base-exchange properties of soils. *Soil Sci., 53*, 1-14.
- Misopolinos, N. D., and Kalovoulos, J. M. (1984). Determination of CEC and exchangeable Ca and Mg in non-saline calcareous soils. *J. Soil Sci., 35*, 93–98.
- Okazaki, R., Smith, H. W., and Moodie, C. D. (1963). Hydrolysis and salt-retention errors in conventional cation – exchange-capacity procedures. *Soil Sci. 96*, 205-209.
- Polemio, M., and Rhoades, J. D. (1977). Determining cation exchange capacity: A new procedure for calcareous and gypsiferous soils. *Soil Sci. Soc. Am. J., 41*, 524–527.
- Reeve, N., and Sumner, M. E. (1971). Cation exchange capacity and exchangeable aluminum in Natal Oxisols. *Soil Soc. Am. Proc. 35*, 38-42.
- Rhoades, J. (1982). Cation Exchange Capacity. Methods of Soil Analysis. Part 2. Agronomy Monographs Nº 9. Madison. American Society of Agronomy. 149- 157.
- Rodríguez, R. O., Sánchez, G. A., Mendoza, E. B., Rodríguez, G. Z., Henríquez, R. M., Rodríguez, P. V., and Guerra, D. E. (2011). Capacidad de extracción de cationes mediante acetato de amonio, acetato de sodio y cloruro de amonio. *Interciencia. 36: (3)*, 219-223.

● Shuman L, M., and Duncan R, R. (1990). Soil exchangeable cations and aluminium measured by ammonium chloride, potassium chloride and ammonium acetate. *Commun in Soil Sci Plant Anal 21*, 1217-1228