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Nota

COMPLEXOMETRIC TITRATION WITH POTENCIOMETRIC INDICATOR TO DETERMINATION OF CALCIUM AND MAGNESIUM IN SOIL EXTRACTS⁽¹⁾

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SUMMARY

This study proposes a method of direct and simultaneous determination of the amount of Ca^{2+} and Mg^{2+} present in soil extracts using a Calcium Ion-Selective Electrode and by Complexometric Titration (ISE-CT). The results were compared to those obtained by conventional analytical techniques of Complexometric Titration (CT) and Flame Atomic Absorption Spectrometry (FAAS). There were no significant differences in the determination of Ca^{2+} and Mg^{2+} in comparison with CT and FAAS, at a 95 % confidence level. Additionally, results of this method were more precise and accurate than of the Interlaboratorial Control (IC).

Index terms: ion selective electrode, automatic titrator, potentiometry

RESUMO: *TITULAÇÃO COMPLEXOMÉTRICA COM INDICADOR POTENCIOMÉTRICO PARA DETERMINAÇÃO DE CÁLCIO E MAGNÉSIO EM EXTRATOS DE SOLO*

Neste trabalho foi proposto um método para determinar de forma direta e simultânea a quantidade de Ca^{2+} e Mg^{2+} trocáveis presente em extratos de solos, empregando-se eletrodo íon seletivo de Ca e titulação complexométrica (EIS-TC). Os resultados dessas determinações

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foram comparados aos dados obtidos por meio de técnicas analíticas convencionais de Titulação Complexométrica (TC) e Espectrometria de Absorção Atômica com Chama (FAAS). Não houve diferenças significativas nas determinações dos íons Ca^{2+} e Mg^{2+} em relação aos métodos TC e FAAS, com 95 % de confiança. Adicionalmente, o método apresentou melhor precisão e exatidão quando seus resultados foram comparados aos do Controle Interlaboratorial (CI).

Termos de indexação: eletrodo íon seletivo, titulador automático, potenciometria.

INTRODUCTION

One of the main problems in laboratory soil analysis is the selection of the determination method of ions of interest in the extracts. Methods should be quick, highly accurate and cheap. Many studies have been conducted with this purpose for several types of analytes, and the constant improvement of equipment and analytical methods contribute to continuous revisions and reevaluations in this area.

Most laboratories determine the exchangeable calcium and magnesium by complexometric titration with EDTA in the presence of metallo-chromic indicators Calcon or Murexide for Ca^{2+} and Eriochrome Black T for total hardness ($\text{Ca}^{2+} + \text{Mg}^{2+}$), where Mg^{2+} is obtained by difference (Raij, 1966; Embrapa, 1997; Cantarella et al., 2001; Embrapa, 2005). Another common method is the determination by Flame Atomic Absorption Spectrometry with (FAAS) (Williams et al., 1966; Macphee & Ball, 1967; Boeira et al., 2004, Embrapa, 2005).

Other methods are also proposed for determination of these ions in soil, such as Spectrophotometry (Coelho & Gargantini, 1969; Nogueira et al., 1996), Atomic Fluorescence (Dagnall et al., 1971) and ICP-OES (Bernardi et al., 2003). Potentiometric methods have been also used to analyze different compounds in soil, such as boron (Carlson & Paul, 1969), sulfate (Goetzen & Oster, 1972), chloride (Ferreira et al., 1996a), nitrogen (Ferreira et al., 1996b) and potassium (Grygoliwicz-Pawlak, 2006). In this case, the analysis takes place by means of ion selective electrodes (ISE). Unlike the classical analytical methods, analyses with these sensors are very fast and cheap and allow the direct determination of electrolytes such as Ca and Mg in aqueous media (Christiansen, 1976; Imato et al., 1989; Beli & Zirino, 1993; Chen & Adams, 1998; Saurina et al., 2002; Simões, 2008; Metrohm, 2010a) and some complex matrices, e.g., milk (Metrohm, 2010b) and rocks (Kotek & Dlezal, 1980).

The purpose of this study was to propose a methodology for the determination of exchangeable calcium and magnesium in soil extracts by Ion Selective Calcium Electrode and Complexometric Titration (ISE-CT). The results were compared to those obtained by conventional analytical techniques such as Complexometric Titration (CT), Flame Spectrometry Atomic Absorption (FAAS) and even results of Interlaboratory Control (IC).

MATERIAL AND METHODS

The ISE-CT method for Ca^{2+} and Mg^{2+} determination in soil extracts was tested for precision and accuracy. Precision was evaluated by variance analysis in triplicate measurements of six samples and accuracy by comparing the average Ca^{2+} and Mg^{2+} concentrations obtained by IES-CT with two conventional methods (CT and FAAS). In addition, the proposed method was also compared with average Ca^{2+} and ($\text{Ca}^{2+} + \text{Mg}^{2+}$) of the IC of the state commission for agronomic laboratory analysis of Paraná (CELA-PR).

Sample Preparation

Firstly, soil samples were dried in an air-circulating oven at 40 °C and sieved (2 mm). The extracts were prepared with 10 cm³ soil in 50 mL KCl 1 mol L⁻¹ extraction solution.

Extraction of exchangeable Ca^{2+} and Mg^{2+}

The mixture of 10 cm³ soil sample with 50 mL of potassium chloride solution (KCl) 1 mol L⁻¹ was agitated in a rotating shaker for 15 min at 120 rpm. After extraction, the samples were left to stand for 8 hours for complete settling and aliquots were decanted for analysis.

Analysis by Ion Selective Electrode and Complexometric Titration (ISE-CT)

The analyses were performed with an automatic titrator (Titrand 809, Metrohm), Ion Selective Calcium Electrode (ISE-Ca) and reference electrode Ag/AgCl (saturated KNO₃ electrolyte bridge) to titrate a solution containing 10 mL KCl 1 mol L⁻¹ (blank) or soil extract, 0.5 mL magnesium sulfate heptahydrate (MgSO₄·7H₂O) and calcium chloride dihydrate (CaCl₂·2H₂O) solutions, all at a concentration of 0.0125 mol L⁻¹, as well as 4 mL ammonia buffer solution pH = 10.0 (aqueous solution containing 60 % of NH₄OH and 1.26 mol L⁻¹ NH₄Cl) and 50 mL of deionized water. The dynamic titration was performed by automatic dispenser (Dosino 800, Metrohm) with a solution of Ethylenediaminetetraacetic Acid disodium salt (EDTA-Na₂) 0.0125 mol L⁻¹, at a dose rate of 5 mL min⁻¹ and a sign of deviation of 20 mV min⁻¹ was established.

Analysis by conventional methods

The CT and FAAS analyses were performed using the solutions and procedures proposed by Embrapa (2005). CT analyses were carried out using automatic burette (Jekins, precision of 0.01 mL), titrating 10 mL of soil extract with 0.0125 mol L⁻¹ EDTA solution. FAAS determinations were conducted at a dilution of 0.2 mL of the extract in 10.0 mL of deionized water plus 1.0 mL of 5 % Lanthanum Oxide (La₂O₃). Seven-point calibration curves were established (Ca: 0; 0.5; 1.0; 2.0; 3.0; 4.0 and 5.0 mg L⁻¹; Mg: 0; 0.05; 0.10; 0.20; 0.30; 0.40 and 0.50 mg L⁻¹), maintaining the same proportion of La₂O₃ solutions used in diluted samples. Analysis were carried out at wavelengths of 422.7 nm and 285.2 nm for Ca and Mg, respectively, using air/acetylene flame. The determination coefficients (R²) of the calibration curves were 0.99833 for Ca and 0.99751 for Mg.

Parameters

The accuracy of the methods was examined by the coefficient of variation of triplicates. The ISE-CT method was compared with CT and FAAS by analysis of variance (F test) for which the treatment effect was considered. The comparison with the Interlaboratory Control (IC) was measured by determining the relative error.

The analytical sensitivity for each method was determined by calculating the detection limits (DL) and quantification limits (QL). DL is three and QL is ten times the standard deviation of the blank readings (extraction solution of 1 KCl mol L⁻¹), divided by the slope of calibration curve (response variation by concentration variation) for the range of 0.5–5 cmol_c dm⁻³ for each ion.

RESULTS

Statistical analysis revealed no significant difference between the concentrations obtained by ISE and the CT and FAAS methods for Ca²⁺ (p = 0.7790) and (Ca²⁺ + Mg²⁺) (p = 0.2621) determinations, at a confidence level of 95 %.

DISCUSSION

The CV values were below 8 % for Ca²⁺ concentrations and total hardness (Ca²⁺ + Mg²⁺) by the method ISE-CT. Comparatively, the CT analysis resulted in CV of up to 20 % and 17 %, respectively, for these values and FAAS in up to 16 % and 22 %, for the same measures. Furthermore, the CVs were higher for samples at low Ca²⁺ concentration by CT and FAAS. In the determination of (Ca²⁺ + Mg²⁺) by CT this effect was not observed, unlike for FAAS, where CV of two samples at lower concentration was 15 and 18 %, respectively. For IC the CV was high at low concentrations for both parameters (Table 1), reflecting the fact that the analyses in most of the 30 partner laboratories of IC were based on CT or FAAS.

In terms of accuracy, values of ISE-CT were closest to IC for Ca²⁺ and for (Ca²⁺ + Mg²⁺), values of FAAS were closest to IC, followed by ISE-CT and CT.

By comparing the concentration values of Ca²⁺ and (Ca²⁺ + Mg²⁺) to six samples analyzed by each method with the IC values, the relative error was lowest by ISE-CT, suggesting greater accuracy of this method (Table 2). Furthermore, the regression equations showed linearity of the ISE-CT, as well as the other two methods, with the IC values, in the range studied.

Table 1. Mean concentrations of Ca²⁺ and (Ca²⁺ + Mg²⁺) and their coefficient of variation (CV%) determined by ion selective electrode and complexometric titration (ISE-CT), Complexometric titration (CT), Flame Atomic Absorption Spectrometry (FAAS) and average results of Interlaboratory Control (IC)

Sample	Ca ²⁺				(Ca ²⁺ + Mg ²⁺)			
	ISE-CT	CT	FAAS	IC	ISE-CT	CT	FAAS	IC
	cmol _c dm ⁻³ (CV %)							
1	0.69 (3.64)	0.47 (18.22)	0.44 (10.66)	0.63 (26.48)	0.79 (3.64)	0.69 (1.00)	0.71 (18.52)	0.96 (27.31)
2	1.03 (0)	0.48 (20.09)	0.92 (10.48)	1.11 (14.68)	1.51 (3.98)	1.46 (4.93)	1.69 (15.02)	1.92 (13.53)
3	2.86 (4.54)	2.11 (7.11)	3.06 (4.61)	3.10 (10.51)	4.19 (6.71)	4.20 (17.21)	5.01 (10.01)	5.09 (9.83)
4	3.51 (0.74)	3.06 (3.04)	3.87 (16.49)	3.95 (9.61)	4.94 (6.56)	4.69 (6.43)	5.76 (22.31)	5.93 (7.34)
5	4.21 (1.79)	3.28 (3.09)	4.02 (2.52)	4.65 (11.24)	6.39 (5.24)	6.26 (6.24)	5.48 (4.99)	7.55 (9.98)
6	5.96 (2.73)	4.77 (2.33)	5.68 (2.66)	6.29 (10.66)	8.31 (7.15)	8.34 (3.79)	7.28 (5.18)	9.53 (8.81)

Average (n = 3 for ISE-CT, CT, and FAAS; n = 30 for IC)

Table 2. Characteristics of analytical determinations of Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ by different methods

Method	Regression Equation	R ²	Range	DL	QL	Relative error
			————— cmol _c dm ³ —————		%	
Ca ²⁺						
ISE-CT	$\hat{y} = -0.0047 + 1.0821 \text{ x}$	0.9985	0.00-5.96	0.08	0.25	5.25-11.14
CT	$\hat{y} = 0.2992 + 1.2657 \text{ x}$	0.9952	0.47-4.77	0.08	0.24	22.53-56.76
FAAS	$\hat{y} = 0.2014 + 1.0423 \text{ x}$	0.9934	0.44-5.68	0.01	0.07	1.29-30.16
(Ca ²⁺ + Mg ²⁺)						
ISE-CT	$\hat{y} = 0.1869 + 1.1427 \text{ x}$	0.9994	0.79-8.31	0.16	0.51	12.8-21.35
CT	$\hat{y} = 0.3131 + 1.1350 \text{ x}$	0.9980	0.69-8.34	0.22	0.60	12.49-28.13
FAAS	$\hat{y} = 0.1982 + 1.2406 \text{ x}$	0.9681	0.71-7.28	0.06	0.28	1.57-27.42

x: concentration of Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ in cmol_c dm⁻³, by each method; y: concentration of Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ in cmol_c dm⁻³, by CI; R^2 : correlation coefficient; DL: detection limit; QL: quantification limit; Relative error: error of the method compared to IC.

The DL and QL of ISE-CT are close to CT, while those of FAAS were the lowest.

Although ISE-CT is already a method commonly applied for the determination of these ions in other sample types, this methodology had not been established for soil analysis so far. Therefore, this study shows that this method is reliable for Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ determination in soil extracts, in the concentration range studied.

Figure 1 depicts the typical curves obtained for Ca^{2+} and Mg^{2+} concentrations in KCl 1 mol L⁻¹ solution (blank) and in soil extract of one of the samples. The points EP₁ and EP₂ correspond to the concentrations of Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$, respectively, in cmol_c dm⁻³.

The initial presence of Ca^{2+} and Mg^{2+} in blank is detectable (Figure 1), since the addition of 0.5 cmol_c dm⁻³ of each cation to the blanks extracts and samples was needed to make them detectable. Otherwise, the blank result would be displayed as incorrect, preventing the sample readings. This measure ensures that the detected signal exceeds the quantification limit, and the sensitivity of the method is adequate. Figure 1b represents the curve obtained for one soil sample, where the Ca^{2+} and $(\text{Ca}^{2+} + \text{Mg}^{2+})$ concentrations are the results of the subtraction of the sample EP's from the blank EP's. The result of concentration of Mg^{2+} is given by subtracting the EP of Ca^{2+} from the EP of $(\text{Ca}^{2+} + \text{Mg}^{2+})$. Some authors have reported difficulties in the analysis of these

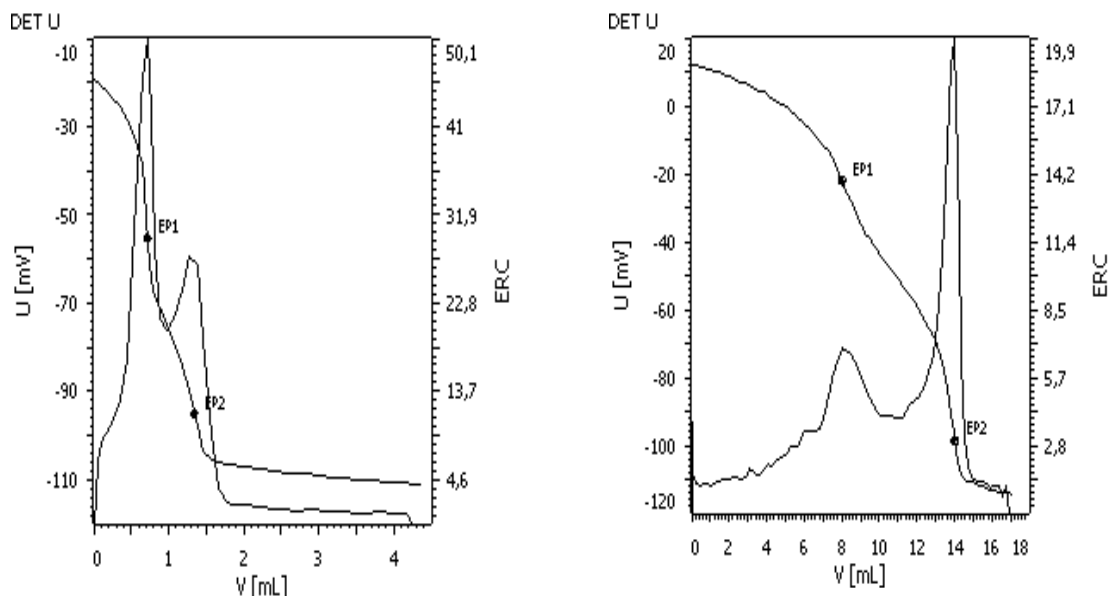


Figure 1. Curves obtained by ISE-CT and Ca^{2+} ($\text{Ca}^{2+} + \text{Mg}^{2+}$) in (a) blank samples and (b) soil extract.

cations by FAAS (Raij et al., 2001; Boeira et al., 2004) and CT (Raij, 1966). In the first place, difficulties are caused by the formation of KCl deposits in the burner slit of the spectrophotometer which frequently require a system shutdown for cleaning, delaying the analyses. Moreover, samples often have to be diluted to perform the readings in the linear range of the calibration curve. In relation to CT, there are several problems of interference, mainly due to the presence of the elements manganese, copper, iron, and aluminum. These, at appreciable quantities, make the determination of the turning point of the Murex difficult, which is the indicator used in Ca^{2+} determination. The Eriochrome black-T indicator, used in total hardness determination, interferes with the analysis by preventing the turn to blue in titrations with EDTA (Raij, 1966). For the ISE-CT method, there were apparently no such problems since the end point is determined by the sudden change in current at the equivalence point during titration (Skoog et al., 2008), unlike by CT, where this point is determined visually.

This method was tested in routine analyses of the Laboratory of Soils and Plant Nutrition of Embrapa Florestas and proved entirely suitable, since the analysis can be processed automatically. Furthermore, Ca^{2+} and Mg^{2+} are determined simultaneously, which also reduces the number of measurements. Thus, the analysis time was about half the time of CT. Compared to FAAS, times are similar but ISE-CT is more advantageous when working with highly concentrated samples, avoiding the need to dilute them. This is because, unlike FAAS, ISE-CT is a direct method that requires no calibration curve.

The ISE-CT method was not tested to determine the ions Ca^{2+} and Mg^{2+} with soil extracts originating from resin extraction, due to the fact that this method is not used in the laboratory routine analyses. However, it is believed that there is no barrier to analyze this type of extract, because the conditions are the same as those in the extraction with KCl, where the ammonia solution is sufficient to avoid interferences by other ions.

CONCLUSIONS

The determination method of exchangeable calcium and magnesium in soil extracts using Calcium Ion Selective Electrode and Complexometric Titration (ISE-CT) is accurate, precise and applicable when compared to Complexometric Titration (CT) and Flame Atomic Absorption Spectrometry (FAAS). Besides, the results obtained by this method were more precise and accurate than by the Interlaboratory Control (IC). Therefore, this study indicates that the ISE-CT method is reliable for Ca^{2+} and Mg^{2+} determination in soil extracts, in the concentration

range studied. The analysis time spent with ISE-CT was approximately half of the period required for CT and similar to FAAS.

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