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Use of a Ca-selective electrode in the determination of total Ca in the production of crude sugar. Preliminary studies.

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ABSTRACT: The determination of the total calcium in juice, syrups, and other products of the sugar industry is investigated. Total calcium and free calcium is determined by AAS and employing Ca-selective electrode respectively. A coefficient is obtained for the relation of total calcium with respect to free calcium. The coefficient is employed to determine the content of total calcium in accordance with the following equation.

Ca (tot)

= K

Ca (free)

Relative error is less than 5 %.

KEYWORDS: Ion-selective electrode; Ca-selective electrode; Atomic Absorption Spectrometry; sugar juice.

Introduction

The use of a massive form of the Calcium ion-selective electrode in the sugar production process is

limited by the existence in the sugared fluids, of other products not only free calcium, but also different compounds which contain calcium, eg. phosphates, organic acids, aminoacids and proteins.¹ This makes it impossible to give values of total calcium in juice, molasses in the sugar industry.⁵ The express analysis of the content of calcium by an ion-selective electrode (ISE) would be able to control the considerable presence of this element in different stages of the sugar production² process and so avoid scaling in equipment and apparatus and the loss of sugar in final molasses.^{1,3}

In our work we determine the relation between free calcium and total calcium in juices, molasses and crude sugar. We employ this relation to determine total content of calcium in the sample by ISE.

Materials and methods

In the realization of this study a calcium ion-selective electrode was prepared using an ether derivative of 1,2,3 trihydroxysulfonic acid mixed with polyvinylchloride and dissolved in cyclohexanone to make up a laminated matrix which is fixed to a plastic tube. The experiments were carried out at $298 \pm 1\text{K}$ using a Ag/AgCl electrode as a reference electrode, which was to a digital millivoltmeter MV-88, whose error in measuring does not exceed 0.1 mV. The reagents used where CaCl_2 , MgCl_2 , Cyclohexanone, SnCl_2 , all analytical grade and polyvinylchloride chromatographic grade.

The determination of the total calcium in the samples and model solutions were done in an atomic absorption spectrometer AAS-3 at a wavelength of 422.7 nm.

Results and discussions

The elaborated calcium ion-selective electrode presented a electrochemical behavior in correspondence with Nernst relationships, can be used for describing electrode potentials ranging from 0.1 mol/L to 3.10^{-6} mol/L with an average slope of 27.4 mV/decade close to the theoretical value for divalent ions. The electrode response was instantaneous with a maximum permissible potential deviation of $\pm 1\text{mV}$.

For the determination of calcium in the samples taken from Panama sugar factory these were: Some juices of purifier, mixed juice, clarified juice, molasses and crude sugar. In the case of the concentrated syrup (molasses) and the crude sugar, the respective dilution of the solutions were made (5 and 10% w/r respectively).

The results were as follow:

Table 1 - Determination of total calcium (AAS) and free calcium (ISE) in mgL-1

Sample	Purifier			Mixed Juice			Clarified Juice			Molasses (5 % w/r)		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
1	525	328	1.60	470	356	1.32	580	356	1.63	2800	1840	1.52
2	540	356	1.52	505	356	1.42	530	356	1.49	2500	1840	1.36
3	550	356	1.54	555	356	1.56	510	356	1.43	3600	2360	1.53
4	465	356	1.31	570	386	1.48	545	386	1.41	2450	1840	1.33
5	640	356	1.80	510	350	1.45	545	356	1.53	3100	1840	1.68
Average	544	350.4	1.55	522	360.8	1.45	542	362	1.50	2890	1945	1.48

Note: 1. AAS determination.
 2. ISE determination.
 3. Calculate Coefficient.

The value of the average coefficient for juices and syrups is :

$$K_{av} = \frac{K_{pur} + K_{mix} + K_{clar} + K_{mol}}{4} \quad (1)$$

$$K_{av} = 1.497$$

This coefficient can serve as a base for calculation in the determination of the total calcium:

$$Ca_{tot} = K_{av} \cdot Ca(\text{free}) \quad (2)$$

By employing equation (2) the following results are obtained.

Table 2 - Calculated values by (2) and experimental values (AAS) mg/L

Sample	Purifier			Mixed Juice			Clarified Juice			Molasses (5 % w/r)		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
1	525	492	6.2	470	534	13.5	580	534	7.9	2800	2760	1.3
2	540	534	1.1	505	534	5.7	530	534	0.7	2500	2760	6.4
3	550	534	2.9	555	534	3.7	510	534	4.7	3600	3540	1.7
4	465	534	14.9	570	579	1.5	545	579	6.2	2450	2760	1.2
5	640	534	16.5	510	525	2.9	545	534	2.0	3100	2760	1.0
Average	544	526	3.3	522	541	3.6	542	543	0.2	2890	2418	1.0

Notes: 1. AAS determination
 2. Calculated
 3. Relative error

It can be clearly seen that between the average calculated values and the average values of total calcium (AAS), the relative error does not surpass 4%.

In the case of crude sugar the results calculated and those obtained by AAS, maintained the following correspondence.

Table 3 - Calculated values by (2) and experimental values (AAS) mg/L in crude sugar

Sample	AAS	ISE	Coefficient	Calculated	% error
1	620	-	-	-	-
2	570	472	1.21	552	3.1
3	520	434	1.20	508	2.3
4	540	472	1.14	552	2.2
5	530	472	1.12	552	4.1
Average	556	463	1.17	542	2.5

In this table the relative error is less 5%

Conclusions

The preliminary results obtained in our work permit in a very quick way to determine the concentration of total calcium in the production process of sugar by using an ion-selective electrode sensitive to calcium. Total concentration can be determined in an indirect manner based on the fact that it is possible to find a correlation coefficient that can be employed in the calculation of Ca(tot).

It's necessary to reaffirm more than ever the validity of the methodology used by increasing the determination in different stages of the year where the raw material changes its calcium compositions in dependence of characteristic of the juice.

GONZÁLEZ GARCÍA, J., EGONOV, V. V., DEL TÓRO DÉNIZ, E., MARTINÉZ SÁEZ, S., RAMOS VEGA, A. Uso de um eletrodo seletivo de cálcio na determinação do total de cálcio na produção de açúcar cristal. Estudos preliminares. *Ecl. Quím (São Paulo)*, v.22, p.193-197, 1997.

RESUMO: Foi investigada a determinação do total de cálcio em sucos, melaços, xaropes e outros produtos da indústria açucareira. O cálcio total eo cálcio livre foram determinados, respectivamente, por espectroscopia de absorção atômica (AAS) e empregado eletrodo seletivo de cálcio. Foi obtido no coeficiente para relação entre o cálcio total e o cálcio livre. Este coeficiente foi utilizado na determinação do conteúdo total de cálcio, segundo equação:

Ca (total)

= K

Ca (livre)

Com um erro relativo menor que 5%.

PALAVRAS-CHAVE: Eletrodo de íon seletivo; espectroscopia de absorção atômica; caldo de cana.

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