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CALCIUM DETERMINATION BY PERMANGANOMETRY AND EDTA COMPLEXATION

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OBJECTIVES

This study is part of a project that aims to perform the isotopic separation of Lithium, using the ion exchange process. In the developed procedure, Calcium Acetate is used as a displacer for the formed Lithium band. Therefore, some samples collected from the column have a high concentration of calcium that interferes with the determination of the 6Li/7Li ratio. To obtain better precision in isotopic analyses, it was necessary to employ a quick and practical method for determining calcium in these samples. Therefore, this study aims to identify the best method for determining the calcium present in samples from isotopic separation columns via ion exchange for its subsequent removal. For comparison, two classic methods were chosen, permanganometry and complexation with EDTA.

METHODS AND PROCEDURES

For determination by permanganometry, the methodology developed by Burin[1] and collaborators (2008) was used. At a rate of 50 mL of the sample from the isotopic separation column was added with 50 mL of ultrapure water. The pH was adjusted to 5.5 with NH_4OH. After heating until boiling, 4.2% (NH4)2C2O_4 was added and the calcium precipitated. The precipitate was filtered and washed with NH4OH. The filtrate was collected from the filter paper with 3.85% H2SO_4 in a beaker. To determine Ca in this solution, a 0.01M $KMnO_4$ solution was used, standardized with a K2C2O_4 solution in an acidic medium at 80ºC. Standardization was carried out in triplicate for greater data reliability. Once this was done, the sample was titrated with this permanganate at 75ºC. Sample titration was also performed in triplicate.

The second method adopted was Standard Method 3500 of determination with EDTA, the same samples collected from the separation column were diluted (1 mL of the original solution to 50 mL) and adjusted to pH 12 with NaOH. About 3 g of EDTA was diluted in 1 L of ultrapure water. To prepare the standard calcium solution, 0.1 g of $CaCO_3$ diluted in a few drops of HCl was weighed and then carefully diluted in 20mL of ultrapure water. This solution was heated to 90ºC for a few minutes and the medium was alkalinized. The EDTA solution was standardized in triplicate with this solution, using murexide as an indicator. pH 12 calcium samples were titrated with standardized EDTA.[2]

RESULTS

The standardization of $KMnO_4$ with K2C2O_4 can be defined by the reaction: 2KMnO4 + 5K2C2O_4 + 8H_2SO_4 ↔ 6K_2SO_4 + 2MnSO^4 + 10 CO2 +8H2O. The concentrations obtained for the $KMnO_4$ solutions were around 0.01 and 0.009 mol/L. To determine Ca through permanganometry, the equation is obtained: 2$KMnO_4$ + 5CaC_2O_4 + 8H_2SO_4 ↔ K_2SO_4 + 2$MnSO_4$ + 5$CaSO_4$ + 10 CO_2 + 8H_2O.

In this reasoning, the calcium concentrations in the samples were calculated and obtained according to the following table.

Samples	Ca concentration (mg/L) in triplicate titrations		
	1ª	2ª	3ª
S-1686	1732,18	1299,17	1563,13
S-1706	1641,68	1729,99	1920,93
S-1707	1431,15	1439,50	1417,10
S-1714	1995,35	2015,71	1985,17

Table 1: Ca concentrations in samples by titration with $KMnO_4$ in triplicate.

For determination by EDTA complexation, the concentrations in mol/L of EDTA through standardization with CaCO3 were between 0.011 and 0.010. The Ca concentrations obtained are described in the table below.

Samples	Ca concentration (mg/L) in triplicate titrations		
	1ª	2ª	3ª
S-1686	195,17	195,17	191,02
S-1706	145,34	194,34	191,02
S-1707	196,00	197,67	195,17
S-1714	193,51	186,87	188,53

Table 2: Ca concentrations in samples by titration with EDTA in triplicate.

CONCLUSIONS

The determination of calcium in the samples obtained is best used by permanganometry. In total, around 250 mL of 0.01M KMnO4 solution were used per sample. However, despite the large volume spent and the longer experimental time, the results obtained were more reliable. When determining with EDTA, around 70 mL were spent per sample and titrations are faster when compared to permanganometry. However, the results obtained were not satisfactory, since approximately the same volume of EDTA was used for all samples, when they have different concentrations of Ca. These results will later be compared with analyzes to be carried out using a flame photometer. This way, it can be concluded that the determination that demonstrated results of a high degree of reliability was that of permanganometry, and that the determination by EDTA must not be discarded as it has the potential for such analysis, however, a study for improvement is necessary. technique in order to obtain satisfactory results.

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