

# Comments on Chemical Analysis of Limestone and Dolomite Using Capillary Electrophoresis

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## Abstract

Comments on the determination of calcium and magnesium in limestone, dolomite and other related materials using capillary electrophoresis is presented. As stated and discussed, the use of highly sensitive capillary electrophoresis technique for the chemical analysis of major concentration of calcium and magnesium content in limestone and dolomite samples is never justified in comparison with the well established EDTA complexometric titration methods. Complexometric titration methods satisfy all the essential requirements of: Reliability (accurate and precise, comparable, traceable) Applicability (applicable to diverse sample matrices) and Practicability (simple, rapid, cost-effective, no requirement of standards and calibration of instrument, no expensive instrumentation and are widely recommended for the determination of calcium and magnesium at percentage level for such matrices. Surprising, there is no comment or discussion by the authors in their manuscript on complexometric titration methods. There are contradictory and highly misleading statements.

**Keywords:** Capillary electrophoresis; Calcium; Magnesium dolomite; Limestone

## Comments

I have read the above cited paper [1], all the cited papers in references therein and available published literature on the above subject very carefully. Undersigned developed an indicator for the titrimetric determination of calcium and magnesium with ethylenediaminetetraacetate in water [2], its indicator properties [3] and further extended its application in Dolomite, Limestone, Magnesite, Phosphatic and Silicate Matrices [4]. Based on my experiences gained so far, I would like to share my comments as follows: As on today, the EDTA titration methods are commonly used for the determination of calcium and magnesium in limestone, dolomite, water samples and other related materials. The various methods/techniques used in the determination of calcium and magnesium in the Certification of Standard Reference Materials, such as Dolomitic limestone 88b, BCS No. 368 Dolomite, BCS-CRM No. 513 Limestone etc. are well documented in certificate of their analysis. EDTA complexometric method for determination calcium and magnesium in lime and limestone products has been thoroughly investigated and is widely accepted. Complexometric titration methods and various techniques of titrations are well documented in the commonly available book Vogel, A Textbook of Quantitative Inorganic Analysis. Indicators namely, Eriochrome Black T [5-7], murexide [8], calcon [9,10], the indicator of Patton and Reeder [11], calmagite [12], Arsenazo I [13] are well known for complexometric titrations. Ordinarily the EDTA procedure is designed to follow routine separations, that is, single dehydration of silica and a single precipitation with  $\text{NH}_4\text{OH}$  of the combined oxides of iron and aluminum. For expediency, the assays can be run directly without prior separation of the combined oxides of iron and aluminum by using the complexing action of EDTA at appropriate pH levels. As reported in

ASTM-document [13], Designation: C 25-06, Standard test methods for chemical analysis of limestone, quick lime and hydrated lime. The precision of this test method was tested by ten laboratories using three limestone and one dolomite reference samples. The results are summarized as follows: The overall precision (1sigma) between laboratories (reproducibility) and within laboratories (1 sigma): for CaO are  $\pm 0.31$  and  $\pm 0.24$  absolute units and for MgO are  $\pm 0.28$  and  $\pm 0.22$  absolute units, respectively. Moreover, titration methods are regarded as absolute methods in analytical chemistry [14,15].

As claimed and stated in manuscript by Mohanty et al. [1] quote "The developed analytical protocol is cheaper, faster and accurate compared to the existing analytical methods using ICP-OES and AAS as it does not require any gases during analysis and avoids all types of interferences" unquote. In view of the stated facts as above in 3rd para, the claim of authors is absolutely incorrect and highly misleading. In general, complexometric titration methods satisfy all the essential requirements of: Reliability (accurate and precise, comparable, traceable) Applicability (applicable to diverse sample matrices) and Practicability (simple, rapid, cost-effective, no requirement of standards and calibration of instrument, no expensive instrumentation (simple glasswares, burette, pipettes, etc.), and are widely recommended for the determination of calcium and magnesium at percentage level for such matrices. Surprising, there is no comment or discussion by the authors of the cited paper [1] in their manuscript on complexometric titration methods.

As stated and discussed in this manuscript [1] on Page 2029, 2nd para, quote "capillary electrophoresis (CE) is hybrid technique multispecies analysis and also stated in 3rd para of the manuscript" unquote. The use of highly sensitive capillary electrophoresis technique for the determination of calcium and magnesium content in limestone and dolomite samples is never justified. On Page 2030, of the manuscript, as stated, quote "Dilute solutions (1-30 ppm) can be easily analysed using CE with good reproducibility, but analysis of

concentrated solutions often lead to peak broadening and hence poor reproducibility of the results” unquote. Moreover, from the reproducibility data reported are significantly different (nearly twice), reproducibility data (% RSD) for calcium as Ca and for magnesium as Mg by CE technique are 0.9 and 1.7, on the contrary, %RSD values are 1.7 (actual figure should be 1.8) and 3.2 (actual figure should be 3.29, i.e., 3.3), respectively. In Dolomite BCSNo.368 sample (All results relate to the dried (110°C, Correct certified value of CaO, 30.8% (average)  $\pm$  0.086 (Standard Deviation) and corresponding Ca value is  $22.01 \pm 0.06$  (standard deviation), and for MgO, 20.9 (average)  $\pm$  0.15 (standard deviation) and corresponding Mg value is  $12.6 \pm 0.09$ . As reported in the manuscript, on Page 2032, the certified values of Ca as  $22.01 \pm 0.17$  and Mg as  $12.6 \pm 0.14$ , are incorrect and wrongly quoted. As per the convention, the values of major element concentrations in minerals or rocks are reported in terms of their oxides. The same convention of reporting their concentration is adopted in their certificate of analysis of CRMs. Instead, the authors of the cited paper 1 adopted to report their analytical results in terms of elemental form. In my opinion, this is simply to fabricate the values of standard deviations with their average values of calcium and magnesium contents in CRMs for comparison purpose as reported in the manuscript and to mislead the scientific analytical community. The certificate of analysis of Limestone (NML CRM No.71.1) is not available on NML website. The information available on the NML website on the analysis values are as follows: Limestone (No.71.1) (revalidated), Silica, 0.52%, Calcium oxide, 55.10%, Magnesium oxide, 0.50%, Loss on ignition, 43.48% (There is no information, whether the values are ‘as is basis’ or ‘dried basis’). The corresponding reported certified values of Ca as 39.38% and Mg as 0.30% in Limestone (NML CRM No.71.1) are correctly quoted. The values of associated standard deviations in Ca  $\pm$  0.29 and Mg  $\pm$  0.09 appears totally incorrect.

As per the published literature, common trace elements including calcium and magnesium in the reference materials are commonly determined by flame-atomic absorption spectrophotometer while ICP-OES is most suitable for the determination of traces of elements forming refractory oxides, such as REEs, etc. [16-18]. ICP and AA spectrophotometric methods suffer from chemical, physical, and spectral interferences including wavelength absorbance, inconsistencies in the introduction of the dissolved sample into the instrument, and overlapping and unresolved wavelength peaks. AAS and ICP techniques are never recommended for the analysis of calcium and magnesium at higher concentration levels due to their unacceptable high % RSD [13]. X-ray spectrometric methods require that the chemical and physical compositions of the sample closely match the reference materials used to calibrate the instrument, but the availability of certified reference materials is limited.

## Conclusion

The reported analytical protocol for the determination of calcium and magnesium in limestone and dolomite using capillary

electrophoresis does not satisfy any of the three essential requirements of a methodology: reliability, applicability and practicability. There are contradictory and highly misleading statements.

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