



Internal standard addition calibration: Determination of calcium and magnesium by atomic absorption spectrometry



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ABSTRACT

Internal standard addition (ISA) is a new calibration method that combines the principles of internal standardization and standard additions. The current work demonstrated the effectiveness of ISA for the determination of Ca and Mg in biodiesel samples and certified reference materials (CRMs) by flame atomic absorption spectrometry. Manganese and Sr were selected as internal standards for Mg and Ca, respectively. Results for Ca and Mg in CRMs using ISA were in agreement with certified values at the 95% confidence level (*t*-test). The relative standard deviations ($n = 12$) were ca. 6% for both analytes. For comparison purposes, Ca and Mg were also determined by the traditional methods of external standard calibration (ES), standard additions (SA) and internal standardization (IS). Recoveries obtained with ISA (Ca: 93–109%; Mg: 100–106%) were similar to those found with IS (Ca: 100–112%; Mg: 98–105%), but significantly better than ES (Ca: 219–291%; Mg: 111–120%) and SA (Ca: 97–127%; Mg: 106–128%). Results for Ca and Mg determined in biodiesel and CRMs using ISA were more accurate and more precise than those obtained with ES, SA and IS.

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1. Introduction

Except when an absolute method of determination is available, choosing the most adequate calibration strategy is essential in any quantitative chemical analysis [1]. Among the main calibration methods employed in quantitative instrumental analysis, the most important are the external standard calibration (ES), standard additions (SA) and internal standardization (IS) [2]. The first one is the simplest, but it is the most susceptible to errors caused by fluctuations in operating conditions and/or matrix effects. On the other hand, SA and IS can minimize these errors, significantly improving accuracy and precision [3].

The standard addition method is useful when the analyte is present in a complex matrix and the matrix-matching approach cannot be used [4]. However, it presents some limitations: (i) spiked analyte concentrations must be within the linear working range; (ii) species of spiked analyte and sample analyte must be similar; (iii) it is time-consuming (convenient for a small number of samples); and (iv) large sample volumes are required to prepare a series of standard solutions, restricting its application in some cases.

The IS method has been used to minimize errors caused by instrumental drift and to reduce chemical matrix effects. It combines the straightforwardness of ES without the need for matrix-matching.

However, the selection of an adequate internal standard species that presents similar physical–chemical properties to the analytes is not a trivial task. Moreover, the element selected as internal standard must be absent, or occur at very low concentrations in the samples [5,6].

Some works in the literature have combined the benefits of SA and IS by plotting the analyte-to-internal standard signal ratio as instrumental response (the so-called analytical signal) versus the added concentration of analyte to the sample. In this case, the internal standard species is added to all series of sample solutions at a known and fixed concentration [7,8]. It is important to mention that the pre-requisites for the selection and use of an internal standard are also valid here, which sometimes can be considered restrictive for a large scale routine analysis.

Standard dilution analysis (SDA) is a new calibration method recently proposed in the literature [9] that combines the principles of IS and SA. The theory and equations of the SDA method were adapted to the internal standard addition (ISA) calibration employed in this work. In SDA, a solution containing the analytical sample and a standard mixture containing the analyte and an internal standard (solution 1) is mixed with another solution also containing the analytical sample and the blank (solution 2). As solution 1 is diluted by solution 2 in the same container, many calibration points are generated on-the-fly. Because the amount of analytical sample never changes (both solutions 1 and 2 have 50% of sample), a matrix-matching is obtained and only the standard solution is in fact diluted. The observed analyte signal (S_A) will result from the quantity present in the sample (sam) and the

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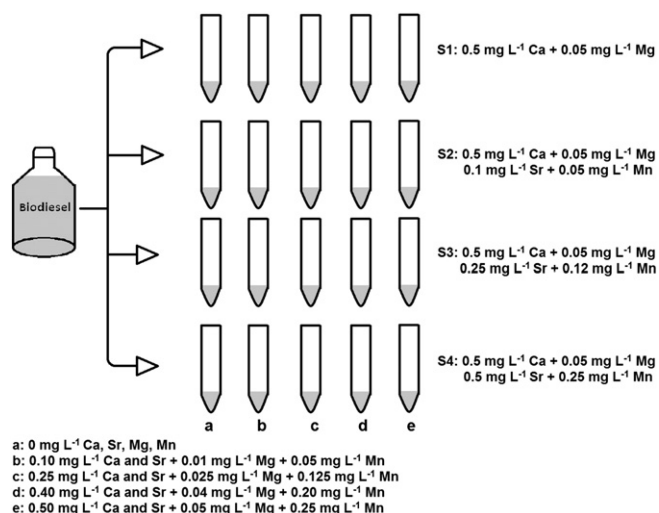


Fig 1. Scheme of sample preparation to evaluate the performance of the ISA method spiked with different concentrations of Sr and Mn.

concentration of added standard (std). On the other hand, the observed internal standard signal (S_i) will come from the standard solution alone. The obtained signals are related to the concentrations by the calibration

sensitivity (m) of the respective calibration curve equations, $S_A = m_A C_A$ and $S_i = m_i C_i$. While applying the SDA method, one uses the ratio of the analyte to internal standard signals according to Eq. (1) [9]:

$$\frac{S_A}{S_i} = \frac{m_A C_A^{\text{std}}}{m_i C_i} + \frac{m_A C_A^{\text{sam}}}{m_i C_i} \quad (1)$$

If the term (S_A/S_i) is plotted versus ($1/C_i$), a linear relationship is obtained, where intercept and slope will be ($m_A C_A^{\text{std}}/m_i C_i$) and ($m_A C_A^{\text{sam}}/m_i$), respectively. Because C_A^{std}/C_i is known from the preparation of solution 1, the analyte concentration in the sample is easily found by applying Eq. (2).

$$C_A^{\text{sam}} = \frac{\text{slope}}{\text{intercept}} \times \frac{C_A^{\text{std}}}{C_i} \quad (2)$$

As described above, SDA is carried out using only two solutions. To further confirm the SDA hypothesis, we have applied ISA to the determination of Ca and Mg by flame atomic absorption spectrometry in five biodiesel samples and in certified reference materials (CRMs) of milk, botanical tissues, biological tissues, flours and biodiesel. All samples and CRMs were also analyzed by comparative calibration methods (ES, SA and IS) to check the performance of ISA. It is important to note that different from SDA, the application of ISA requires the preparation of several standard calibration solutions;

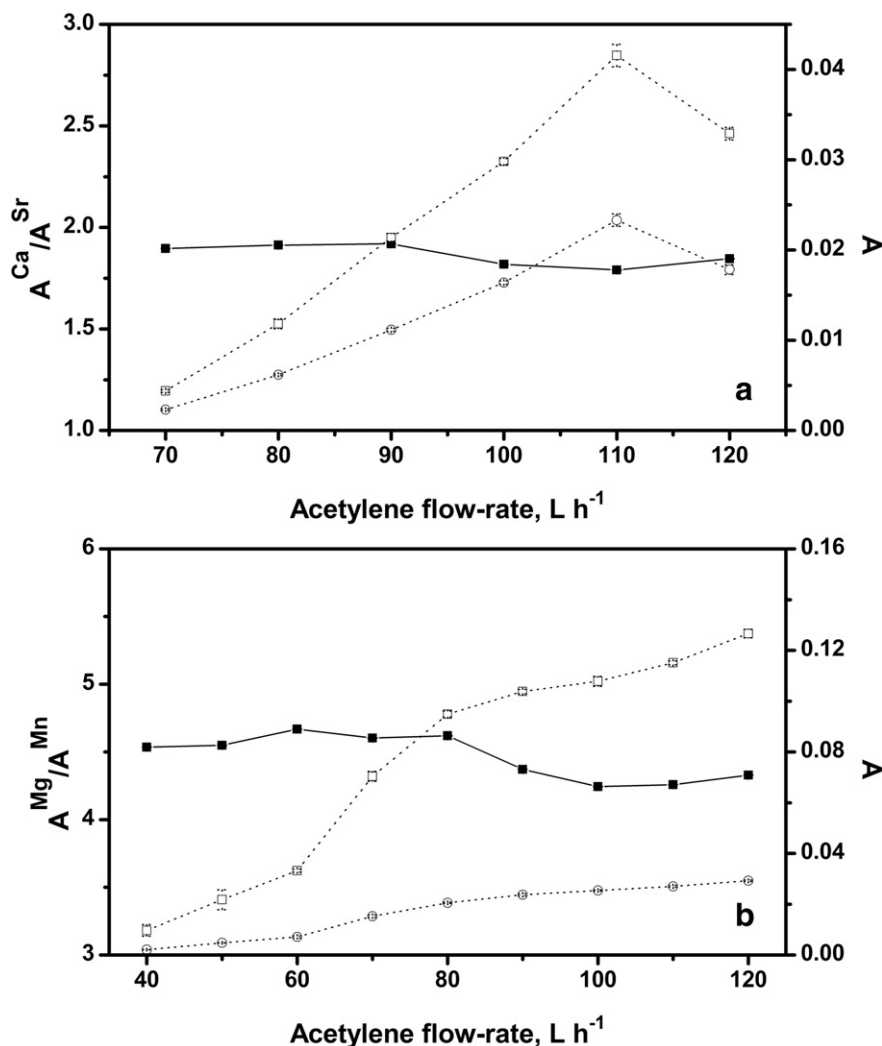


Fig 2. Influence of variation of acetylene flow-rate on: a) A^{Ca} (□) A^{Sr} (○) and $A^{\text{Ca}}/A^{\text{Sr}}$ ratio (■); b) A^{Mg} (□) A^{Mn} (○) and $A^{\text{Mg}}/A^{\text{Mn}}$ ratio (■).

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