



# Standard dilution analysis of beverages by microwave-induced plasma optical emission spectrometry



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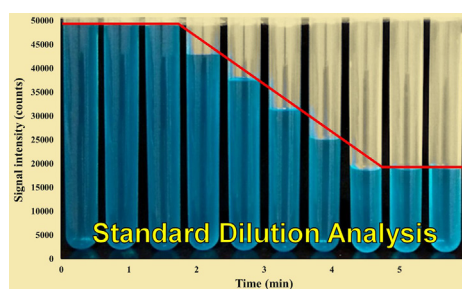
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## HIGHLIGHTS

- Only two calibration solutions for recoveries between 90 and 99%.
- Accuracies comparable or even superior to traditional calibration methods.
- Simple sample dilution with 1% v v<sup>-1</sup> HNO<sub>3</sub>.
- Less calibration points result in higher LODs.
- Internal standardization, matrix matching and in-line dilution.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, standard dilution analysis (SDA) is combined with microwave-induced plasma optical emission spectrometry (MIP OES) to determine seven elements in coffee, green tea, energy drink, beer, whiskey and cachaça (Brazilian hard liquor). No sample preparation other than simple dilution in HNO<sub>3</sub> 1% v v<sup>-1</sup> is required. Due to relatively low plasma temperatures, matrix effects may compromise accuracies in MIP OES analyzes of complex samples. The method of standard additions (SA) offers enhanced accuracies, but is time-consuming and labor intensive. SDA offers a simpler, faster approach, with improved accuracies for complex matrices. In this work, SDA's efficiency is evaluated by spike experiments, and the results are compared to the traditional methods of external calibration (EC), internal standard (IS), and standard additions (SA). SDA is comparable to the traditional calibration methods, and it provides superior accuracies for applications involving ethanol-containing beverage samples. The SDA-MIP OES procedure is effective. Using only two calibration solutions, it may be easily automated for accurate and high sample throughput routine applications.

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## 1. Introduction

Calibration is one of the most critical steps in any analytical procedure [1]. It usually requires several standard reference solutions, which can affect sample throughput. Ideally, these solutions

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should be prepared in the same medium as the sample to prevent matrix effects (*i.e.*, matrix-matching). However, matching complex matrices such as beverages containing various amounts of alcohol is often an insurmountable challenge to the analyst.

For determinations involving simple matrices, accurate results may be achieved by employing external standard calibration (EC) and standard reference solutions prepared in a common solvent. This strategy is simple and efficient for most applications, but it can provide inaccurate results when combined with matrix-sensitive methods. On the other hand, poor accuracy caused by variations in sample viscosity and its effects on nebulization, sample transport and/or atomization can be minimized by employing the traditional method of internal standardization (IS) [2–4]. In IS, a species presenting physical–chemical properties similar to the analyte (*i.e.* an internal standard, IS) is added to blank, standard reference and sample solutions. The analyte-to-IS signal ratio is then used as the dependent variable (*y*-axis) of the calibration curve. If the analyte and the IS experience the same fluctuations during the analysis, then using their signal ratio rather than the analytical signal alone can significantly improve accuracy and precision [2,4]. The main limitations of the IS method are related to its inability to correct for matrix effects and the difficulty to find ideal IS species for different applications.

For methods severely affected by matrix effects, standard additions (SA) is the most commonly used strategy to ensure reliable results [5–7]. By preparing the standard reference solutions using the sample as solvent, one can guarantee the same medium in all determinations. The analyte concentration in the sample is then determined by the *x*-axis intercept of the calibration curve. The SA method is one of the most efficient strategies to correct for rotational effects (*i.e.*, variations in the analytical signal caused by concomitant species) [8] and it is widely used in all chemical analysis subfields [5–8]. On the other hand, SA is time-consuming and it becomes unpractical when analyzing several samples. In addition, it cannot correct for fluctuations in temperature, sample transport, nebulization and sample volume.

Standard dilution analysis (SDA) is a new method based on a different calibration approach. It combines SA and IS to simultaneously improve accuracy and sample throughput in complex matrix determinations [9]. Different from the traditional EC, IS and SA methods, only two solutions are required in SDA calibrations. Solution 1 contains 50% sample and 50% of a standard solution containing the analytes and an internal standard. Solution 2 has 50% sample and 50% blank. Analyte and IS signals are continuously monitored and many calibration points are generated in “real time” as Solution 2 is added to the same tube containing Solution 1. Because the amount of sample never changes (both Solutions 1 and 2 contain each 50% sample), only the standards are diluted. This matrix-matching effect contributes to improved accuracies, and the presence of an IS minimizes signal fluctuations due to differences in sample viscosity [9,10].

The SDA calibration curve is built by plotting the analyte-to-IS signal ratio on the *y*-axis, and the reciprocal of the IS concentration on the *x*-axis (*i.e.*,  $S_A/S_{IS}$  vs.  $1/C_{IS}$ ). Eqs. (1)–(4) show the mathematical treatment used to calculate the analyte concentration in the sample. The analytical signal ( $S_A$ ) arise from both the sample (*sam*) and the standard (*std*), while the IS signal ( $S_{IS}$ ) comes from the standard only. These signals are related to the respective concentrations by the calibration curve sensitivities (*m*):  $S_A = m_A C_A$  and  $S_{IS} = m_{IS} C_{IS}$ . By taking the analyte-to-IS signal ratio,  $S_A/S_{IS}$ :

$$\frac{S_A}{S_{IS}} = \frac{m_A C_A}{m_{IS} C_{IS}} = \frac{m_A (C_A^{sam} + C_A^{std})}{m_{IS} C_{IS}} = \frac{m_A C_A^{sam}}{m_{IS} C_{IS}} + \frac{m_A C_A^{std}}{m_{IS} C_{IS}} \quad (1)$$

If we consider  $S_A/S_{IS}$  as the dependent variable (*y*-axis) and  $1/C_{IS}$

as the independent variable (*x*-axis), the slope and intercept of this calibration curve will be:

$$\text{Slope} = \frac{m_A C_A^{sam}}{m_{IS}} \quad (2)$$

$$\text{Intercept} = \frac{m_A C_A^{std}}{m_{IS} C_{IS}} \quad (3)$$

Finally, the analyte concentration in the sample is calculated from the values of slope and intercept by rearranging Eqs. (2) and (3):

$$C_A^{sam} = \frac{\text{Slope}}{\text{Intercept}} \times \frac{C_A^{std}}{C_{IS}} \quad (4)$$

The efficiency of the SDA method at improving accuracy and sample throughput has recently been demonstrated for UV–VIS molecular absorption spectroscopy and inductively coupled plasma optical emission spectrometry (ICP OES) [9]. Considering complex samples and the potential matrix effects in a relatively low temperature (*ca.* 5000 K) microwave-induced plasma (MIP) [11], the SDA method is an interesting alternative to SA in MIP OES applications. In the present work, we combine SDA with the plasma stability of MIP OES to determine seven elements in beverage samples. The  $N_2$  MIP is tolerant to high solvent loads [12,13], which allows for a sample preparation procedure based on simple dilution with  $HNO_3$  1% *v v*<sup>-1</sup>. Complex matrix samples of coffee, green tea, energy drink, beer, whiskey and cachaça (Brazilian hard liquor) are analyzed by SDA–MIP OES and the results are compared with values obtained with the traditional methods of EC, IS and SA.

## 2. Experimental

### 2.1. Instrumentation

An Agilent 4200 MP-AES (Agilent Technologies, Santa Clara, CA, USA) was used in all determinations. The sample introduction system is composed of a SPS 3 automatic sampler, solvent-resistant tubing, a double-pass cyclonic spray chamber and the inert OneNeb nebulizer. A liquid  $N_2$  Dewar was used as plasma gas source. The same nebulization gas flow rate and plasma observation position were used for all analytes in SDA determinations: 0.75 L *min*<sup>-1</sup> and 0, respectively. The plasma observation position is based on stepper motor positions and has no specific unit. In this case, 0 approximately corresponds to the center of the plasma.

Because the 4200 MP-AES collects data sequentially (*i.e.*, one wavelength at the time), we have used the optimization feature in the MP Expert software for all SDA determinations. This feature is used in common applications to define the best conditions of nebulization gas flow rate and plasma observation position for each individual analyte. In SDA, it allows for continuous, multi-element and real-time signal acquisition (SDA's main requirements). The sequentially recorded emission signals are then exported as CSV files for MS Excel data processing.

For comparison, all analytes were also determined by the traditional methods of EC, IS and SA. Depending on the sample matrix, either aqueous or ethanolic multi-element solutions were used to determine the best conditions (Tables 1 and 2) for each analyte and the internal standard (yttrium). In this case, the instrument's normal acquisition mode was used to determine Al, Co, Cr, Cu, Mn, Ni and Zn in six beverage samples.

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