Microchemical Journal 124 (2016) 662–667

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Standard dilution analysis in flow system: Sodium determination by flame atomic emission spectrometry

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ARTICLE INFO

Article history:
Received 1 October 2015
Accepted 8 October 2015
Available online 21 October 2015

Keywords:
Standard dilution analysis
Flow-injection analysis
Calibration

ABSTRACT

Standard dilution analysis (SDA) is a new calibration method that combines the principles of internal standardization and standard additions. The current work evaluated the feasibility of SDA automation using a flow-injection system (FIA). The FIA-SDA system was applied to sodium determination in biodiesel samples and certified reference materials (CRMs) by flame atomic emission spectrometry (FAES). Lithium was employed as internal standard in all determinations. The results for Na determination in five CRMs using FIA-SDA were in agreement with certified values at the 95% confidence level (*t*-test). For comparison purposes, Na was also determined by the traditional methods of external standard (ES), standard additions (SA) and internal standardization (IS). Recoveries showed increased accuracy following the sequence ES (181–202%) < IS (67–72%) < SA (111–126%) < FIA-SDA (94–98%). FIA-SDA provided more accurate and precise results than ES, SA and IS for Na determination in biodiesel and CRMs by FAES.

1. Introduction

In analytical chemistry, instrumental methods generally require careful calibration for determining the concentration of an analyte in an unknown sample [1,2]. External standard calibration (ES) is the most commonly used calibration method due its simplicity of application and interpretation [3]. However, this method is susceptible to errors mainly caused by variations in instrumental parameters and/or matrix effects which can deteriorate precision and/or accuracy. These drawbacks can be circumvented by using other types of calibration such as matrix matching, standard addition (SA) and internal standardization (IS) [4–6].

A novel calibration method called standard dilution analysis (SDA), that combines the principles of the traditional methods of SA and IS was recently proposed in the literature [7]. It can be performed by providing the detector with a solution containing a constant amount of sample and a varying amount of standard solution containing both analyte and internal standard. SDA was applied for the determination of FD&C dye Blue No. 1 in mouthwash by spectrophotometry, and Al, Cd, Co, Cr, Cu, Fe, Ni and Pb in water, nitric acid, mouthwash, wine, and cola by inductively coupled plasma optical emission spectrometry (ICP OES). The procedure was based on manually combining two solutions (*e.g.* A and B). Solution A, containing 50% sample and 50% standard mixture (analyte plus internal standard), is mixed with solution B, which contains the sample and the blank. After mixing the two solutions (by pouring solution B into the same tube containing solution A), many calibration points are generated on-the-fly as solution A is diluted by solution B. In this case, only the standard solution is in fact diluted and the sample matrix never changes (both solutions A and B have 50% sample), which results in an efficient matrix-matching procedure. Details on the mathematical approach for calculating the concentration of analyte in SDA determinations are described elsewhere [7]. Despite its efficiency and relatively high sample throughput, the SDA method is all manual. The analyst must pay close attention to the different phases of signal acquisition (*i.e.*, introduction of solution A, gradient zone, and after solutions A and B are completely mixed) in order to ensure enough data points for calibration. The automation of the SDA method is therefore an interesting approach to minimize errors and further improve sample throughput, since time and conditions of solution mixing can be made highly reproducible.

Considering that flow-injection analysis (FIA) is an excellent technique to manage solutions [8], the present work reports on the development of a combined automated FIA-SDA system for real sample applications. The method is applied to sodium determination in biodiesel samples and certified reference materials (CRMs) of milk, biological tissues and biodiesel by flame atomic emission spectrometry (FAES) employing Li as internal standard [2,9]. The efficiency of the FIA-SDA system is also checked by comparing its results with values obtained with the traditional methods of ES, SA and IS.

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http://dx.doi.org/10.1016/j.microc.2015.10.019
0026-265X/

2. Materials and methods

2.1. Reagents, analytical solutions and samples

High purity deionized water obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q™ Academic® deionizer system (resistivity 18.2 MΩ cm, Millipore, Bedford, USA) was used to prepare all solutions.

Analytical solutions were prepared by appropriate dilution of 1000 mg L^{-1} Na and Li stock solutions (SpecSol, São Paulo, Brazil). Distilled ethanol was used for biodiesel samples dilution. Nitric acid 70% (JT Baker, Phillipsburg, USA) and H_2O_2 30% v v^{-1} (Merck, Darmstadt, Germany) were used for CRMs digestion.

All solutions were stored in high-density polypropylene flasks (Nalgene, Rochester, USA). All plastic containers and glassware materials were decontaminated by soaking in 10% (v v^{-1}) HNO_3 for at least 24 h, and then rinsing abundantly in deionized water before use.

Biodiesel samples provided by the Monitoring and Research Center of Fuel Quality, Biofuels, Oil and Derivatives (CEMPEQC, Araraquara, Brazil) were stored in amber glass flasks in a refrigerator (about 5 °C) before analysis. A mass of 2.0 g biodiesel samples and 2.0 g biodiesel standard oil (Conostan, Baie-D'Urfé, Canada) were directly weighed into 15-mL polypropylene graduated flasks (Corning, New York, USA) and the volumes were made up to 10 mL with distilled ethanol [10,11].

All CRMs (1549 Non-Fat Milk Powder, 8435 Whole Milk Powder, 1577b Bovine Liver, and 2976 Mussel Tissue) from the National Institute of Standards and Technology (Gaithersburg, USA) were prepared by microwave-assisted wet digestion. Sample masses of *ca.* 200 mg were accurately weighed and transferred to microwave flasks followed by 3.0 mL HNO_3, 1.0 mL H_2O_2 and 2.0 mL of deionized water. Then, the mixtures were heated using the following five-step microwave program: (1) 15 min from 0 to 600 W; (2) 5 min at 600 W; (3) 15 min from 600 to 800 W; (4) 5 min at 800 W and (5) 20 min at 0 W (cooling). After cooling, the digests were transferred to 25 mL volumetric flasks and diluted to the mark with deionized water.

2.2. Instrumentation

An Analyst 100 Perkin Elmer flame atomic absorption spectrometer (Shelton, USA) equipped with a 50-mm burner head was used for sample nebulization and analyte excitation. An air-acetylene flame was employed for Na and Li excitation. The optimum air-acetylene flow-rates for Na and Li excitation was a 4:2 (air:acetylene) ratio. Acetylene with 99.7% purity (Air Liquid, São Paulo, Brazil) was used as fuel gas.

The emission intensities from Na and Li were measured at 586.98 nm and 667.43 nm, respectively, using an USB 650 Red Tide Ocean Optics spectrometer (Dunedin, FL, USA). The acquisition of emission signals by the Ocean Optics spectrometer (SpetraSuite software) employed a 50-ms integration time in high-speed mode (6000 spectra recorded by each analytical cycle).

An IPC-8 Ismatec peristaltic pump (Zurich, Switzerland) furnished with Tygon® tubes was used for pumping solutions.

A Multiwave 3000 Anton Paar (Graz, Austria) microwave oven with a rotor of 48 reaction PFA vessels (internal volume of 50 mL) was used to digest all CRMs.

2.3. The flow system

The FIA-SDA system comprised a peristaltic pump, Tygon® pumping tubes, a manual injector-commutator [12], a flame atomizer, a fiber-optic spectrophotometer, polyethylene tubing (i.d. 0.8 mm), coiled reactor and accessories. The flow diagram of the simultaneous Na and Li signal acquisition system is shown in Fig. 1. The operation of the injector-commutator IC involves the sequential introduction of solutions A and B in the system. In the position specified in the figure, an aliquot of solution A (S_A) selected by the loop L_1 is injected into the water carrier stream (C). The established sample zone reaches the atomizer and a steady-state emission signal is measured. After 150 s, the IC is switched and the solution B (S_B) selected by the loop L_2 is injected into the carrier C. Passage of the sample zone through the flame results in a steady-state signal. After baseline restoration, another cycle can be started. A typical signal profile obtained with the proposed flow system is depicted in Fig. 2.

2.4. Analytical procedure

The SDA method [7] requires just a blank and two analytical solutions (A and B) for each sample. Solution A is a mixture of standards (analyte plus internal standard) and sample (1:1 ratio by volume), and solution B is a mixture of sample and blank solutions (1:1 ratio by volume). The solutions must be simultaneously measured in order to obtain a typical SDA graph [7]. Considering the flow system in Fig. 1, the injected sample volume (length of the sampling loops) and the length of reactor coil were evaluated to ensure well-defined steady-state

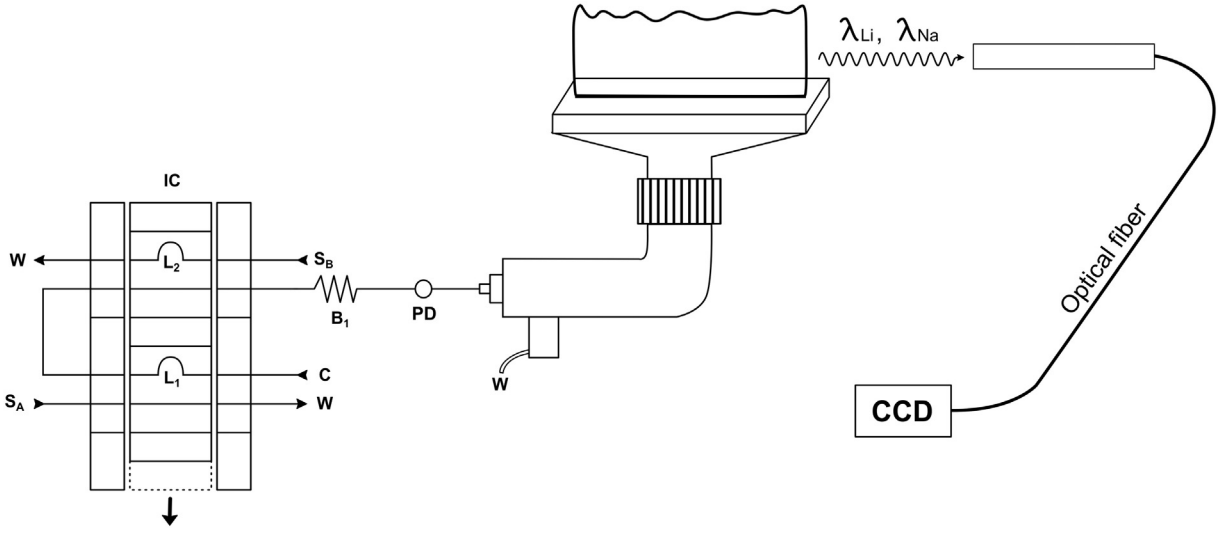

Fig. 1. Flow diagram of the FIA-SDA system for sodium determination. IC: injector-commutator, L_1, L_2: sampling loops (2.5 mL), B_1: coiled reactor (110 cm); C: blank solution (1.0 mL min^{-1}), S_A: solution A (1.0 mL min^{-1}), S_B: solution B (1.3 mL min^{-1}), PD: pulse dampener, W: wastes; CCD: detector (586.98 and 667.43 nm). The downward arrows indicate the movement of the central part of IC.