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Automatable on-line generation of calibration curves and standard additions in solution-cathode glow discharge optical emission spectrometry

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ABSTRACT

Two methods are described that enable on-line generation of calibration standards and standard additions in solution-cathode glow discharge optical emission spectrometry (SCGD-OES). The first method employs a gradient high-performance liquid chromatography pump to perform on-line mixing and delivery of a stock standard, sample solution, and diluent to achieve a desired solution composition. The second method makes use of a simpler system of three peristaltic pumps to perform the same function of on-line solution mixing. Both methods can be computer-controlled and automated, and thereby enable both simple and standard-addition calibrations to be rapidly performed on-line. Performance of the on-line approaches is shown to be comparable to that of traditional methods of sample preparation, in terms of calibration curves, signal stability, accuracy, and limits of detection. Potential drawbacks to the on-line procedures include signal lag between changes in solution composition and pump-induced multiplicative noise. Though the new on-line methods were applied here to SCGD-OES to improve sample throughput, they are not limited in application to only SCGD-OES—any instrument that samples from flowing solution streams (flame atomic absorption spectrometry, ICP-OES, ICP-mass spectrometry, etc.) could benefit from them.

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1. Introduction

In recent years, a large number of compact plasma sources that make use of solution electrodes [1] have been developed based on the design originally reported by Cserfalvi and co-workers [2]. One such device, the atmospheric-pressure solution-cathode glow discharge (SCGD), has garnered significant attention due to the advantages it offers over conventional plasmas for atomic optical emission spectrometry (OES) [3–11]. The SCGD is both inexpensive and simple, requires no compressed gases or sample-solution nebulizer, and operates at low direct-current power (~70 W). Despite its simplicity, the SCGD exhibits performance competitive with larger, more complex sources; detection limits are generally on par with, and in some instances, better than those achievable with radially viewed inductively coupled plasma (ICP)-optical emission spectrometry [6,7,9].

Regrettably, the SCGD suffers more from matrix interferences than does the ICP [5]. As a consequence, only relatively simple samples have been analyzed accurately with simple calibration methods [12–14]. More complex samples have necessitated use of standard

additions in order to obtain accurate results [5,15–22]. Unfortunately, standard additions, though capable of overcoming the matrix interferences, are typically tedious, time-consuming, and reduce sample throughput. Methods that automate or increase the speed at which standard-addition analyses can be performed are therefore highly desirable for use with SCGD-OES.

Although automation is a common current theme in analytical instrumentation, most modern instruments automate only the sample-introduction and data-collection processes. As a result, the main bottleneck to analysis remains the off-line preparation of calibration standards and samples. To reduce human error and the time required for sample preparation and analysis, several studies have focused on instruments that prepare calibration standards and samples on-line, or obviate the need for several standards to be prepared. Among these studies are methods based on flow-injection [23,24], which enable on-line standard additions and calibration to be performed. Unfortunately, these methods suffer from poorer precision than traditional analyses and are difficult to fully automate. Other methods focused on the use of multiple peristaltic pumps to mix solutions on-line to generate linear concentration gradients from which calibration curves can be derived [25,26]. Though these techniques promote rapid calibration and standard additions, they suffer from inaccuracies caused by washout time of the pumping systems. Further, because continuously

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changing concentration gradients were used, the concentration delivered to the detector did not remain constant long enough to yield good precision.

Starn and Hieftje [27] investigated the use of gradient high-performance liquid chromatography (HPLC) pumps for on-line solution preparation and delivery for atomic absorption spectrometry and ICP-OES [28]. These studies used stepped gradients to generate specific concentrations of a stock standard solution on-line, and were shown to exhibit performance comparable to traditional methods of calibration. Unfortunately, due to limitations of the available HPLC pumps, flow resolution was restricted and there were only two sample inlet lines; as a result, application of the method to standard additions was unsuccessful.

Here, a system similar to that of Starn and co-workers [27,28] was employed to enable automated, on-line generation of calibration curves and standard-additions plots with SCGD-OES. The new system uses a quaternary-gradient HPLC pump capable of providing and proportioning flows from up to four solution inlet lines. This system performed on-line mixing of a sample solution, stock standard and diluent, which enables standards and samples of specific concentrations to be prepared in a rapid and automated fashion. Results from the system were critically compared to traditional methods of calibration and standard addition and found to be comparable. Given that HPLC pumps are expensive to purchase and maintain, the method was extended to a system of three

peristaltic pumps. This inexpensive arrangement could perform the same functions of the gradient HPLC pump and also provides analytical results comparable with traditional methods of calibration. Potential drawbacks to both methods (lag between changes in solution composition and pump-induced multiplicative noise) are described and evaluated.

2. Experimental

2.1. Pumps and equipment for on-line calibration systems

Fig. 1(A) and (B) shows schematic diagrams of the two setups used to perform on-line calibrations and standard additions with the SCGD. The first of these two systems, displayed in Fig. 1(A), employs a quaternary, gradient, HPLC pump (Hitachi, Japan, model L-7100) as a solution mixing and delivery device. This module is a dual-plunger type, series connection reciprocating pump that can provide solution flows from 0.001 to 10.000 mL min⁻¹ in 0.001 mL min⁻¹ increments with $\pm 2\%$ accuracy. It is equipped with four separate, solenoid-controlled solution inlets through which the fraction of total flow contributed from each line can be adjusted in increments of 1% with a range from 0 to 100%. The pump is also fitted with an onboard dynamic (stirring-mode) solution mixer with an approximate void volume of 2.0 mL. Solution delivery and flow ratios were automated with the system's onboard

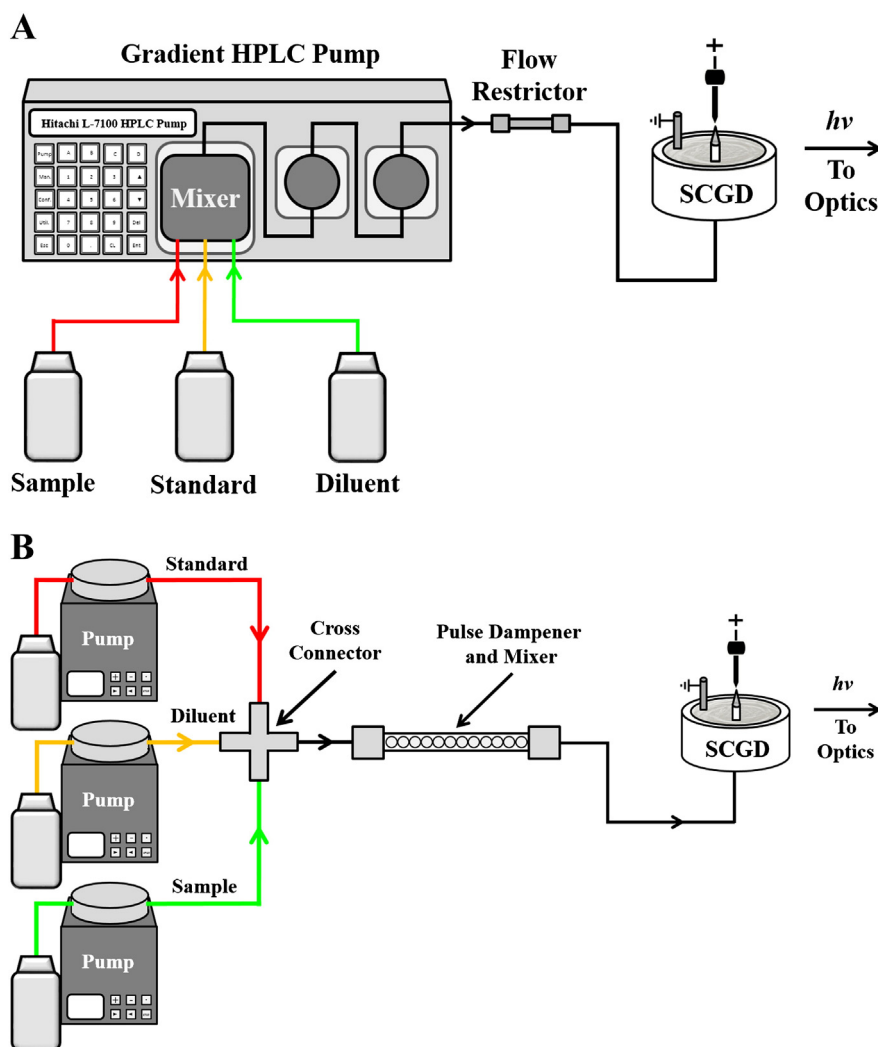


Fig. 1. Schematic diagrams of the two systems used for on-line calibration interfaced to the SCGD. Panel (A) exhibits the gradient HPLC pump system, while (B) shows the peristaltic pump system.

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