Spatially resolved measurements to improve analytical performance of solution-cathode glow discharge optical-emission spectrometry

Andrew J. Schwartz, Steven J. Ray, George C.-Y. Chan, Gary M. Hieftje

PII: S0584-8547(16)30253-1
DOI: doi: 10.1016/j.sab.2016.10.004
Reference: SAB 5152

To appear in: *Spectrochimica Acta Part B: Atomic Spectroscopy*

Received date: 21 June 2016
Revised date: 24 August 2016
Accepted date: 1 October 2016

Please cite this article as: Andrew J. Schwartz, Steven J. Ray, George C.-Y. Chan, Gary M. Hieftje, Spatially resolved measurements to improve analytical performance of solution-cathode glow discharge optical-emission spectrometry, *Spectrochimica Acta Part B: Atomic Spectroscopy* (2016), doi: 10.1016/j.sab.2016.10.004

Spatially Resolved Measurements to Improve Analytical Performance of Solution-Cathode Glow Discharge Optical-Emission Spectrometry

Andrew J. Schwartz,[1] Steven J. Ray,[1,2], George C.-Y. Chan,[1,3] and Gary M. Hieftje[1]*

[1]*Department of Chemistry, Indiana University, Bloomington, IN 47405, USA.*

[2]*Present address: Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260, USA.*

[3] *Present address: Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.*

Corresponding Author E-mail: hieftje@indiana.edu; Fax: +1 812 855 0958; Tel.: +1 812 855 2189

Abstract

Past studies of the solution-cathode glow discharge (SCGD) revealed that elemental and molecular emission are not spatially homogenous throughout the source, but rather conform to specific zones within the discharge. Exploiting this inhomogeneity can lead to improved analytical performance if emission is collected only from regions of the discharge where analyte species emit strongly and background emission (from continuum, elemental and/or molecular sources) is lower. Effects of this form of spatial discrimination on the analytical performance of SCGD optical emission spectrometry (OES) have been investigated with an imaging spectrograph for fourteen atomic lines, with emphasis on detection limits and precision. Vertical profiles of the emission intensity, signal-to-background ratio, and signal-to-noise ratio were collected and used to determine the optimal region to view the SCGD on a per-element basis. With optimized spatial filtering, detection limits ranged from 0.09–360 ppb, a 1.4–13.6 fold improvement over those obtained when emission is collected from the full vertical profile (1.1–840 ppb), with a 4.2-fold average improvement. Precision was found to be unaffected by spatial filtering, ranging from 0.5–2.6% relative standard deviation (RSD) for all elements investigated, closely comparable to the 0.4–2.4% RSD observed when no spatial filtering is used. Spatial profiles also appear useful for identifying optimal line pairs for internal standardization and for flagging the presence of matrix interferences in SCGD-OES.

Keywords: Solution-Cathode Glow Discharge, Optical-Emission Spectrometry, Instrumentation, Spatial Discrimination

Introduction

Studied as sources for atomic optical emission spectrometry (OES) for over twenty years [1, 2], solution-electrode glow discharges (SEGD), a class of atmospheric-pressure glow discharge where one or both electrodes is a flowing liquid, have garnered a great deal of interest within the spectrochemistry community [3-5]. Among the many SEGD designs reported in the literature [3-5], those based on the original system of Cserfalvi and co-workers [1, 2], often referred to as the electrolyte-cathode discharge or solution-cathode glow discharge (SCGD), have demonstrated important advantages over conventional plasma sources for solution analysis, such as inductively coupled plasma (ICP). Unlike the ICP, the SCGD is compact, utilizes no compressed or flowing gases, does not require a nebulizer and operates at low direct-current power.

Though initial evaluation of the SCGD and similar sources yielded poor figures of merit compared to the ICP [1, 2, 6-8], a myriad of advancements have bolstered analytical performance and expanded applicability. Reduction in cathode diameter [9], reversal of the discharge polarity [10], and solution modification [11-13] have improved limits of detection with SCGD-OES. Methods to overcome matrix effects and boost sample throughput have been realized through automated calibration schemes [14] and