Spectrochimica Acta Part B 64 (2009) 1185–1193

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Simultaneous multielement detection in particle beam/hollow cathode-optical emission spectroscopy

C. Derrick Quarles Jr., R. Kenneth Marcus *

Department of Chemistry, Biosystems Research Complex, Clemson University, Clemson, South Carolina 29634-0973, United States

ARTICLE INFO

Article history:
Received 1 July 2009
Accepted 21 August 2009
Available online 31 August 2009

Keywords:
Particle beam
Hollow cathode
Optical emission spectroscopy
Simultaneous multielement analysis
Metallomics

ABSTRACT

Presented here is the development of a particle beam/hollow cathode-optical emission spectroscopy source that has been interfaced with a high resolution polychromator for use as a species-specific detector for chromatographic separations. Use of the high resolution JY RF-5000 polychromator allows simultaneous, multielement analysis; a necessary requirement for comprehensive speciation analysis. Parametric optimization was performed for the nebulization conditions, desolvation temperature, glow discharge current and pressure, and the source block temperature (vaporization) using nitrate salts containing lead, nickel, and silver. Peak area, height, and width were recorded for optical emission of Pb (I) 220.35 nm, Ni (I) 341.41 nm, and Ag (I) 338.28 nm in order to determine optimal peak characteristics under chromatographic separation conditions. Response curves for a multielement salt solution containing Pb, Ni, and Ag were obtained using the optimized conditions, with detection limits for triplicate injections of 2.2, 0.17, and 0.19 ng, respectively. The ability to monitor multiple elements simultaneously reveals the existence of interelement matrix effects that have not been noted previously in hollow cathode devices. The ability to monitor metals and non-metals is demonstrated towards the future application of this system as a tool for metallomic studies.

1. Introduction

Metals account for less than 2% of the total body weight in the human body, but contribute to crucial roles such as structural/stabilization of compounds/proteins, binding substrates for regulation, enzyme catalysis, oxygen transport, signal transduction, and controlling redox reactions [1–4]. Current challenges are ongoing in the determination of metal content, speciation, localization, and use within organisms to give a better understanding to the factors that govern metal binding and selectivity within them [1,4]. Unlike metals in the earth's crust, the abundance of metals in the human body is on the trace level [3]. The ability to detect and identify trace amounts of metals within a given compound is a primary goal of metal speciation, but this only tells a small part of the story. The ability to analyze and detect not only the metal, but also to deduce the entire make-up of the compound or protein based on the total elemental composition, is the more relevant information regarding the function of the compound/protein. This laboratory refers to this type of methodology as "comprehensive speciation".

Typically, metal speciation is performed using high-performance liquid chromatography (HPLC) or capillary electrophoresis (CE) coupled with inductively coupled plasma-optical emission or mass spectrometry (ICP-OES/MS) [5,6]. These techniques lack the ability to detect non-metals such as carbon, hydrogen, nitrogen, and oxygen with high sensitivity due to constant backgrounds in/from the plasma [7,8], particularly when they are present in the chromatographic mobile phases. Common tools in proteomics, matrix assisted laser desorption ionization (MALDI) and electrospray ionization MS (ESI MS) provide fundamental information as it applies to proteins, but these techniques only give the molecular information and do not readily yield the inorganic/elemental information needed to gather a full picture of the protein–metal interaction [9]. Relative to atomic spectroscopy methods, they suffer from poor sensitivity and quantification power due to the complex matrix effects from biological samples/buffer systems. Techniques supplying both molecular and atomic information would be very powerful contributors in the field of metallomics.

This laboratory has previously developed a liquid chromatography-particle beam/hollow cathode-optical emission spectrometer (LC-PB/HC-OES) that can analyze inorganic and/or organic samples, providing empirical formulas based on element ratios (including C, H, N, O, S, and metals), with detection limits on the single ng mL^{-1} level and below [10–13]. The PB/HC-OES system combines the excitation properties of a glow discharge (GD) source with the solvent removal capabilities of the particle beam (PB) to allow dry analyte particles to reach the hollow cathode (HC) GD region [7]. Use of the PB allows work in an inert (discharge gas) atmosphere plasma, in the absence of solvent remnants, which makes it possible to detect "gaseous" elements and non-metals such as C, H, N, O, S, and P with high

* Corresponding author. Tel.: +1 864 656 5011; fax: +1 864 656 0567.
E-mail address: marcusr@clemson.edu (R.K. Marcus).

0584-8547/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2009.08.004

sensitivity. Previous experiments using monochromator detection system include determinations of metal salts and organometallic compounds, as well as the non-metal detection of proteins and amino acids based on C and H content [11–18]. Improvements have been made by substituting the monochromator with a polychromator, allowing for simultaneous, multielement detection, thus reducing data collection times, sample sizes, and the dependence on chromatographic retention times to substantiate elemental correlations. In addition, the use of a nitrogen-purged spectrometer permits enhanced detection of many of the non-metal elements at more sensitive transitions that lie in the vacuum-UV region of the spectrum.

Presented here is the evaluation of the PB/HC-OES using the polychromator from a JY RF-5000 as the detector. This instrument was originally operated as an rf-GD-OES instrument used for solids analysis, but the commercial rf-GD source has been removed and the new HC source added in its place. Direct mounting of the PB/HC with the polychromator required changes to the source block geometry; as a result optimization of working parameters was needed. Nitrate salts (silver, lead, and nickel) were chosen for the optimization studies, because they present a range of physical, chemical and spectroscopic properties. The ability to monitor Cu (I) and Ar (I) during analysis provides insights into interesting interelement and matrix effects; effects that were not observed using the monochromator. Spectroscopic and temporal responses of the elemental constituents of different proteins are presented to demonstrate the utility of this approach in metallomics. These studies set the groundwork for using this system as a detector across the breadth of metal speciation.

2. Experimental

2.1. Sample preparation and solution delivery

High-purity (18.2 MΩ-cm) Barnstead Nanopure (Dubuque, IA) water and HPLC grade methanol (EMD Chemicals, Cincinnati, OH) were used for preparation of metal salt samples and as the mobile phase solutions. Stock solutions (1000 μg mL^{-1}) of lead nitrate, nickel nitrate, and silver nitrate (Sigma-Aldrich, St. Louis, MO) were prepared in 50% HPLC grade methanol and 50% Nanopure water and stored at room temperature in the dark. Protein solutions of hemoglobin, myoglobin, and cytochrome *c* (Sigma-Aldrich) were prepared in 0.1% trifluoroacetic acid (TFA) (Fisher Scientific, Fair Lawn, NJ). A Waters (Milford, MA) model 510 high-performance liquid chromatography pump with a six-port Rheodyne 7125 (Rohnert Park, CA) injection valve using a Rheodyne 10 μL injection loop was used for delivery of sample solutions to the PB interface.

2.2. Particle beam interface

A Thermabeam (Extrel Corporation, Pittsburgh, PA) particle beam interface (Fig. 1) was used to introduce the sample into the hollow cathode glow discharge source [7]. This interface consists of a thermoconcentric nebulizer, a desolvation chamber, and a two-stage momentum separator. Liquid flow enters the nebulizer through a fused-silica capillary (100 μm i.d.) positioned inside of a metal tube that has a DC potential applied across its length. This potential creates thermal energy that is transferred to the coaxial flow of He gas, which passes across the tip of the capillary to affect aerosol generation. This spray enters the desolvation chamber, which is wrapped with heating tape for variable temperature control. The particle-containing gas stream is then introduced into a two-stage momentum separator that removes low mass gas molecules (solvent and He nebulizer gas), delivering dry analyte particles (<10 μm size [19,20]) to the HC source volume.

2.3. Hollow cathode glow discharge source

The HC glow discharge design was altered slightly from the one employed in previous works [10–13,15–19,21,22]. The HC was machined from a bulk copper rod with an inner diameter of 3.5 mm

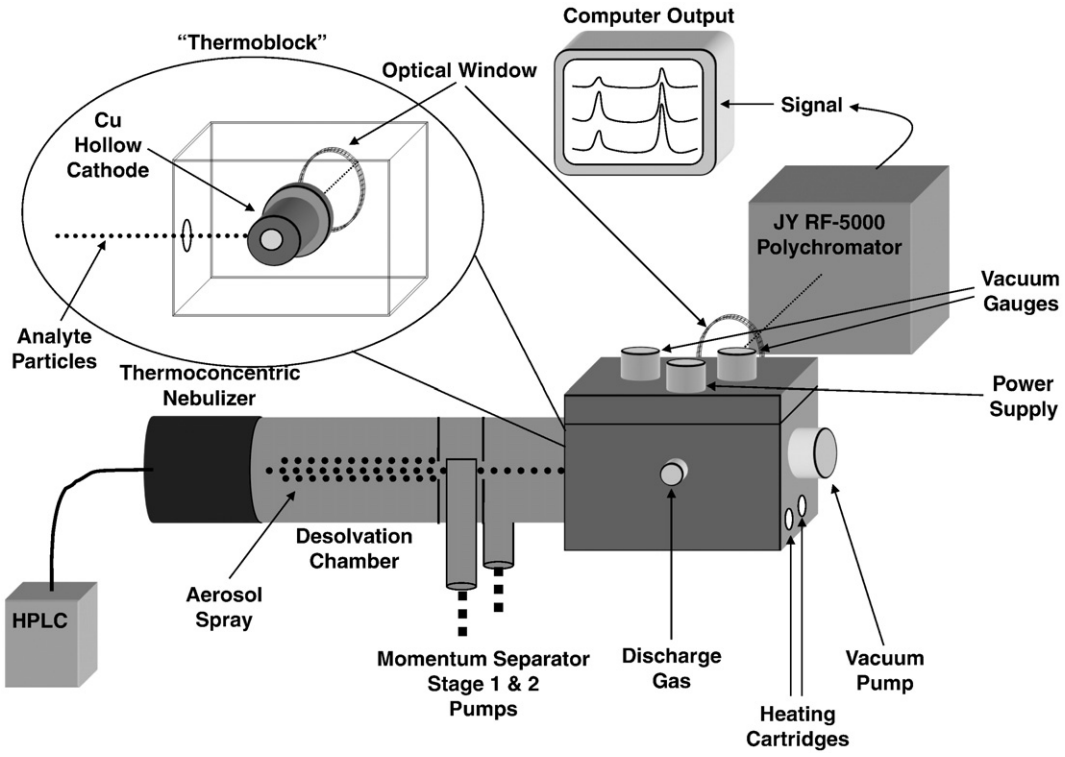

Fig. 1. Diagrammatic representation of HPLC-PB/HC-OES system.