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The Characterization of an Electrothermal Vaporization-Direct Current Plasma Atomic Emission Spectrometer for the Determination of Boron, Cadmium, Copper, Iron, and Lead

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ABSTRACT

A graphite rod electrothermal vaporizer used to introduce microliter-sized samples into a direct current plasma (DCP) atomic emission spectrometer is reported in this work. Several important experimental conditions were found to be important in achieving good analytical performance from the electrothermal vaporization (ETV-DCP) system. A combination of lowered plasma electrode sleeve gas flow rates, when compared to that commonly used in the DC plasma jet, and relatively low carrier gas flow rates resulted in very good analytical performance. Relative precision for the ETV-DCP instrument using B, Cd, Cu, Fe, and Pb solutions ranged between 4% and 10%. Limits of detection (LOD) lower than 100 pg were achieved for these elements, roughly an order of magnitude better than other ETV-DCP studies that used commercial graphite boat/furnace combinations. In addition, good calibration linearity was observed, with 2–4 orders of magnitude linearity for the elements investigated.

Key Words: Electrothermal vaporization; Direct current plasma; Sample introduction; Atomic emission spectrometry.

INTRODUCTION

Electrothermal vaporization (ETV) has been routinely investigated as an approach to introduce samples into atomic emission sources for elemental determinations. It has been extensively and successfully applied to inductively coupled plasmas (ICP) and inductively coupled plasma-mass spectrometers (ICP-MS), with benefits including improved sample transport efficiency, excellent absolute limits of detection (LOD), and applicability to the direct determination of elements in solid samples.^[1–6] The use of ETV for sample introduction into the direct current plasma (DCP) has received much less attention.^[7–12] These published studies have identified ETV carrier gas flow rates, DCP viewing zone, and the angles of the plasma jet electrodes as key parameters in obtaining reasonable emission signals and good performance. However, only limited explorations of the carrier gas flow rate and DCP plasma jet conditions were presented, with most studies employing conditions typical of the use of pneumatic nebulization (PN) with the DCP.

Sneddon et al. employed a modified, commercial graphite furnace atomizer, introducing samples onto a microboat contained in a graphite tube.^[7–10] In their work, only limited explorations of the impact of carrier gas flow were mentioned, with the majority of the discussion focusing on the choice of a 0.6 L/min flow rate for the determination of copper.^[9] Data were not presented for the other four elements studied or in their other published work

on the determination of Au and Hg in algal cells.^[7,8] No explorations on the impact of DCP plasma jet conditions were mentioned.

Elliot et al. also interfaced a modified commercial graphite furnace for sample introduction into a DCP.^[11] The performance of their instrument was studied using Al, Cu, and Mn solutions, optimizing the observation region and using relatively high carrier gas flow rates (ranging from 2.2 to 2.8 L/min). Their results showed good precision (~6% RSD), but relatively high LODs. Little data were presented on the influence of carrier gas flow rates on ETV-DCP performance and no exploration of the DCP plasma jet conditions were mentioned.

Buckley and Boss developed a tungsten filament vaporizer and interfaced it with a DCP.^[12] Samples of 1 μ L were rapidly vaporized from a tungsten filament to reduce the width of sample emission profiles. Good emission signals were obtained using high carrier flow rates (about 3.5 L/min) and by narrowing the angle of the DCP plasma jet anodes. No alteration of any other DCP plasma jet operating condition was mentioned. Excellent absolute LODs were reported, reaching the picogram level for the elements studied, but the relative precision of their system was high (10–14% RSD), likely a result of manually pipetting 1 μ L samples.

In this paper, we describe an ETV-DCP system based on a carbon rod atomizer, onto which sample volumes as large as 40 μ L can be introduced. The ETV working head, contained within a simple glass bell housing, is coupled directly to the DCP sample introduction tube. This work explores the influence of carrier gas flow rates, carbon rod design, and DCP sleeve gas flow rates on the performance of the ETV-DCP system. The results in this paper show improved absolute LOD, when compared to previous published data and very good relative precision, ranging from 4% to 10% RSD for the five different elements studied.

EXPERIMENTAL

Instrumentation

The ETV-DCP system used in this work was based on a Beckman SpectraSpan V (Thermo-Elemental, Waltham, MA) DCP containing a single channel Echelle spectrometer with a reciprocal linear dispersion of 0.082 mm/nm and a Hamamatsu Model R292 photomultiplier tube (Hamamatsu Corporation, Bridgewater, NJ). The plasma jet compartment of this instrument was modified to fit the ETV assembly and provide rapid coupling of the ETV to the plasma sample introduction tube. The ETV working head was a Varian CRA-61 Carbon Rod Atomizer (Varian, Inc., Palo Alto, CA), whose



temperature was controlled using a Perkin-Elmer HGA-2200 (Perkin-Elmer, Wellesley, MA) graphite furnace controller and power supply. The working head was mounted in a custom-built aluminum base and was enclosed in a custom bell housing made from Pyrex glass, as illustrated in Fig. 1. The ETV bell housing was attached directly to a modified DCP glass sample introduction tube using an 18/9 glass ball and socket combination. The total distance between the carbon rod and the DCP viewing zone was approximately 20 cm. Wavelength alignment in the spectrometer was performed using aqueous elemental standards that were pneumatically nebulized with a standard DCP ceramic nebulizer or by using appropriate hollow cathode lamps that were focused on the spectrometer entrance slit.

One-piece, pyrolytically coated graphite rods were custom manufactured by Poco Graphite, Inc. (Decatur, TX). The graphite rods (length: 2.56 in., diameter: 0.18 in.) were designed with two different sample cup dimensions, allowing maximum sample volumes of 10 μ L (cup diameter: 0.08 in., depth: 0.09 in.) and 40 μ L (cup length: 0.56 in., width: 0.08 in., depth: 0.09 in.)

Data Collection

Transient emission signals were collected by connecting the analog output of the spectrometer to a chart recorder and also to a 12 bit A/D converter

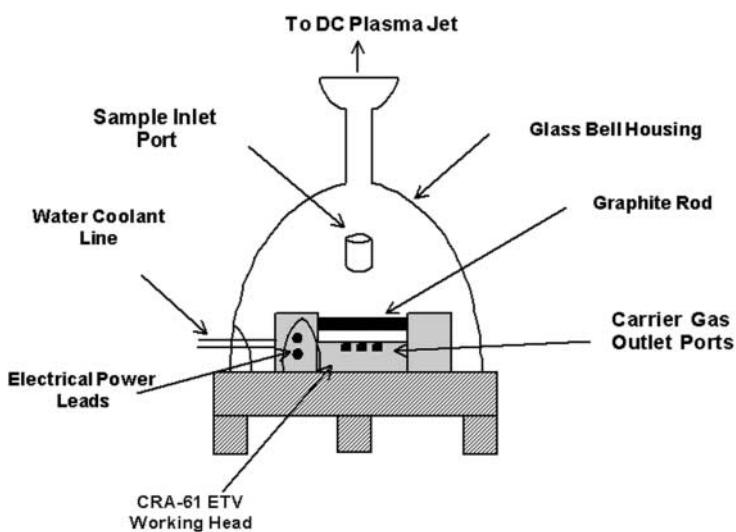


Figure 1. Diagram of ETV working head, mount and bell housing assembly.



interfaced with an IBM compatible personal computer. A signal pulse from the ETV controller was used to trigger the PC collection of data immediately prior to the vaporization of samples into the DCP. Unkelsope Level 2 Plus software (UNKEL Software, Inc., Lexington, MA) was used for the computer data collection.

Chemicals and Solutions

All elemental standards used were serially diluted from 1000 $\mu\text{g}/\text{mL}$ stock standards prepared using high-purity solid salts and trace-metal grade acids. Water used in the work was purified to 18 $\text{M}\Omega$ resistivity using a Millipore Milli-Q (Millipore Corporation, Billerica, MA) water purification system. Polyethylene bottles, glassware, and volumetric flasks were cleaned using dilute nitric acid, followed by rinsing with the same high purity water used in the preparation of elemental standard solutions.

Procedure

The performance of the ETV-DCP instrument was investigated using five different elements, including B, Cd, Cu, Fe, and Pb. Samples of aqueous standards in the range of 5–30 μL were manually transferred with a micropipet onto the graphite rod through an access hole in the glass bell housing. After depositing the sample, a temperature program specific to the element of interest was applied to the graphite rod to vaporize the sample. The vaporized sample was transported into the DCP jet using argon carrier gas introduced beneath the graphite rod inside the ETV working head. Carrier gas flow rates were experimentally optimized for each individual element of interest. All final temperature programs and carrier flow conditions ultimately used for ETV-DCP performance measurements are shown in Table 1. The final operating conditions of the plasma jet as well as the spectral measurement parameters for elemental emissions are shown in Table 2. Transient analyte emission signals were evaluated using both peak height and area measurements.

RESULTS AND DISCUSSION

ETV Temperature Program

The final ETV temperature programs shown in Table 1 were developed by initially using time/temperature conditions commonly employed in graphite



Table 1. ETV final experimental parameters.

		B	Cd	Cu	Fe	Pb
Drying stage	Temperature (°C)	110	125	130	125	120
	time (sec)	30	20	20	20	20
Ashing stage	Temperature (°C)	350	250	875	400	450
	time (sec)	40	30	30	30	30
Vaporization stage	Temperature (°C)	2,300	1,100	2,100	2,400	1,600
	time (sec)	5	6	6	6	7
Ar carrier gas	Flow rate (L/min)	1.0	0.2	0.7	1.0	0.8
	pressure (psig)	20	20	20	20	20

furnace atomic absorption spectrophotometry (GFAAS) determinations.^[13] These temperatures were experimentally optimized using 5 µL samples of each element at a concentration of 1 µg/mL. A particular emphasis was made on studying the ashing and vaporization steps of the temperature program. An ETV carrier gas flow rate of 1.0 L/min was used to transport samples to the DCP. The DC plasma jet was operated with electrode sleeve gas flow rates of ~1.0–1.5 L/min, sufficient to maintain a well-defined, “thermally pinched” plasma, as commonly used with standard pneumatic nebulizers for the DCP.

Table 2. DCP Experimental conditions.

Element	Wavelength (nm)	Order
B	249.773	90
Cd	228.802	98
Cu	324.759	69
Fe	259.940	86
Pb	368.438	61
Plasma jet operating current	7 A	
Plasma jet operating voltage	~40 V	
Electrode sleeve pressure	50 psig	
Electrode sleeve flow rates	0.75 L/min	
Plasma viewing zone	~2 mm below edge of “halo” discharge	
Entrance slit (W × H in µm)	50 × 300	
Exit slit (W × H in µm)	100 × 300	



The key consideration in choosing an ashing temperature was preventing the loss of analyte prior to the vaporization stage. Ashing temperatures were varied, beginning with a temperature of approximately 200°C and increasing temperatures in 50°C intervals. The peak area emission signal was measured during the vaporization stage of the temperature program. A decrease in the peak area of the element's emission indicated the temperature at which premature vaporization each element occurred. Ashing temperatures were chosen to be approximately 100°C lower than the highest temperature in which no premature elemental loss was observed.

Vaporization temperatures were studied similarly, beginning at relatively low temperatures (~900°C) and raised incrementally in 50°C steps. As temperature increased, peak area emission signals also increased, reaching a plateau in which no further change in the peak area was observed. The plateau indicated complete vaporization of the element from the surface of the graphite rod. Vaporization temperatures chosen for this study were approximately 100°C higher than beginning of the peak area signal plateau. A typical ETV signal-time response for Cu with appropriate temperature programing is shown in Fig. 2.

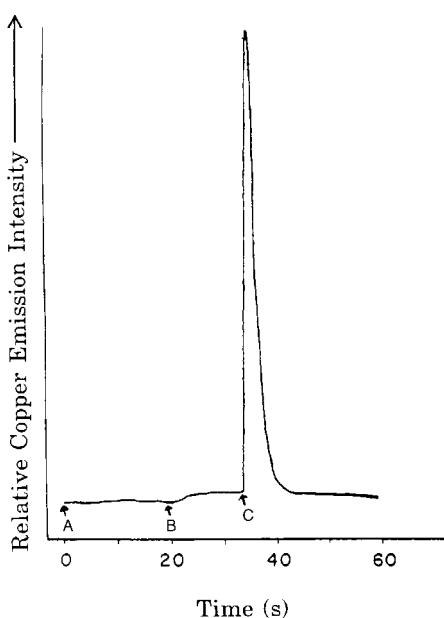


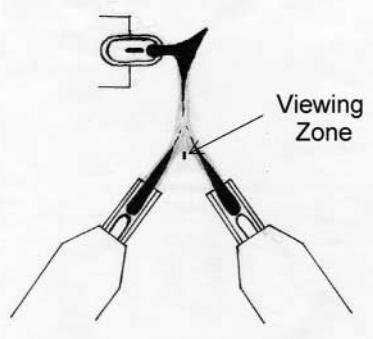
Figure 2. ETV-DCP emission signal response from copper. (A) drying stage; (B) ashing stage; and (C) vaporization stage.



DCP Electrode Sleeve Gas Flow Rates

The DC plasma jet was initiated with ETV carrier gas flow rates in the range of 1.0–1.5 L/min, causing the formation of a plasma whose legs were much less well defined than that expected from a DCP used with pneumatic nebulizers, as shown in Fig. 3(A). The crux of the inverted “Y” of the plasma was wider, less well defined, and possessed a grainy “halo” bordering into the excitation region of the plasma. Increasing the sleeve gas flow rates served to “thermally pinch” the discharge and create well-defined plasma legs, shown in Fig. 3(B). However, when the sleeve gas flows were increased, noticeable decreases in emission signals were observed from elements vaporized into the DCP. Experiments conducted to investigate the relationship of Cu emission vs. that of sleeve gas flow rate, showed that rates of 0.70–0.80 L/min gave the

A. Low Electrode Sleeve Gas Flow Rate



B. Normal Electrode Sleeve Gas Flow Rate

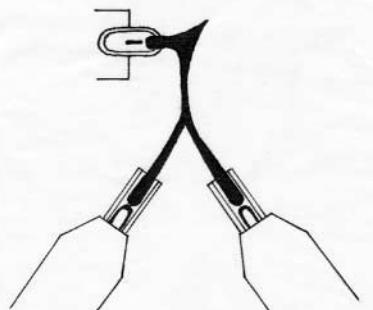


Figure 3. DCP Jet with variation in sleeve gas flow rates. (A) low sleeve gas flow rates (0.80 L/min) and (B) normal sleeve gas flow rates (1.5 L/min).



best emission signals, even though they resulted in a plasma discharge considered less thermally pinched. At flow rates lower than 0.6 L/min, the plasma jet became unstable and frequently extinguished, so further sleeve flow decreases were not explored. At higher sleeve gas flow rates, signals continually declined, with decreases nearing a factor of 2 when the sleeve gas flow rates reached levels creating a “thermally pinched” plasma (1–1.5 L/min). Similar results were observed with all other elements studied. As a result, all subsequent ETV-DCP measurements were made with low sleeve flow rates of 0.70–0.75 L/min. The final plasma viewing position chosen for these studies, shown in Fig. 3(A), was ~2 mm below the edge of the grainy halo at the crux of the plasma’s inverted “Y” juncture, where optimum emission signals were observed under the low sleeve flow conditions.

In a standard DCP jet that has a well-defined boundary between the sample excitation zone and the plasma legs, pneumatically nebulized samples skirt around the plasma legs and are excited by conduction of energy from the plasma legs to the viewing zone.^[14,15] At high sleeve gas flow rates, it is believed that the plume vaporized from the ETV tends to skirt rapidly around the legs of the “thermally pinched” plasma causing relatively poor conduction of energy from the plasma to the vaporized analyte. In the lower flow plasma, the vaporized analyte penetrates further into the plasma legs allowing greater conduction of energy from the plasma to the analyte. This improved interaction more increases the efficiency of excitation of the analyte element and thus results in a more intense emission signal than the more “thermally pinched” plasma.

ETV Carrier Gas Flow Rates

A third parameter considered essential to the achievement of good emission signals with our ETV-DCP instrument was that of sample carrier gas flow rate. Using DCP electrode sleeve gas flow rates of approximately 0.7 L/min and the temperature program conditions listed in Table 1, studies of the impact of carrier gas flow rate on the emission signal were conducted for B, Cd, Cu, Fe, and Pb. Five microliter samples of aqueous standards at 1 $\mu\text{g}/\text{mL}$ concentration were vaporized and transported into the DCP with variable carrier gas flow rates. The resulting relationship between carrier gas flow rates and relative emission signals for each of the elements studied are shown in Figs. 4 and 5. All emission signals were normalized to fit the same graph scale.

From element-to-element, there are significant differences in the carrier gas flow rates that give the best emission signals. Cadmium, shown in Fig. 4, gave best emission signals at carrier flow rates between 0.05 and 0.5 L/min, substantially decreasing above this flow range. Cu and Pb, Figs. 4 and 5, respectively, required flow rates that were between approximately



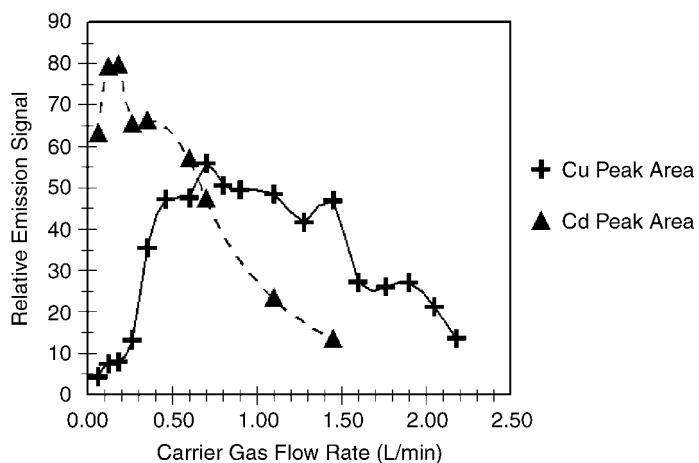


Figure 4. Effect of ETV carrier gas flow rate on Cd and Cu emission signals.

0.5–1.0 L/min. A rapid, nearly 10-fold loss in signal occurred when the flow rates were reduced to those optimal for Cd, with a more gradual decline at rates higher than 1.0 L/min carrier gas flow rate. Optimal signals for B and Fe were observed at flow rates between 1.0 and 1.2 L/min. As a result, all measurements assessing the performance of our ETV-DCP system were made at carrier gas flow rates considered best for each individual element.

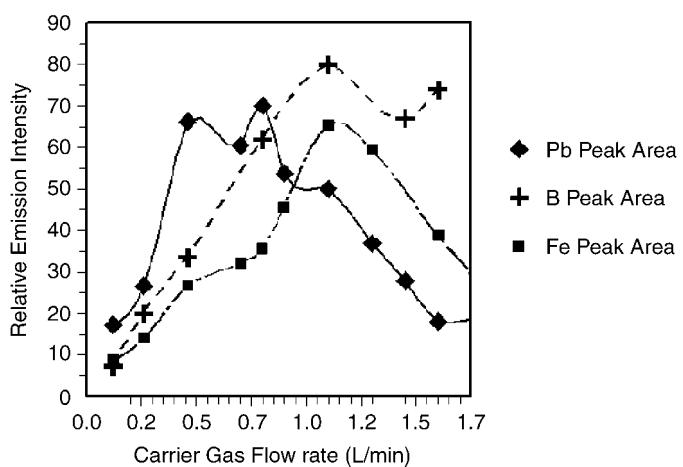


Figure 5. Effect of ETV carrier gas flow rate on B, Fe, and Pb emission signals.



If simultaneous determinations of two or more elements were to be attempted using ETV-DCP, compromises in both the vaporization temperatures and carrier gas flow rate will likely worsen the overall performance of the ETV-DCP instrument. Grouping elements with similar vaporization temperatures and carrier gas flow rate requirements, such as B and Fe, would provide conditions that would give good, though not optimum, performance for each element.

ETV-DCP Precision

In assessment of the quantitative performance of the ETV-DCP system, difficulties were encountered in pipetting samples into the cup on the standard, small volume graphite rod. The best observed precision when using these rods ranged from 7% RSD to 15% RSD, in large part due to the difficulty in precisely transferring samples into the very small diameter cup as well as the high random error contribution associated with the delivery of 5 μ L of liquid by a micropipet.

To improve the precision of sample transfer into the cup on the graphite rod, a new rod was constructed, with the potential to allow the transfer of sample sizes up to 40 μ L in volume. The larger cup size enabled greater ease in precisely positioning the sample into the cup and the delivery of larger volumes of sample. The overall precision for a fixed mass of Cu improved from 7.1% RSD for a 5 μ L sample of 1 μ g/mL Cu to 4.3% RSD for a 10 μ L sample of 0.5 μ g/mL Cu. Similar improvements in precision were observed with the other elements studied. Thus, the modified graphite rod design was used for all further quantitative investigations of the ETV-DCP instrument's analytical performance.

The short-term precision of the ETV-DCP instrument was explored for each of the five elements using the final experimental conditions shown in Tables 1 and 2 and the modified rod design. A total of 12 and 15 replicate 10 μ L samples of 1.0 μ g/mL concentration were used to determine the short-term precision of each element using peak area measurements. Overall, the %RSD for the five elements investigated ranged from roughly 4% to 10%, with typical %RSDs of 7–8% for B and Cd and 9–10% for Fe and Pb. Further improvements might be expected if larger volumes of sample were used.

Limits of Detection

The LODs for the ETV-DCP instrument were also measured. All LOD studies were performed using 10 μ L samples of blanks and aqueous standard solutions whose concentrations were \sim 0.050–100 μ g/mL. LODs were

calculated by determining the concentration (or mass) of an aqueous standard required to give a peak area signal three times the standard deviation of the blank noise. At least 12 blank measurements were used for each LOD determination. Both absolute LODs and concentration LODs were determined for the ETV-DCP.

Our ETV-DCP instrument gave concentration LODs in the low part-per-billion range, equivalent to or slightly better than that of PN into the DCP or the ICP. When comparing our results to that of GFAAS, B, Cu, and Fe were slightly better than GFAAS, while Cd and Pb were an order of magnitude worse. Only Cu, Fe, and Pb could be compared to previous studies involving ETV-DCP instruments. For those three elements, concentration LODs are roughly an order of magnitude better than those reported by Barnes^[11] or Sneddon,^[9,10] whose systems were constructed using conventional graphite furnace working heads and power supplies. When compared to the results reported by Buckley and Boss using a tungsten filament vaporizer to introduce samples into the DCP, the concentration LODs were of comparable magnitude. Our ETV-DCP gave values for LODs roughly one order of magnitude higher than the best reported values from ETV-ICP experiments for B, Cd, and Cu, but gave comparable LODs for Fe and Pb.

Table 3 shows a comparison of the absolute LOD values for the five elements that were explored. The absolute LODs show one of the benefits of ETV sample introduction when coupled to plasma emission sources, that of improved absolute amounts of analyte detectable when compared to PN sample introduction. Comparing our ETV-DCP results vs. that of the absolute LODs obtainable via PN into the DCP or ICP, improvements ranging from 20- to 400-fold were observed in absolute LODs.

ETV-DCP results in this study compared to previously published ETV-DCP studies that used conventional GFAAS components also showed improvements of an order of magnitude in absolute LODs. However, in comparison to the work of Buckley and Boss, the ETV-DCP results of this study were roughly an order of magnitude higher. Comparing ETV-DCP to ETV-ICP, the absolute LODs for B, Cd, and Cu in our experiments were roughly an order of magnitude higher than the best ETV-ICP results, though Pb and Fe were very close in magnitude. GFAAS absolute LODs were better by approximately an order of magnitude for the elements Cd, Cu, and Pb, but ETV-DCP was an order of magnitude better for B and Fe.

The combination of reduced sleeve gas flow rates and reductions in the carrier gas flow rates were believed largely responsible for improved LODs when compared to previous efforts involving GFAAS component based systems for vaporization into the DCP. In the work of Buckley and Boss, the use of the tungsten vaporizer instead of a graphite rod or furnace allowed more rapid vaporization of the analyte element.^[12] The rapid vaporization



Table 3. ETV-DCP absolute limits of detection.

Element	ETV-DCP				GFAAS (pg) ^[17]
	This study (pg)	Other work (pg)	PN-DCP (pg) ^[16]	PN-ICP (pg) ^[17]	
B	100	—	8,000	3,000	10
Cd	80	—	5,000	1,500	1
Cu	5	150 ^[11] /100 ^[9] /0.2 ^[10]	2,000	1,500	0.35
Fe	20	2 ^[10]	7,000	6,000	20
Pb	90	400 ^[12]	20,000	60,000	300
					15



reduced the peak width of the transient emission signal, resulting in a more concentrated packet of analyte reaching the plasma, thus gaining a greater signal-to-noise ratio. A combination of the rapid vaporization characteristics of a tungsten filament vaporizer with optimization of the carrier gas and electrode sleeve gas flow rates might serve to lower the LOD of ETV-DCP even further, approaching the performance of ETV-ICP.

Calibration Linearity

Good calibration linearity was observed using the conditions previously described. The limit of quantitation (LOQ) was determined by the concentration of element at 10 times the LOD. The limit of linearity for each calibration plot was the concentration in which noticeable rollover due to self-absorption occurred in the calibration. In all cases, linear calibration was observed over 2–4 orders of magnitude in concentration, with typical concentration ranges from 0.05 to 30 $\mu\text{g}/\text{mL}$ for Fe to 0.1–100 $\mu\text{g}/\text{mL}$ for B, Cd, Cu, and Pb linear dynamic ranges were all similar to that of Fe, with the exception that the LOQ for Cu was a factor of 10 lower than Fe.

CONCLUSION

This work demonstrates that a simple and relatively inexpensive electro-thermal vaporizer based on a carbon rod atomizer can be interfaced successfully with a DCP with excellent absolute LODs, good precision, and good calibration linearity. ETV sample introduction can also be used to minimize or eliminate sample decomposition and to allow matrix modification of complex samples. Combining the good observed analytical performance with the potential for minimal sample preparation will allow the use of this ETV-DCP system for trace level determinations of elements in samples, either directly from the solid state or with minimal sample preparation, thus helping to reduce the time bottleneck and most error-prone step in most analytical methods.

Though advantageous in many respects, ETV-DCP does have some shortcomings. First, the ETV introduction system is certainly not as simple to operate, when compared to that of standard PN-DCP or ICP instruments. Also, different optimum carrier gas flow rates and ETV temperature programs serve to limit the performance of ETV-DCP in its application to simultaneous multielement determinations. Sacrifices in performance will be made when compromise conditions of carrier gas flows and temperature programing are chosen, though with prudent grouping of elements with similar characteristics.

of vaporization, good performance in simultaneous multielement determinations at part-per-billion concentrations is possible.

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