Geoscience Canada

Machinations:
D.C. Plasma Atomic Emission Spectrometry In Geochemical Applications

Ian D. Brindle and Xiao Chun Le

Volume 17, Number 1, March 1990

URI: https://id.erudit.org/iderudit/geocan17_1fea03

See table of contents

Publisher(s)

The Geological Association of Canada

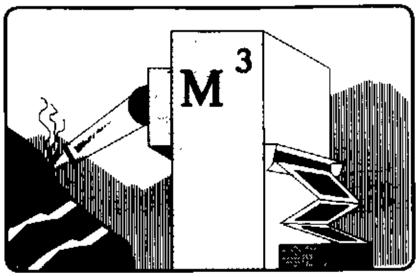
ISSN

0315-0941 (print)
1911-4850 (digital)

Explore this journal

Cite this article

Brindle, I. D. & Le, X. C. (1990). Machinations:: D.C. Plasma Atomic Emission Spectrometry In Geochemical Applications. *Geoscience Canada*, *17*(1), 41–46.



Machinations

D.C. Plasma Atomic Emission Spectrometry in Geochemical Applications

Ian D. Brindle and Xiao-chun Le
Chemistry Department
Brock University
St. Catharines, Ontario L2S 3A1

Introduction

Plasma atomic emission spectrometry is a useful tool for analytical chemistry. Commonly used sources include inductively-coupled plasma (ICP), direct current plasma (DCP), microwave-induced plasma (MIP), and capacitively-coupled microwave plasma (CMP). These sources have largely displaced arc and spark excitation sources. Spex Industries introduced the first commercially available DCP in mid-1960s. Variations of DCP devices were elaborated in the 1960s and in 1970 a new DCP source design was described with an inverted "V" flame-like configuration (Valente and Schrenk, 1970). Temperatures in the plasma were about 6000 K with a d.c. source operating at 300 V and 10 A and the plasma required less than 2.5 L·min^{-1} of argon.

In 1974, a plasma source was introduced by SpectraMetrics called the "Spectrajet II". This, in turn, was replaced by the SpectraJet III. This is a three-electrode d.c. plasma. The three electrodes consist of a front and a rear graphite anode and a top tungsten cathode, forming an inverted "Y" plasma when operating. The cathode forms the "leg" of the "Y". The electrodes are located inside water-cooled blocks and can be moved relative to each other *via* argon-activated pistons. This design results in improved stability and better detection limits than previously reported for the DCP. Of particular value is the stability of the plasma in the presence of varying solvent types such as those containing large amounts of salts, organics, high acid or alkaline concentrations. The sample excitation region and photometric observation area of the SpectraJet III is centered uniquely in the crook of the Y where spectral contribution from the plasma continuum is minimal. The plasma requires less than 1000 W of power and is sustained by a low voltage of approximately 40 V and a current of 7.5 A after ignition. Approximately 8 L·min^{-1} of commercial grade (99.5%) inert argon is used as the plasma support gas. The argon performs three functions in the SpectraJet III: (i) it is used as the support gas through each electrode to form the plasma and to sustain the thermal pinch effect of the plasma; (ii) it is used as the nebulizer and aerosol carrier gas; and (iii) it actuates the piston used to move the electrodes into position for ignition.

Compared with the two-electrode plasma, the three-electrode plasma has proved to be superior in terms of improved stability and lower background (Reednick, 1979; Decker, 1980). Recent modifications by ARL, the present manufacturer of these machines, have improved the concentricity of the graphite anodes within the alumina sleeves, but little other modification has been made to the plasma source.

Other designs include three-phase DCP (Masters and Piepmeier, 1985) and rotating arc DCP (Hara and Parsons, 1985). They result in an extended interaction between the sample aerosol and arc discharge. A conical DCP has recently been described in a design based on the three-electrode DCP (Meyer, 1987). The linear dynamic range and detection limits for six elements studied, according to the reports (Meyer, 1987), were improved compared with the commercial DCP source. More recently, a six-electrode d.c. plasma device has been described (Shields *et al.*, 1988) in which the nebulized sample is passed through the plasma and the emission is viewed above the current carrying arc.

Detection System

With temperatures as high as 10,000 K, the DCP sources provide an extremely rich spectrum. One is not limited to ground state transition lines, but can choose from first or even second ionization state lines for detection. This provides an opportunity to determine a wide variety of elements. On the other hand, it also increases occurrences of spectral interferences. To solve this problem, a resolving device capable of reliably isolating the line of interest is required.

The combination of a DCP and an echelle grating spectrometer for AES has proved a good match (Zander, 1986). The echelle grating spectrometer consists of an echelle grating and a prism which sorts the spectrum by order of diffraction. The compact spectrum that results from the echelle makes possible the simultaneous determination of as many as twenty-four elements. This is accomplished by a bank of photomultipliers behind a casette which contains slits at the appropriate positions; fibre optics will eventually be used to direct the emission lines to the photomultipliers. Thus, in principle, almost all of the wavelengths of most of the elements could be available in twenty wavelength sets. In addition, the spectrum can be intercepted by a mirror and directed into a Polaroid camera. Thus qualitative analysis can be performed on samples.

Searching for the peak in the DCP has always been a technique that has required a fine touch. In addition, the rather older SpectraSpan microprocessor requires long integration and background scanning times, which means that analyses have taken much longer than necessary to perform. More recent versions of the SpectraSpan V have an improved aquisition system. This year, ARL has just introduced a new machine, the SpectraSpan VII, which promises to be more versatile than previous models and incorporates innovations from ARL and is controlled by an IBM PS/2.

Sample Introduction System

Because of inherent problems that often restrict detection limits and produce interference effects, sample introduction has been called "the Achilles' heel of atomic spectroscopy" (Browner and Boorn, 1984). Sparkes and Ebdon (1986) have reviewed sample introduction as a key problem for DCP techniques. Therefore, a variety of sample introduction techniques have been developed and evaluated for the introduction of liquid, solid, and gaseous samples to a DCP jet.

Liquid sample introduction has traditionally been the method of choice. Approximately 1-2 mL·min^{-1} of sample solution is taken with transport efficiency of approximately 15% (Decker, 1980) and droplet size of the aerosol described as between 3-10 μm (Zander, 1982a) and 1-20 μm (Mohamed *et al.*, 1981). This overall sample loading is relatively higher than both ICP and flame AAS (Browner and Boorn, 1984).

To improve transport efficiency of analyte to the plasma, electrothermal vapourization (ETV) techniques were studied (*e.g.*, Ng and Caruso, 1985). Transport of the sample by electrothermal vapourization is much simpler than those involving liquid sampling. A microlitre amount ($\geq$ 5 μL) of the sample is introduced into a graphite or metallic (W, Ta, Pt) vapourization cell. During the high-temperature vapourization step, the sample vapour is formed and transported by carrier gas from ETV to DCP. A transient signal is thus obtained, since the sample is vapourized in one pulse under optimal conditions. Because of desolvation by ETV, more efficient introduction of analyte directly into the excitation region of the DCP is achieved, resulting in higher sensitivities, especially for volatile materials (elements or compounds). Relatively low transport efficiencies of less volatile and carbide-forming species were improved by the addition of volatilizing gases, such as freons, halocarbon, and volatile halides, to the argon carrier gas. On the other hand, to prevent some volatile elements or compounds from vapourizing during the sample drying stage, sodium sulphide, nickel salts, and iodine were added to stabilize mercury, arsenic and selenium, and volatile alkyl lead compounds, respectively. This introduction method complements the conventional pneumatic nebulizer for micro-amount, high-salt-content samples, and viscous solutions, and can be applied to solutions with suspended particles and solid samples.

Direct analysis of solid samples eliminates the need for sample digestion. This has recently gained attention because it reduces sample preparation time and minimizes contamination and loss of analyte. A DCP, having high excitation temperature, showed advantages for atomization and excitation of slurry samples. Particle size-dependent effects were observed in the case of slurry introduction (Mohamed *et al.*, 1981; Sparkes and Ebdon, 1988). Therefore, small particle size for the slurry introduction method is necessary in order to obtain adequate precision (Mohamed *et al.*, 1981; Sparkes and Ebdon, 1988). The introduction of high salt solutions creates fewer problems in the DCP than in the ICP, thus brines can be aspirated into the plasma without degradation of performance.

Hydride generation (HG) has proved to be an effective sample introduction method for atomic spectrometry (Nakahara, 1983). This technique was combined with d.c. arc emission spectrometry (Erdey *et al.*, 1955), AAS (Holak, 1969), ICP-AES (Thompson *et al.*, 1978), and DCP-AES (Miyazaki *et al.*, 1979). For DCP-AES, hydrides produced in the hydride generator by the reaction of the hydride-forming elements and a reducing agent (sodium tetrahydroborate (III)), are introduced in a stream of argon through a modified sample tube into the DCP (Boampong *et al.*, 1987). In the hydride generation process, analytes are preconcentrated and separated from the sample matrix. Therefore, spectral interferences are eliminated or reduced and the sensitivity is improved by a factor of approximately 20 over the direct aqueous nebulization (Sparkes and Ebdon, 1986). Hydride generation in conjunction with DCP-AES has been used in the determination of arsenic (*e.g.*, Boampong *et al.*, 1987) antimony (*e.g.*, Peramaki and Lajunen, 1988), selenium (*e.g.*, Hayrynen *et al.*, 1985), germanium *e.g.*, Brindle *et al.*, 1989), tellurium (Hayrynen *et al.*, 1985), and tin (Brindle and Le, 1988). Similar applications include cold vapour (Lajunen *et al.*, 1985) and chloride formation (Miyazaki *et al.*, 1979) for mercury and arsenic, respectively.

Another interesting sample introduction technique is chromatography. The DCP-AES instrument functions as a multi-element detector when coupled directly to a chromatograph. Van Loon (1979) has reviewed the combination of chromatography and atomic spectrometry; Carnahan *et al.* (1981) have summarized the application of plasma emission spectrometry in chromatography. This application can be done in two ways: (i) independent collection of chromatographic fractions followed by analysis, where the chromatography represents a preconcentration/separation step in the preparation of the sample; and (ii) direct introduction of the column effluent into the analytical instrument. The DCP is tolerant of a wide range of gas flow rates and of gas and solvent types. Gas chromatography (GC) (*e.g.*, Panaro *et al.*, 1987), high performance liquid chromatography (HPLC) (*e.g.*, Uden *et al.*, 1978), gel filtration chromatography (*e.g.*, Gardiner *et al.*, 1983), and ion exchange chromatography (*e.g.*, Epstein *et al.*, 1987) have been coupled with DCP-AES.

An HPLC system can be easily coupled to a DCP system because the flow rates can be adjusted to those required by the nebulizer and samples can be separated in a relatively short time. Uden *et al.* (1978) have found that the standard nebulization system was sufficient for eluents used in ion-exchange and reversed-phase chromatography, but a new nebulizer had to be designed to avoid the formation of carbon deposits when organic solvents are used in adsorption chromatography. Also, a combination of HPLC-hydride-generation-DCP has been described for determination of total tin and organo-tin species (Brindle and Le, 1988).

A new technique, laser ablation DCP-AES, has been used (*e.g.*, Mitchell *et al.*, 1985) for the direct determination of metals in solid samples. These preliminary studies have demonstrated excellent selectivity and sensitivity, low detection limits, and little interference in sample analysis.

DCP and Other Plasma Sources

The ICP has been extensively studied and has proved extremely useful for inorganic major, minor, and trace analysis (*e.g.*, Boumans, 1987). According to Greenfield *et al.* (1986), ICP-AES has been applied to the analysis of "almost every material under the sun". In order to assess the DCP, a number of authors (Zander, 1986; McHard *et al.*, 1984) compared DCP with ICP. For AES, the DCP source is superior to the ICP source in terms of instrumental and operational costs, and versatility for organic, high-salt content and slurry sample introduction, whereas ICP is less prone to matrix effects and has slightly better or similar precision than DCP (Zander, 1986). ICP is more advanced than DCP from both a theoretical and practical point of view, partly due to its wider availability. Recent adoption of the d.c. plasma atomic emission method for the analysis of waste waters, by the United States Environmental Protection Agency, will lead to wider acceptance in academic institutions.

The basic characteristics, capabilities and limitations of the commercial DCP are summarized in Table 1.

Applications of DCP-AES

Because of the characteristics, listed in Table 1, DCP-AES has been applied to determine a variety of elements in environmental, geological, metallurgical, clinical, biological, industrial, and other samples (Table 2).

Table 1 Advantages and Limitations of the DCP

Detection limits	usually comparable with those of ICP. This characteristic allows DCP-AES to determine directly trace elements in samples.
Linear dynamic range	at least three orders of magnitude. With sample dilution procedure, the simultaneous determination of major, minor, and trace elements is possible.
Precision	relative standard deviations of about 1.5% for most elements in aqueous solutions at concentrations well above the detection limits.
Stability	acceptable both long-term and short-term.
Versatility	can tolerate a number of organic solvents and can also accept solutions which contain more than 10% dissolved solids.
Excitation region	this region is small and thus makes its use with conventional spectrographic and spectrometric equipment difficult. However, with an echelle grating spectrometer, this is no longer a problem.
Excitation processes	these are greatly affected by elements with low ionization potentials, for example, alkali and alkaline earth metals (Johnson *et al.*, 1980; Nygaard and Gilbert, 1981; Fox, 1984; Miller *et al.*, 1984) and pose greater problems in the DCP than in the ICP.

Table 2 Applications of DCP-AES to Various Geological Matrices

Elements Determined	Sample Analyzed	Comments	Reference
Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn, Ba, Cr, Cu, Ni, Sr, V, Zn	Silicate rocks	Lithium metaborate fusion of samples and cesium buffering to reduce interference	Bankston *et al.*, 1979
Be, Al, Si, Fe, Zn, Nb, Sn, Ta, W	Minerals	Introduction of suspensions of finely powdered samples (10 µm diameter) to the DCP	Derie, 1984
Major, trace, REEs	Rocks	Rapid determination of 29 petrologically important elements, 2% RSD for 22 elements, 5% for 6 elements, 6% for Rb	Feigenson and Carr, 1985
U	Phosphatic materials	A 2% oxalic acid adjusted to pH 4.5 with triethanolamine was used quantitatively to back-extract U from trioctylphosphine oxide in cyclohexane. This sample pretreatment method overcame matrix interferences	Norman *et al.*, 1983
Si, Fe, Al, Ca, Mg, Mn, Ti, K, Na, P	Soil	Li or Na buffering was recommended. The results for the 10 elements were satisfactory for routine analysis when compared with those obtained by chemical methods	Shen *et al.*, 1983
Transition elements	Soils and sludges	Discussion of matrix interferences, use of EIE buffers recommended	Schramel, 1988
Be, Co, Cr, Ga, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Ti, V, Zr, La, Y, Yb	Rocks	Lab-made "two-jet plasmatron" was used. Matrix interferences were the same order as the random error of analysis	Yudelevich *et al.*, 1985
Cu	Ores	Laser ablation technique was used for solid sample direct introduction	Mitchell *et al.*, 1985
Al, Ca, Fe, Mg, Si, Ti	Geological materials	A 2-electrode DCP was used. Samples analyzed included lunar rocks and soils	Golightly and Harris, 1975
Major, minor, REEs	Ore concentrates	Simple calibration	Johnson and Sisneros, 1982
La	Geological samples	Review of available methods	Kantipuly and Westland, 1988
B	Rocks	Matrix interferences were minimized by carefully selecting the most suitable line for each samples and/or by cation exchange. The results were compared with those obtained by azomethine H method	Lajunen *et al.*, 1987
Cr, Cu, Mg, Mn, Ni, Pb	Coal	Slurry introduction with extremely small (less than 20 µm) coal particle size. Quantitative agreement between experimental and certified values	McCurdy *et al.*, 1985
Ba, Sr	Sediments	Li, Na, K, or Cs alone did not completely eliminate matrix interferences. Lithium, from preliminary fusion, and lanthanum together removed interferences	Bowker and Manheim, 1982
Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, La, Ce, Dy, Yb	Estuarine sediments	Lithium metaborate fusion of samples. Lithium also served as EIE buffer	Cantillo *et al.*, 1984
Ba, Ca, Cd, Cr, Cu, Fe, Mg, Na, Ni, Pb, Sr, V, Zn	Sediments, waters, marine organisms	Stray light and spectral interferences from Ca and Mg were observed. Compensation for the interferences using simple linear correction or matrix matching was reported	Grogan, 1983
Cd, Cr, Cu, Pb, Ni, Zn	Seawater, ocean sediments	Na, Ca, and Mg in seawater increased both background and signal. EIE buffering minimizes the matrix effects	Nygaard, 1979

Table 2, continued

Elements Determined	Sample Analyzed	Comments	Reference
Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Tl, Pb	Saline waters	Enhancement effects were studied by using an empirical approach combined with statistical analysis	Eastwood *et al.*, 1980
Fe, Ni, Sc	Saline matrices	Sodium-induced emission enhancement was studied. A partial thermodynamic equilibrium instead of a local thermodynamic equilibrium was suggested	Eastwood *et al.*, 1982
K, Na, Ba, Sr, In, Al, Ca, Cr, Pb, Mn, Ni, Mg, Cu, Si, B, Cd, Be, P	Natural waters	Interferences from stray light due to the presence of Ca and/or Mg can be compensated by using a simple linear correction. Two- and three-electrode DCP systems were compared and the latter offered advantages of improved stability and lower background	Johnson *et al.*, 1979
As, B, C, P, Se, Si	Natural waters	No significant interference from natural water and waste water sample matrix	Urasa, 1984
Cr	Waters	Speciation of Cr(III) and (VI) via HPLC	Krull *et al.*, 1983
Cd, Cu, Fe, Hg, Ni, Pb, Zn	Coastal seawater	Non-aqueous sample introduction to the DCP. Effects of organic solvents were studied	Gilbert and Penney, 1983
U	Ground- and mine waters	Standard addition and matrix matching methods were recommended for reducing the enhancement effects due to Na and Ca	Greene *et al.*, 1985
Au	Algal cells	ETV introduction of 0.2-0.6 mg of samples to DCP	Greene *et al.*, 1986
Hg	Algal cells	ETV introduction of 0.6-0.9 mg of solid sample to DCP. The addition of sulphur-containing alga or cysteine modified the sample and allowed a reproducible mercury signal to be obtained	Mitchell *et al.*, 1986
Ge	Ferrous dusts	Determination by hydride generation using ammonium peroxidisulphate to overcome interferences	Brindle and Ceccarelli-Ponzoni, 1987

Easily ionized elements (EIEs) in samples enhance emission signals (*e.g.*, Decker, 1980; Miller *et al.*, 1984), and, although emission line to background ratios are often improved, this enhancement effect has been generally regarded as a nuisance due to its unpredictability (*e.g.*, Skogerboe and Urasa, 1978; Cantillo *et al.*, 1984).

A number of authors have ascribed the signal enhancement effect by EIEs to suppression of populations of ionized analyte by EIE-donated electrons (Johnson *et al.*, 1979). Subsequent research, however, showed that intensities of both atomic and ionic emission lines were enhanced and that the addition of EIE appeared to have little influence on electron densities measured in the analytical zone (Eastwood *et al.*, 1982; Zander and Miller, 1985). A number of mechanistic models suggest possible explanations of this complex phenomenon (Johnson *et al.*, 1980; Hendrick *et al.*, 1986).

To minimize the interference caused by EIE, matrix matching of samples, blanks, and standards (Cantillo *et al.*, 1984), standard additions or internal standards (Johnson *et al.*, 1980), EIE buffers (*e.g.*, Eastwood *et al.*, 1982), and removing EIEs by ion exchange (Lajunen *et al.*, 1987) have been proposed. EIE buffering is the most widely applied technique, where samples and standards are typically spiked with excess amounts of EIEs, such as salts of lithium (Skogerboe and Urasa, 1978), sodium (Urasa, 1984), potassium (Golightly and Harris, 1975), cesium (Bankston *et al.*, 1979), and lithium-lanthanum mixture (Fox, 1985) to minimize signal differences due to EIEs. However, these methods have not always been successful since enhancement effects due to EIEs are very complicated (Miller *et al.*, 1984). In the determination of hydride-forming elements, EIEs have been used to enhance signals by simultaneously aspirating a solution of EIE into the plasma along with the hydride. With appropriate alkali elements, 40-115% signal enhancement was achieved in the determination of arsenic, antimony, germanium, lead and tin by hydride generation DCP-AES (Brindle and Le, 1989). Brindle and Le (1989) have introduced a modification of the introduction system that reduces interferences from EIEs in the determination of transition elements by DCP-AES. Two pump/nebulization systems were used which introduced analyte and EIEs separately into the plasma, thus eliminating the need to introduce the EIEs into the sample during preparation.

Conclusion

Determination of elements in geological matrices by DCP-AES provides a reasonable alternative to the ICP-AES systems. The system is robust and relatively cheap to operate and, for some applications, provides superior performance. Modifications made to the machine over the last few years should improve long-term stability and will speed up analysis time.

References

Bankston, D.C., Humphris, S.E. and Thompson, 1979, Major and minor oxide and trace element determination in silicate rocks by direct current plasma optical emission echelle spectrometry: Analytical Chemistry, v. 51, p. 1218-1225.

Boampong, C., Brindle, I.D. and Ceccarelli-Ponzoni, C.M., 1987, Determination of arsenic by hydride generation in the d.c. plasma atomic emission spectrometer — determination of arsenic (II) and arsenic (V) as total arsenic: Journal of Analytical Atomic Spectrometry, v. 2, p. 197-200.

Boumans, P.W.J.M., 1987, Inductively Coupled Plasma Emission Spectrometry: J. Wiley, New York.

Bowker, P.E. and Manheim, F.T., 1982, Analysis of barium and strontium in sediments by d.c. plasma emission spectrometry: Applied Spectroscopy, v. 36, p. 378-382.

Brindle, I.D. and Ceccarelli-Ponzoni, C.M., 1987, Germanium determination by hydride generation atomic emission spectrometry: simultaneous signal enhancement and interference suppression: Analyst, v. 112, p. 1547-1550.

Brindle, I.D. and Le, X-c., 1988, Determination of trace amounts of tin by hydride generation direct current plasma atomic emission spectrometry: Interference reduction by L-Cystine: Analyst, v. 113, p. 1377-1381.

Brindle, I.D., Le, X-c. and Li, X-f., 1989, Convenient method for the determination of trace amounts of germanium by hydride generation direct current plasma atomic emission spectrometry: Interference reduction by L-Cystine and L-Cysteine: Journal Analytical Atomic Spectrometry, v. 4, p. 227-232.

Brindle, I.D. and Le, X-c, 1989, Application of signal enhancement by easily ionized elements in hydride generation direct current plasma atomic emission spectrometric determination of arsenic, antimony, germanium, tin and lead: Analytical Chemistry, v. 61, p. 1175-1178.

Browner, R.F. and Boorn, A.W., 1984, Sample introduction: the Achilles' heel of atomic spectroscopy?: Analytical Chemistry, v. 56, p. 786A-798A.

Cantillo, A.Y., Sinex, S.A. and Helz, G.R., 1984, Elemental analysis of estuarine sediments by lithium metaborate fusion and direct current plasma emission spectrometry: Analytical Chemistry, v. 56, p. 33-37.

Carnahan, J.W., Mulligan, K.T. and Caruso, J.A., 1981, Element-selective detection for chromatography by plasma emission spectrometry: Analytica Chimica Acta, v. 130, p. 227-241.

Decker, R.J., 1980, Some characteristics of a three electrode d.c. argon plasma source for optical emission spectrometry: Spectrochimica Acta, v. 35B, p. 19-31.

Derie, R., 1984, Analysis of mineral suspensions by d.c. plasma emission spectrometry: Analytica Chimica Acta, v. 166, p. 61-69.

Eastwood, D., Hendrick, M.S. and Sogliero, G., 1980, Applications of d.c. argon plasma emission spectroscopy to saline waters: a study of enhancement effects: Spectrochimica Acta, v. 35B, p. 421-430.

Eastwood, D., Hendrick, M.S. and Miller, M.H., 1982, Wavelength-dependent enhancement of DCP metal lines by saline matrices: Spectrochimica Acta, v. 37B, p. 293-302.

Epstein, M.S., Koch, W.F., Epler, K.S. and O'Haver, T.C., 1987, Determination of phosphorus in copper-based alloys using ion-exchange chromatography and direct-current plasma emission spectrometry: Analytical Chemistry, v. 59, p. 2872-2876.

Erdey, L., Gegus, E. and Kocsis, E., 1955, Spectrochemical analysis of solutions by means of hollow electrodes: Acta Chimica Hungarica, v. 7, p. 343-360.

Feigenson, M.D. and Carr, M.T., 1985, Determination of major, trace and rare-earth elements in rocks by DCP-AES: Chemical Geology, v. 51, p. 19-27.

Fox, R.L., 1984, Enhancement errors in the determination of platinum group metals in alumina-based matrices by direct-current plasma emission spectrometry: Applied Spectroscopy, v. 38, p. 644-647.

Fox, R.L., 1985, Non-alkali metal interferences in the determination of platinum group metals by d.c. plasma emission spectrometry: Spectrochimica Acta, v. 40B, p. 287-291.

Gardiner, P.E., Bratter, P., Negretti, V.E. and Schulze, G., 1983, Use of direct current argon plasma as a detector in gel filtration chromatography of biological fluids: Spectrochimica Acta, v. 38B, p. 427-436.

Gilbert, T.R. and Penney, B.A., 1983, Determination of trace elements in non-aqueous samples by d.c. plasma emission spectrometry: Spectrochimica Acta, v. 38B, p. 297-302.

Golightly, D.W. and Harris, J.T., 1975, Spectrographic analysis of geological materials with an argon plasma jet: Applied Spectroscopy, v. 29, p. 233-240.

Greene, B., Uranga, A. and Sneddon, J., 1985, Observations on the determination of uranium in waters by direct current argon plasma emission spectrometry: Spectroscopy Letters, v. 18, p. 425-436.

Greene, B., Mitchell, P.G. and Sneddon, J., 1986, Direct determination of gold in solid algal cells by direct current argon plasma emission spectrometry with introduction by electrothermal atomization: Spectroscopy Letters, v. 19, p. 101-111.

Greenfield, S., Hieftje, G.M., Omenetto, N., Scheeline, A. and Slavin, W., 1986, Twenty-five years of analytical atomic spectroscopy: Analytica Chimica Acta, v. 180, p. 69-98.

Grogan, W.C., 1983, Applications of d.c. plasma emission spectrometer to the analysis of environmental samples: Spectrochimica Acta, v. 38B, p. 357-369.

Hara, L.Y. and Parsons, M.L., 1985, Rotating arc direct current plasma as an emission excitation source: Analytical Chemistry, v. 57, p. 841-845.

Hayrynen, H., Lajunen, L.H.J. and Peramak, P., 1985, Determination of trace concentrations of selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into a direct current plasma source for emission spectrometry: Atomic Spectroscopy, v. 6, p. 88-90.

Hendrick, M.S., Seltzer, M.D. and Michel, R.G., 1986, Laser excited atomic fluorescence for studies of enhancement effects in the direct current plasma: Spectrochimica Acta, v. 41B, p. 335-348.

Holak, W., 1969, Gas-sampling technique for arsenic determination by atomic absorption spectrophotometry: Analytical Chemistry, v. 41, p. 1712-1713.

Johnson, G.W. and Sisneros, T.E., 1982, Determination of rare earth elements in ore concentrate samples using direct current plasma spectrometry: Rare Earth Modern Science and Technology, v. 3, p. 525-529.

Johnson, G.W., Taylor, H.E. and Skogerboe, R.K., 1979, Determination of trace elements in natural waters by the d.c. argon plasma, multi-element atomic emission spectrometer (DCP-MAES) technique: Spectrochimica Acta, v. 34B, p. 197-212.

Johnson, G.W., Taylor, H.E. and Skogerboe, R.K., 1980, Characterization of an interelement enhancement effect in a d.c. plasma atomic emission spectrometry system: Applied Spectroscopy, v. 34, p. 19-24.

Kantipuly, C.J. and Westland, A.D., 1988, Review of methods for the determination of lanthanides in geological samples: Talanta, v. 35, p. 1-13.

Krull, I.S., Panaro, K.W. and Gershman, L.L., 1983, Trace analysis and speciation for chromium (VI) and chromium (III) via HPLC-direct current plasma emission spectroscopy (HPLC-DCP): Journal of Chromatographic Science, v. 21, p. 460-472.

Lajunen, L.H.J., Kinnunen, A. and Yrjanheikki, E., 1985, Determination of mercury in blood and fish samples by cold-vapor atomic absorption and direct current plasma emission spectrometry: Atomic Spectroscopy, v. 6, p. 49-52.

Lajunen, L.H.J., Kurikka, A. and Ojaniemi, E., 1987, Determination of boron in geological samples by direct current plasma atomic emission spectrometry: Atomic Spectroscopy, v. 8, p. 142-144.

Masters, R.A. and Piepmeier, E.H., 1985, Sample entraining 3-electrode argon plasma source for atomic emission spectrometry: Spectrochimica Acta, v. 40B, p. 85-91.

McCurdy, D.L., Wichman, M.D. and Fry, R.C., 1985, Determination of lead in biological samples by hydride generation spectrometry using an aqueous slurry technique: Applied Spectroscopy, v. 39, p. 984-988.

McHard, J.A., Twigg, K.M., Bach, D.T. and Winefordner, J.D., 1984, Determination of trace alkali and alkaline earth metals in orange juice using the dc plasma and the inductively coupled plasma atomic emission techniques: Spectroscopy Letters, v. 17, p. 285-294.

Meyer, G.A., 1987, Conical three electrode d.c. plasma for spectrochemical analysis: Spectrochimica Acta, v. 42B, p. 333-339.

Miller, M.H., Eastwood, D. and Hendrick, M.S., 1984, Excitation of analytes and enhancement of emission intensities in a d.c. plasma jet: a critical review leading to proposed mechanistic models: Spectrochimica Acta, v. 39B, p. 13-56 and references cited therein.

Mitchell, P.G., Ruggles, J.A., Sneddon, J. and Radziemske, L.J., 1985, Direct determination of copper in solids and ores by laser ablation – direct current argon plasma emission spectrometry: Analytical Letters, v. 18, p. 1723-1732; Chemical Abstracts, v. 104, 45097u.

Mitchell, P.G., Greene, B. and Sneddon, J., 1986, Direct determination of mercury in solid algal cells by direct-current argon-plasma emission spectrometry with sample introduction by electrothermal vaporization: Mikrochimica Acta, v. 1, p. 249-258.

Miyazaki A., Kimura, A. and Umezaki, Y., 1979, Determination of arsenic in sediments by chloride formation and d.c. plasma arc emission spectrometry: Analytica Chimica Acta, v. 107, p. 395-398.

Mohamed, N., Brown, R.M. and Fry, R.C., 1981, Slurry atomization d.c. plasma emission spectrometry and laser diffraction studies of aerosol production and transport: Applied Spectroscopy, v. 35, p. 153-164.

Nakahara, T., 1983, Application of hydride generation techniques in atomic absorption, atomic fluorescence and plasma atomic emission spectroscopy: Progress in Analytical Atomic Spectroscopy, v. 6, p. 163-223.

Ng, K.C. and Caruso, J.A., 1985, Electrothermal vaporization for sample introduction in atomic emission spectrometry: Applied Spectroscopy, v. 39, p. 719-726.

Norman, J.D., Stumpe, L.A., Trimm, J.R. and Johnson, F., 1983, Argon plasma emission spectrometry of uranium in phosphatic materials: Journal of the Association of Official Analytical Chemists, v. 66, p. 949-951.

Nygaard, D.D., 1979, Plasma emission determination of trace heavy metals in salt water matrices: Analytical Chemistry, v. 51, p. 881-884.

Nygaard, D.D. and Gilbert, T.R., 1981, Emission line enhancement in a d.c. plasma: Applied Spectroscopy, v. 35, p. 52-56.

Panaro, K.W., Erickson, D. and Krull, I.S., 1987, Determination of methylmercury in fish by gas chromatography – direct current plasma atomic emission spectrometry: Analyst, v. 112, p. 1097-1105.

Peramaki, P. and Lajunen, L.H.J., 1988, Determination of antimony in geological samples using hydride generation and direct current plasma atomic emission spectrometry: Analyst, v. 113, p. 1567-1570.

Reednick, J., 1979, A unique approach to atomic spectroscopy. High energy plasma excitation and high resolution spectrometry: American Laboratory, v. 11(3), p. 53-54, 56-58.

Schramel, P., 1988, ICP and DCP emission spectrometry for trace element analysis in biomedical and environmental samples. A review: Spectrochimica Acta, v. 43B, p. 881-896.

Shen, R., Zhen, C. and Qian, Q., 1983, Application of d.c. argon plasma emission spectrometry to the analysis of soil samples. I. simultaneous determination of macroamount of elements in soil: Fenxi Huaxue, v. 11, p. 599-604.

Shields, J.P., Lee, G.H. and Piepmeier, E.H., 1988, A six-electrode, direct-current, variable length plasma source for atomic emission spectroscopy, Applied Spectroscopy, v. 42, p. 684-692.

Skogerboe, R.K. and Urasa, I.T., 1978, Evaluation of the analytical capabilities of a d.c. plasma – echelle spectrometer system: Applied Spectroscopy, v. 32, p. 527-532.

Sparkes, S. and Ebdon, L., 1986, A selected review of sample introduction techniques for the direct current plasma: ICP Information Newsletter, v. 12(1), p. 1-6.

Sparkes, S.T. and Ebdon, L., 1988, Direct atomic spectrometric analysis by slurry atomization. Part 6: Simplex optimization of a direct current plasma for kaolin analysis: Journal of Analytical Atomic Spectrometry, v. 3, p. 563-569.

Thompson, M., Pahlavanpour, B., Walton, S.J. and Kirkbright, G.F., 1978, Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. Part I. Preliminary studies: Analyst, v. 103, p. 568-579.

Uden, P.C., Quimby, B.D., Barnes, R.M. and Elliott, W.G., 1978, Interfaced d.c. argon-plasma emission spectroscopic detection for high-pressure liquid chromatography of metal compounds: Analytica Chimica Acta, v. 101, p. 99-109.

Urasa, I.T., 1984, Determination of arsenic, boron, carbon, phosphorus, selenium, and silicon in natural waters by direct current plasma atomic emission spectrometry: Analytical Chemistry, v. 56, p. 904-908.

Valente, S.E. and Schrenk, W.G., 1970, The design and some emission characteristics of an economical d.c. arc plasmajet excitation source for solution analysis: Applied Spectroscopy, v. 24, p. 197-205.

Van Loon, J.C., 1979, Metal speciation by chromatography/atomic spectrometry: Analytical Chemistry, v. 51, p. 139A-1150A.

Yudelevich, I.G., Cherevko, A.S., Engelsht, V.S., Pikalov, V.V., Tagiltsev, A.P. and Zheenbajev, Zh.Zh., 1984, A two-jet plasmatron for the spectrochemical analysis of geological samples: Spectrochimica Acta, v. 39B, p. 777-785.

Zander, A.T., 1982, DC plasma emission spectrometry speeds elemental analysis: Industrial Research and Development, February 1982, p. 146-150.

Zander, A.T., 1986, Atomic emission sources for solution spectrochemistry: Analytical Chemistry, v. 58, p. 1139A-1149A.

Zander, A.T. and Miller, M.H., 1985, Electron density spatial profiles of the DCP source: Spectrochimica Acta, v. 40B, p. 1023-1037.

Accepted 18 October 1989.