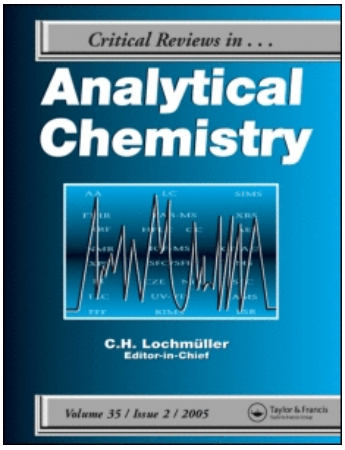

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

A Review of Microwave Plasma Sources in Atomic Emission Spectrometry: Literature from 1985 to the Present

A. E. Croslyn[a]; B. W. Smith[a]; J. D. Winefordner[a]
[a] Department of Chemistry, University of Florida, Gainesville, FL

To cite this Article Croslyn, A. E. , Smith, B. W. and Winefordner, J. D.(1997) 'A Review of Microwave Plasma Sources in Atomic Emission Spectrometry: Literature from 1985 to the Present', Critical Reviews in Analytical Chemistry, 27: 3, 199 — 255
To link to this Article: DOI: 10.1080/10408349708052201
URL: http://dx.doi.org/10.1080/10408349708052201

Critical Reviews in Analytical Chemistry, 27(3):199–255 (1997)

A Review of Microwave Plasma Sources in Atomic Emission Spectrometry: Literature from 1985 to the Present

*A. E. Croslyn, B. W. Smith, and J. D. Winefordner**

University of Florida, Department of Chemistry, P.O. Box 117200, Gainesville, FL 32611-7200; phone: 352/392-0556; fax: 352/392-4651; e-mail: jdwin@chem.ufl.edu

* Author to whom correspondence should be addressed.

ABSTRACT: Microwave plasmas have been used as sources for atomic spectroscopy since the 1970s. Several common forms of this plasma source exist, including the microwave-induced plasma, the capacitively coupled microwave plasma, the surface-wave or surfatron plasma, the microwave plasma torch, and some other unique designs. Although not as popular as the inductively coupled plasma, microwave plasmas offer the advantage of lower initial and operational costs. This review covers the literature on the various forms of the microwave plasma since 1985, including basic principles of microwave plasmas and design descriptions of a variety of systems.

KEY WORDS: microwave plasma, surfatron, MIP, CMP, MPT.

I. INTRODUCTION

There are many excellent reviews on different aspects of microwave plasmas used as sources for atomic emission spectrometry. Reviews which include microwave and other plasmas can be found in the Atomic Spectroscopy Update in the *Journal of Analytical Atomic Spectroscopy*,[1–6] *Analytical Chemistry*,[7–9] the yearly review series on microwave plasmas by Dahmen,[10–16] and others.[17–21] However, we found a need for a review which encompassed a wide variety of microwave plasmas and simultaneously provided a comprehensive overview of the many applications to which these plasmas have been employed. This review attempts to cover both of these areas. A search of the literature on microwave plasmas revealed that a great deal of work had been accomplished in recent years and that there existed a myriad of applications to which microwave plasmas had been applied.

This review will cover microwave plasmas used in atomic emission spectrometry from 1985 to present. This is an attempt to cover as much of the literature as possible, but is not an exhaustive literature review.

1040-8347/97/$.50

In addition, we have omitted the literature dealing with microwave plasmas used in the areas of fluorescence or diamond deposition. The main focus of this review is the microwave-induced plasma due to the overwhelming number of articles on this plasma compared to the other microwave plasmas. Other microwave plasmas covered are the capacitively coupled microwave plasma, the surface-wave or surfatron microwave plasma, the microwave plasma torch, and several other unique designs such as the kilowatt plus, stabilized capacitive plasma, and others.

II. BASIC PRINCIPLES OF MICROWAVE PLASMAS

Microwaves are simply electromagnetic waves in the frequency range from 300 MHz to 300 GHz. The microwave region is unique in the electromagnetic spectrum because at these high frequencies conventional wiring and electronics will not work due to high lead reactances and long transit times. This can also be described as the skin effect, which is a phenomenon in which high frequency (microwave) current travels on the outer surface, or skin, of a metal rather than penetrating it.[25] Therefore, microwave systems transfer energy by means such as antennas, waveguides, and coaxial cables. Microwave systems are used in a wide variety of fields including space telemetry, radar communications, and microwave heating.[26]

Microwaves have both an electric field component and a magnetic field component. The electric field is the force created when two electrons repel one another (Figure 1) and the magnetic field is the force on a moving charge due to other moving charges (Figure 2). When these two forces act simultaneously in the form of waves, the resulting waveform in Figure 3 is created. Characteristics which make one electromagnetic wave different from another include frequency, wavelength, impedance, power density, and phase.[26]

Microwaves are transmitted primarily through four forms. One way is transmission through space using antennas. The other three forms, which find their use in systems used in microwave plasma formation, are waveguides, coaxial cables, and microstrips (Figure 4). A waveguide is simply a hollow metal pipe or box through which the microwaves travel from the source, or magnetron, to the electrode at the receiving end of the waveguide. A coaxial cable consists of inner and outer conductors containing an insulating material through which microwaves can travel. Finally, a microstrip works similarly to a coaxial cable, with top and bottom planar conductors sandwiching an insulator.[26]

A microwave plasma is formed when microwave energy is transmitted from the source (or magnetron) through one of the transmission lines previously described to a discharge tube containing the plasma gas. A plasma consists of a partially ionized gas which is, on average, electrically neutral.[27] Maximum power is transmitted to the plasma by positioning the discharge tube where the plasma is to form at a point where the electric field component is at a maximum. The discharge is then ignited by "seeding" the plasma gas with electrons using a Tesla coil; in some cases, microwave heating of the containment vessel will release electrons from the vessel walls and allow autoignition of the plasma. The plasma is then sustained by collision of the electrons with gas atoms. The free electrons are initially moving in an oscillatory motion in phase with the microwave field. However, when the field changes phase quickly the electrons move

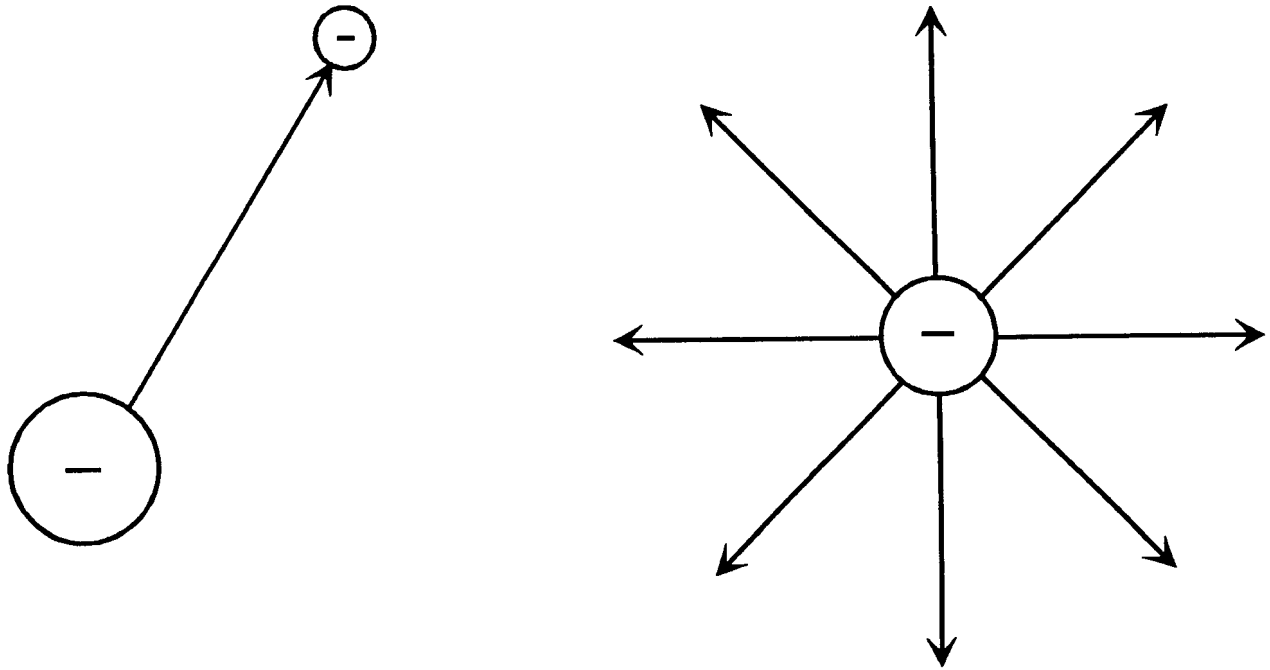

FIGURE 1. Electric fields. (Adapted from Reference 26.)

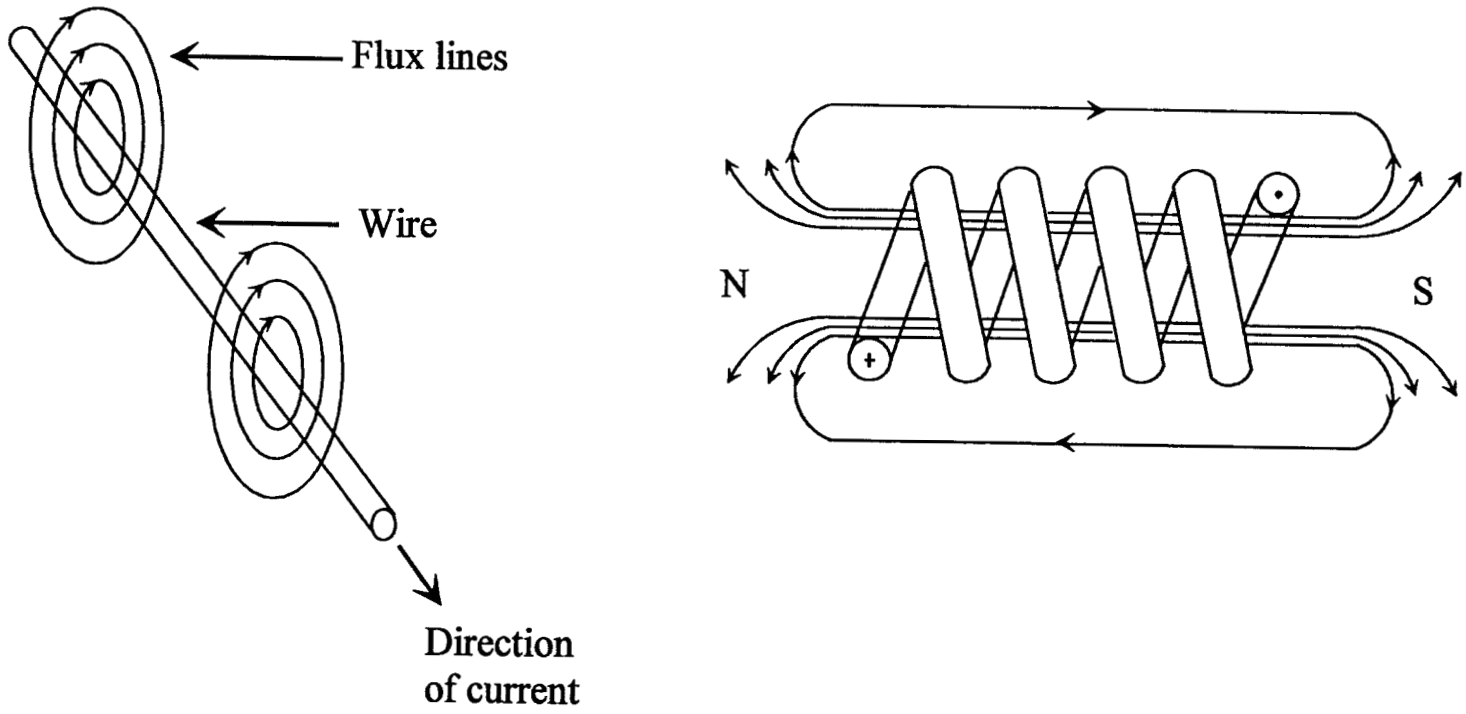

FIGURE 2. Magnetic fields. (Adapted from Reference 26.)

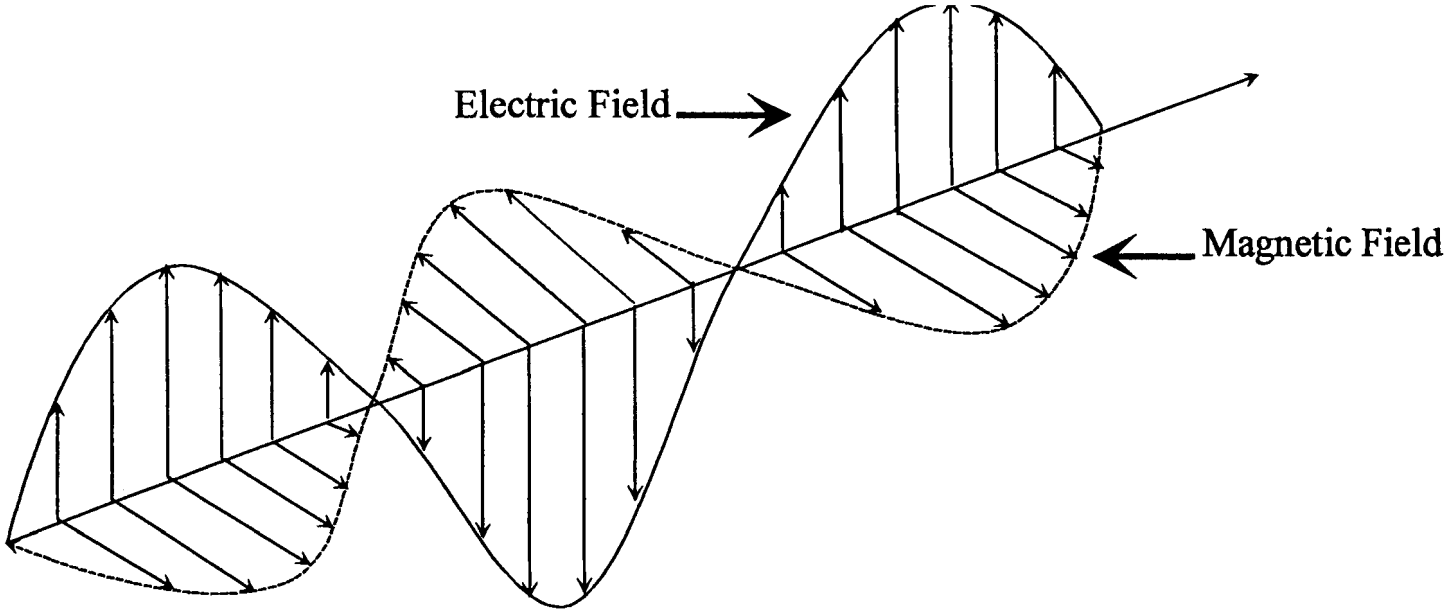

FIGURE 3. Electromagnetic waves. (Adapted from Reference 26.)

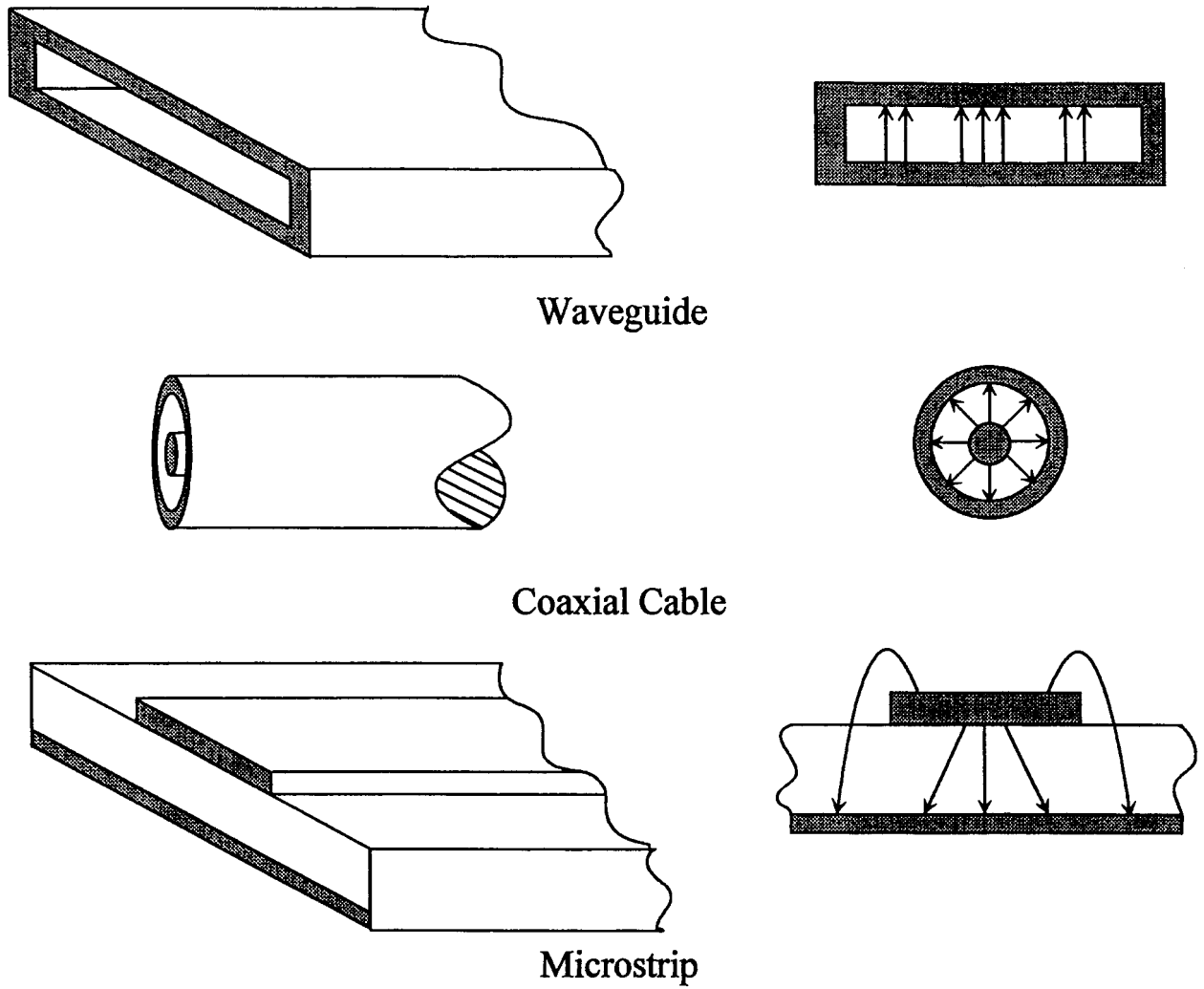

FIGURE 4. Microwave transmission lines. (Adapted from Reference 26.)

out of their oscillatory motion (or out of phase) and begin to collide with the surrounding plasma gas atoms. The plasma is then self-sustaining if a given electron creates at least one new electron by collision before it eventually is recombined.[28]

Microwave plasmas are categorized according to the way in which the microwave energy is transferred from the source to the plasma. For example, the MIP transfers microwave energy through coaxial cables while the CMP uses a waveguide. The specific system designs of the MIP, CMP, MPT, etc. will be described in their respective sections.

Several helpful books containing information on microwave theory are referenced.[22,25,26]

III. MICROWAVE-INDUCED PLASMAS (MIP)

A. Introduction

The microwave-induced plasma (MIP) is the mostly widely used microwave plasma. Beenakker[24] first reported use of this plasma operated in helium and argon at atmospheric pressure in 1976 and as an element-selective detector for gas chromatography in 1977.[29] The MIP is formed by transmitting the microwaves from the generator through a coaxial cable to a resonant cavity. Figure 5 shows a typical Beenakker cavity design. The cavity is constructed from copper due to its high conductivity. Twelve screws hold the removable lid tightly to the fixed bottom for good electrical contact. The silica discharge tube through which the plasma gases flow extends through the center of the cavity where the electric field strength is at a maximum. A 1 mm copper wire loop extending inwardly from the cylindrical wall serves to inductively transfer the power to the cavity. It is fixed to the cavity by a connector and vacuum sealing kit which prevents arcing between the loop and the bottom of the cavity. Tuning is accomplished by two finely threaded screws located in the cylindrical wall opposite the coupling loop and in the bottom wall parallel with the discharge tube.[24]

The microwave generator is equipped with both a power output meter and a reflected power meter. The cavity is tuned to minimum reflected power and the plasma gas passed through the discharge tube. The plasma then autoignites or is ignited with a Tesla coil.[24]

Several excellent reviews on the microwave-induced plasma as a source for atomic emission spectroscopy have been written.[30–32] Overall, MIPs are found to be most often used as detectors for gas chromatography. Their high power densities make them excellent atomization sources for metals and nonmetals alike.[33] They also operate easily at low power. However, MIPs do not accommodate liquid sample introduction well, and sometimes are even extinguished. In addition, optimization of the plasma with frequency is not easy since the resonant cavity frequency is determined by the width of the cavity.[31]

B. Diagnostics

Spectroscopic temperature investigations have been performed by a variety of methods, involving translational, rotational, and surface temperature determinations with various plasma gases;[34] excitation and rotational temperature comparisons for axial and lateral viewing of

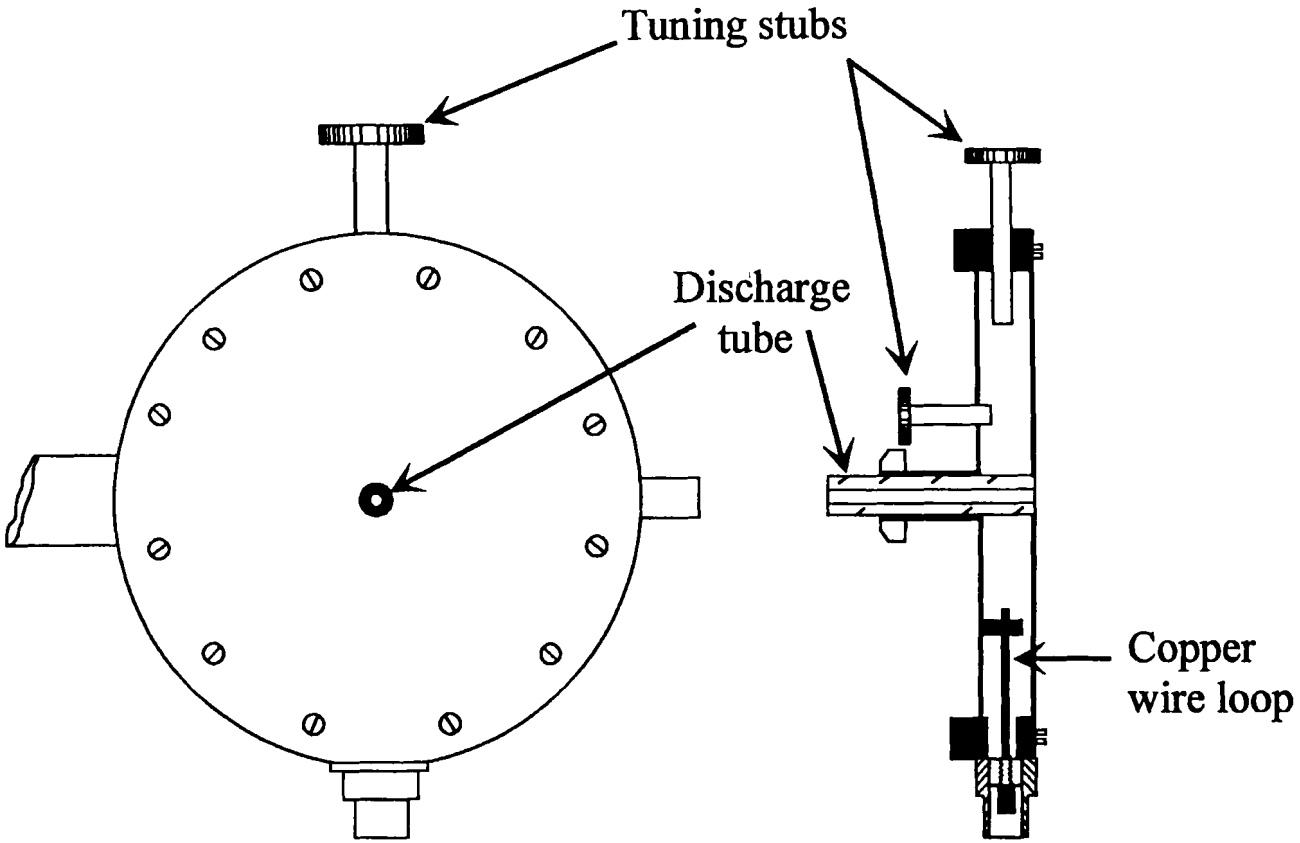

FIGURE 5. Beenakker resonator cavity. (Adapted from Reference 24.)

the plasma;[35] comparison of rotational temperatures using the OH radical versus N2+;[36] and excitation and rotational temperatures in a laminar flow torch.37 Electron number density determinations have been performed for both helium and argon plasmas, with values on the order of 1015 cm^{-3} for both plasmas.[38,39] The influence of pressure on several properties of the MIP has been investigated by Goode et al.[40] The argon excitation temperature, OH rotational temperature, electron number density, and relative line irradiances have been measured with pressures varying from 10 to 760 torr. The variation in pressure was found to have little effect on the spectroscopic temperature (although measurement precision was 10 to 50%). Electron number density was directly proportional to plasma pressure for the range investigated and the relationship between relative line radiance and pressure appeared complex, possibly due to pressure dependent excitation and deexcitation mechanisms. Table 1 summarizes diagnostic determinations for several microwave-induced, surfatron, and capacitively coupled microwave plasmas.

Spatial distribution maps of emission, electronic excitation temperature, rotational temperature, and electron number density were constructed for a helium MIP with varying analyte (helium, argon, carbon dioxide, and methane), analyte flow rate, and applied microwave power by Goode and Emily.[41] Pseudo three-dimensional and contour plots were prepared and used to find associations between emission and temperature or electron number density and atomization. A study by Pak and Koirtyohann of spatial profiles for the helium MIP indicated the possibility of different excitation mechanisms for metals versus nonmetals.[42] Three dimensional maps revealed that metals were excited lower in the plasma with a dip in emission intensity at the center of the plasma; nonmetals did not exhibit the same dip and were excited higher in the plasma. Application of MIPs to nonmetal determinations has also been discussed in terms of fundamental aspects of the plasma by Carnahan and coworkers.[43] Clay and Niemczyk studied iron emission in a nitrogen/rare gas MIP and demonstrated differences in excitation mechanisms with nitrogen concentrations above 3% due to the presence of nitrogen metastables.[44] Matousek et al. mapped the spatial distribution of emission in an argon plasma and found that metal deposition on the discharge tube walls at high microwave powers was a major source of analyte loss.[45] Hieftje et al. compared spatial profiles for MIP and surfatron systems when easily ionized elements (EIE) were introduced into the plasmas.46 EIEs enhanced analyte emission in the MIP to a higher degree in the MIP than in the surfatron system. The difference between the two systems was attributed to the improved sample injection in the surfatron system.

Excitation mechanisms and deviations from local thermodynamic equilibrium were compared for the MIP versus the ICP by Huang.[47] The most interesting findings of this study showed that the electron temperature in the MIP was much higher than in the ICP, but the electron number density was lower in the MIP; also, the ICP has an overpopulation of free electrons and a gas temperature only slightly lower than the electron temperature, while the MIP exhibited an underpopulation of free electrons and a gas temperature up to an order of magnitude lower than the electron temperature. Deviations from local thermal equilibrium in argon and helium MIPs were also investigated using Thomson scattering and Rayleigh scattering by Hieftje and coworkers.[48]

Table 1: Microwave Plasma Diagnostics

Plasma	Torch i.d. (mm)	Gas	Power (W)	T_{rot} (K)	T_{exc} (K)	n_e x10^{-14} (cm^{-3})	Ref
MIP	4 - 5	Ar	85 - 100	2000 - 2700			97
MIP	4 - 5	He	120 - 180	2200 - 2600			97
MIP	5	Ar	400 - 600	3110 - 3580	14200		35
MIP		He	75	1492 - 1976	6100 - 6700		37
MIP	2	He	85	1270 - 1620			36
MIP	5	He	400			5.75	38
MIP	5	Ar	40			24	38
MIP	2	He	80			6 - 8	39
MIP	2	Ar	85	6100	4500	4 - 16	40
MIP	2	He	85	6100	8800	1 - 2.5	40
MIP		He	350		1600 - 2000	1	47
MIP		Air	400 - 560		4533 - 4730		50
MIP		Ar	100 - 200	600 - 950			34
MIP		He	100 - 400	800 - 1500			34
MIP		O_2	100 - 300	1300 - 2500			34
MIP		He	270	3000	500 - 3000	1.1 - 2.1	41
Surfatron	2	Ar	82	2000	2400	3-4	255
Surfatron	2	He	82	2000	3000	1	255
Surfatron	1	Ar	50	2200	5100	9	259
Surfatron	3	Ar	0 - 200	1500 - 2500	7000 - 8000	3 - 4	256
Surfatron		He-CO_2	50 - 150	1850 - 2210		0.24 - 0.33	257
CMP		He	700	1620	3430	4	223
CMP		He-H_2	700	1800 - 3000	2000 - 5000	4 - 9	224
CMP		N_2	600	2800 - 4300	4900 - 5500	0.01 - 1	226
CMP		Ar	600		4800		226
CMP		Air	600		4600		226

Several studies on the analytical figures of merit of microwave-induced plasmas have been performed. Figures of merit and interelement effects for both air and nitrogen MIPs have been investigated by Urh and Carnahan.[49] Hieftje and Deutsch have also reported analytical characteristics[50,51] and limiting noise sources52 of the microwave-induced nitrogen discharge at atmospheric pressure (MINDAP).

Sanz-Medel et al. conducted a comparison study of a Beenakker cavity, surfatron, and microwave plasma torch to evaluate atomization and excitation capabilities for chlorinated hydrocarbons.[53] Detection limits for the same element differed by no more than 2 to 3 times and the most sensitive source was determined to be the Beenakker cavity. A study by Hieftje and others was performed to test the feasibility of replacing the inductively coupled plasma with the MIP with mass spectrometric detection. This fundamental study indicated that the two major obstacles in this replacement would be to minimize air entrainment into the plasma and to maintain a high ion flux through the interface.[54]

Finally, a review by Hubert, Moisan, and Zakrzewski has provided discussion on the specific problems and common mistakes associated with the supply and measurement of power in the MIP and offers possible solutions.[55] Hieftje et al. have also proposed a method for feedback stabilization of the microwave power supply.[56] Recently, Carnahan and coworkers proposed use of a pulsed 120-Hz, 3 kW, 2.45-GHz generator which could be converted to a continuous-wave output to sustain an MIP.[57]

C. Matrix Effects and Interferences

In addition to the study mentioned in the previous section on the effects of easily ionized elements (EIEs) on spatial emission properties,[46] several other studies concerning EIEs have been performed. EIE effects were studied when aqueous samples (copper, silver, magnesium, lead) were desolvated and nebulized into an MIP by Jin et al.[58] This study concluded that EIE effects within the plasma were more significant than EIE effects during desolvation and nebulization steps. Also, the EIE effect was not correlated with the ionization potential of the EIE, but rather was more dependent on the discharge tube dimensions, species and concentrations of EIEs, the analytical lines used, the method of sample introduction, and other operating procedures. In a study by Matousek, Orr and Selby, the presence of EIEs in an MIP with graphite furnace sample introduction was found to cause either analyte signal suppression or enhancement, depending on the element and type of line (atomic or ionic) monitored.[59] In particular, this study found rubidium and cesium addition (10 m*M*) produced enhancement of copper emission.

Interelement effects were overcome in a MINDAP system by using releasing agents such as those used in flame spectrometry.[51] Hieftje et al. found the depression of calcium signals by sodium, aluminum, and phosphate was remedied by the addition of cesium (in the case of sodium) or EDTA (for aluminum or phosphate). Ducatte and Long found nonmetal emission in a helium MIP can be effected by the presence of carbon dioxide or hydrogen.[60] Decreased signal intensity with carbon dioxide or hydrogen addition for sulfur, phosphorus, chlorine, bromine, and iodine was related to the diminishing excitation properties of the plasma discharge.

Finally, the effects of complex matrices were studied in aqueous samples by Caruso and coworkers.[61] In a comparison

of metal emissions for a 2% HNO3 versus synthetic ocean water matrix, the ocean water matrix solutions had enhanced linear dynamic ranges by 2 to 4 orders of magnitude for many metals.

D. Torch Design

The dimensions of a torch can have a dramatic effect on the properties of a plasma. A demountable tangential flow torch with a unique toroidal shape was investigated with different plasma gases by Michlewicz, Urh, and Carnahan.[62] This torch could be used with a nebulizer for analysis of aqueous solutions, but was not useful in the formation of argon plasmas. Goode et al.[63] observed that a tangential flow torch used with MIP-GC provided self-centering capabilities, increased emission, and improved stability when compared with a capillary torch. Long and coworkers[64] have also demonstrated the use of a tangential flow torch with supercritical CO_2 in an MIP-SFC system. In addition, a simple torch design has been constructed with hand tools and a drill press and investigated by Farrer et al.[65] This simple torch was easily modified from a concentric to tangential flow torch with the insertion of a flow modifier into one end of the torch.

Laminar flow torches have also been used with the microwave-induced plasma. Fielden studied a laminar flow torch for a helium MIP which was used as a detector for gas chromatography.[66] Signal-to-noise ratios for this torch design were studied with varying sheathing gas flow rate, insertion depth, and forward power. Detection limits for carbon, chlorine, and hydrogen were in the low pg/s range (2σ) over a tangential flow design. Similar improvements in detection limits over the tangential flow torch were found by Caruso and coworkers in a study involving a low-flow laminar flow torch.[67]

Torches can be cooled by liquid as well as gaseous outer sheaths. The analytical performance of a water-cooled capillary plasma torch for an MIP-GC was evaluated by Boss and coworkers.[68] This torch system demonstrated lower detection limits and enhanced sensitivity over the tangential flow torch. Matusiewicz and Sturgeon investigated a concentric quartz torch operated with synthetic or hydrocarbon based fluids as coolants which essentially eliminated erosion of the tube by the plasma.69 Finally, Mierzwa et al. developed a torch cooled with thermostated silicon oil; this torch exhibited a decrease in spectral background intensity for nebulized solutions.[70]

A novel torch design, the axial injection torch, has been recently developed and characterized by Quintero and coworkers.[71] Fundamental properties for this waveguide-fed torch were investigated and high volatilization and atomization capabilities were found.

E. Gas Introduction

Gaseous sample introduction is achieved by a variety of methods, including hydride generation, chemical oxidation, electrothermal atomization and graphite furnace. Table 2 provides analytical figures of merit for these sample introduction methods with the MIP. Hydride generation of chlorine and bromine for analysis by MIP-AES was performed by Barnett with nanogram and subnanogram detection limits.[72] Ng et al. determined selenium with a 40 ppb detection limit, and were also able to detect

Table 2: Analyical Figures of Merit for the MIP with Gaseous Introduction

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD (ng)	LOD def'n	RSD (%)	LDR	Ref
Ag	328.1	C	He	100	0.2	0.0006	3 σ	5	0.002-3.0 ng	88
	328.0	E	Ar	90		0.004	3 σ		> 4 orders	96
As	228.8	E	Ar	90	50			1.8		99
	228.8	E	Ar	90		0.120	3 σ			96
	235.0	D	He	100	80	0.8	$2\sigma_{bkgd}$		1.0-500 μg/ml	74
Br	291	A	Ar	30		50	$2\sigma_{bl}$		0.05-50 μg	81
	470.5	A	He	130		1	S/N = 2		0.005-50 μg	82
	470.5	C	He	130		2			3-4 orders	89
	478.6	B	He	500	270				1- 250 μg/ml	77
	470.5	A	He	150	40		$3\sigma_{bkgd}$	0.7	0.2-50 μg/ml	76
	470.5	A	He	100	7.46		3 σ	1.2	3 orders	80
	470.5	C	He	500	20	0.300	$2\sigma_{bkgd}$	3.3	0.25-20 μg/ml	92
	470.5	D	He	100		0.09	$2\sigma_{bl}$	1.4	0.02-200 μg/ml	72
Cd	228.8	C	He	500	0.6	0.010	$2\sigma_{bkgd}$	2.6	0.01-10 μg/ml	92
	228.8	E	He	75-135	2		3 σ		> 3 orders	98
	228.8	E	Ar	90		0.008	3 σ			96
Cl	479.5	B	He	500	210				0.5-500 μg/ml	77
	479.5	C	He	500	8	0.120	$2\sigma_{bkgd}$	3.5	0.25-20 μg/ml	92
	479.5	E	He	50-100		6.2	2 σ		2-3 orders	95
	479.5	C	He	110		2			3-4 orders	89
	479.5	D	He	100		0.3	$2\sigma_{bl}$	1.7	0.1-1000 μg/ml	72
	479.5	A	He	150	120		$3\sigma_{bkgd}$	2	0.5-500 μg/ml	76
Co	240.7	E	Ar	90		0.305	3 σ			96
Cr	425.4	E	Ar	90		0.047	3 σ			96
Cu	324.7	E	Ar	90		0.024	3 σ		> 4 orders	96
	327.4	C	He	500	2	0.030	$2\sigma_{bkgd}$	2.3	0.05-10 μg/ml	92
Fe	238.2	E	Ar	90		0.055	3 σ		> 4 orders	96
Hg	253.6	F	Ar-N_2	40		0.1		5	0.5-5 ng	102
	253.7	F	He	80	0.01	0.0005	$3\sigma_{bl}$	4.5	> 4 orders	103
	253.7	F	He	150-200	0.24		3 σ			101
	253.7	G	He	100		0.0024	3 σ	2.9		104
	253.7	H	He	80		0.016	S/N = 2	2.4	0.5-50 pg	100
I	206.2	C	He	130		0.2		1.9	5-1500 ng	91
	183.0	B	He	60	2.3		3 σ	0.92	3 orders	78
	206.2	C	He	140		2			3-4 orders	89
	253.7	H	He	70	0.74		3 σ	1.05	2-100 ng/mL	104
	206.2	A	He	150	230		$3\sigma_{bkgd}$	1.3	1-500 μg/ml	76
	258.3	C	He	100	800	2.4	3 σ	4.3	1-1500 ng	88
	206.2	E	He	50-100		1.0	2 σ		2-3 orders	95
In	410.2	C	He	75	141		2 σ	5-10	> 3 orders	87
Mn	259.3	E	Ar	90		0.011	3 σ		> 4 orders	96
Ni	352.4	E	Ar	90		0.220	3 σ			96

Table 2: Analyical Figures of Merit for the MIP with Gaseous Introduction

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD (ng)	LOD def'n	RSD (%)	LDR	Ref
Pb	368.3	E	Ar	90		0.056	3 σ		> 4 orders	96
	405.7	E	He	75-135	1		3 σ		> 3 orders	98
S	545.4	C	He	140		100			0.1-10 μg	89
	180.7	A	He	100	0.13		3 σ	1.13	1-10000 ng/mL	107
	496.4	C	Ar	50		90	3 σ		50-500 μg/ml	93
	180.7	I	He	1600	0.4				0.02-100 μg/ml	106
	527.9	E	He	50-100		12.0	2 σ		2-3 orders	95
Sb	217.6	E	Ar	90	20			2		99
	259.8	D	He	100	110	1.1	2 σ_{bkgd}		1-500 μg/ml	74
Se	204.0	E	Ar	90	46			1.5		99
	196.0	D	He	100	40		3 σ	6.7	> 3 orders	73
Sn	317.5	D	He	100	290	2.9	2 σ_{bkgd}		1-500 μg/ml	74
Tl	377.5	E	Ar	90		0.028	3 σ			96

A: Chemical generation; B: Chemical vaporization; C: Electrothermal vaporization; D: Hydride generation; E: Graphite furnace; F: Amalgamation trap; G: Gold trap; H: Cold vapor; I: Reductive pyrolysis

selenium in soils.[73] A miniature hydride generation device was developed by Barnett for the determination of Sb, As, Pb, and Sn.[74] Arsenic has also been studied by Matusiewicz et al.[75] using *in situ* preconcentration hydride generation.

Vaporization of the halides by chemical oxidation has been used in conjunction with helium MIPs. Camuña and others discussed at length the optimum conditions for chemical generation and argon MIP determination of chloride, bromide, and iodide for both continuous flow and flow injection sample introduction.[76] Michlewicz and Carnahan quantitatively determined chloride and bromide concentrations in aqueous solutions by adding sulfuric acid to form the hydrogen halide in a continuously flowing cell.[77] Nakahara and coworkers[78] determined trace iodine by oxidation of aqueous iodine using of 1.0 m*M* sodium nitrite in 5.0 *M* sulfuric acid as the oxidizing agent. They also discussed in a later paper the determination of total iodine in brines and seawaters using several oxidizing agents.[79] Determination of bromide using a variety of oxidizing agents has been investigated. Nakahara et al.[80] found that 100 mmol dm^{-3} potassium persulfate in 5.0 mol dm^{-3} sulfuric acid was the most favorable oxidant for elemental bromide generation, while Abdillahi, Tchanen, and Snook[81] found potassium dichromate in concentrated sulfuric acid as the most appropriate oxidizing agent for an argon MIP. Abdillahi and Snook compared oxidation-vaporization with electrothermal vaporization in the determination of bromide.[82] Both methods resulted in the same detection limit of 1 ng (S/N = 2), with an increase in linear dynamic range for the chemical generation.

Electrothermal vaporization (ETV) for sample introduction into an MIP has been reviewed by Matusiewicz in 1990.[83] This extensive review covers thermal vaporization sample introduction systems, *in situ* pre-concentration, speciation, instrumentation, including commercial MIP systems, and detection limits. Other reviews by Carey and Caruso,[84] Ng and Caruso,[85] and

Matusiewicz[86] cover ETV sample introduction for a variety of plasmas, including the ICP. A unique miniature unit with a heated wire filament was developed by Brooks and Timmons which allowed a liquid sample to be injected, volatilized and analyzed, and subsequent samples injected immediately following without extinguishing the plasma.[87] A tantalum-tip ETV sample introduction device developed by Caruso and coworkers resulted in no analyte recondensation during transport to the plasma and yielded picogram detection limits for Ag, Pb, and I.[88] Graphite rod vaporization was investigated by Abdillahi for nonmetals; nanogram detection limits of 10 μl aqueous samples were obtained for the halides, nitrogen, and sulfide.[89] In addition, an aerosol transport interface with a novel two-position valve has been developed by Matusiewicz et al. which yielded an overall sample introduction efficiency of 24% into the plasma.[90] Barnett and Kirkbright used ETV vaporization in the determination of iodide in hydrochloric acid; nanogram detection limits were achieved for aqueous solutions.[91] Trace determinations of Cd, Cu, Br, and Cl were investigated by Wu and Carnahan using ETV-He-MIP;[92] detection limits found for bromine and chlorine were in the low pg (ppb) levels when lead nitrate was used as the matrix modifier. Trace determination of sulfur by electrothermal evaporation was investigated by Broekaert et al.[93] Detection limits were 90 ng for ETE-MIP (evaporation from tungsten coil) using the 469.413 nm sulfur atom line. In the same study, lower detection limits were obtained for tungsten tube FANES/MONES (Furnace Nonthermal Excitation Spectrometry/ Molecular Nonthermal Excitation Spectrometry) monitoring the 383.73 nm S2 band (17 ng) and carbon tube FANES/MONES monitoring the CS molecular bands (2 ng).

A graphite furnace (GF) has also been used to vaporize sample into an MIP. A review by Matusiewicz and Sturgeon covers AAS, MIP-AES, ICP-MS, and FANES atomic spectrometric detection of hydride forming elements following trapping in a graphite furnace.[94] A graphite furnace has been used by Matousek and coworkers in the study of nonmetals with low nanogram detection limits.[95] Metal analysis using this method was performed by Broekaert et al., with detection limits in the low picogram range.[96] Broekaert et al. also published two companion papers concerned with the study of toroidal argon and cylindrical helium MIPs. The first paper outlined optimum operating conditions and spectroscopic properties of these plasmas using both graphite furnace and pneumatic nebulization sample introduction.[97] The second paper focused on the use of the graphite furnace for use with biological sample analysis.[98] Finally, graphite furnace, pneumatic nebulization, and hydride generation techniques were compared as MIP sample introduction systems for the simultaneous determination of As, Sb, and Se by Tschöpel et al., who achieved sub ng ml^{-1} detection limits with hydride generation followed by hot-trapping in a graphite furnace prior to injection into the MIP.[99]

Mercury analysis has been given considerable attention by MIP-AES researchers. Nakahara and coworkers determined mercury by cold vapor generation with a detection limit of 16 pg and a calibration curve linear from 50 pg to 500 ng.[100] Determination of mercury in natural gas condensate was improved by Snell et al. by removing carbon emission interference which gives artificially elevated mercury levels.[101] This was accomplished by capillary gas chromatography followed by an on-line amalgamation trap with subsequent injection into the MIP. With the mercury-selective amalgamation trap, detection lim-

its were 0.24 μg l^{-1} for dimethylmercury and 0.56 μg l^{-1} for derivatized monomethyl and inorganic mercury. Natarajan determined parts per trillion levels of mercury in aqueous solution using a reduction, aeration, amalgamation, and release procedure into an MIP with Ag wool contained in the amalgamation tube.[102] Mercury determinations in lake water were performed by Nojiri et al. by reducing the mercury in aqueous solution with 10% tin (II) chloride in 1 N sulfuric acid, purging with helium, and collecting in a gold amalgamation trap.[103] Heating the trap while purging with helium swept the mercury vapor into the MIP. The detection limit was 0.01 ng L^{-1}. In addition, atomic fluorescence, absorption, and emission were compared in the determination of mercury by Sturgeon and coworkers.[104] Identical vapor generation and amalgamation procedures were used so that the techniques could be directly compared; instrumental noise-limited detection limits were 0.94, 2.4, and 2.8 pg for AAS, AES, and AFS, respectively. Finally, cold-vapor mercury determination was used for the indirect analysis of iodine in seawater and brine by Nakahara and Wasa.105 A decrease was detected in mercury emission due to the interference of iodine with linear calibration curves for iodine from 2 to 100 ng ml^{-1} and a detection limit of 0.74 ng ml^{-1}.

Sulfur has been determined by converting sulfur-containing compounds in aqueous solution to H2S using noncatalytic reductive pyrolysis by Alvarado and Carnahan.[106] Detection limits for this technique were 30 ppb when monitoring the 921.3 nm line and 400 ppt for the 180.[73] nm line. Sulfur was also determined with detection limits in the low ng ml^{-1} range by Nakahara et al. using continuous-flow generation of H2S by acidification of aqueous sulfide, and sulfur dioxide generation by acidification of aqueous sulfite.[107] Molecular nitrogen in natural gases has been determined with a low pressure MIP 108 as well as gaseous and particulate lead in exhaust gas by MIP-AES and Zeeman furnace AAS.[109]

F. Liquid Introduction

Liquid introduction into an MIP is accomplished through nebulization of an aqueous solution. Table 3 summarizes analytical figures of merit for a variety of nebulizers used with MIP systems. Matusiewicz used a Hildebrand grid nebulizer for introduction of urine into an MIP.[110] No desolvation apparatus was needed, although a large volume of solution was needed to prevent carryover between samples. Long and Perkins used a concentric glass nebulizer and Scott type spray chamber for direct introduction into a low powered MIP.[111] A MAK (named for Meddings, Anderson, and Kaiser) nebulizer was employed in a study of synthetic seawater resulting in ppb detection limits by Ng and Shen.[112] A MAK nebulizer was also used by Michlewicz and Carnahan in the determination of chloride with a 7 ppm detection limit and a linear range of 70 to 210,000 ppm.[113]

Pneumatic nebulization is probably the most popular nebulization technique. Urh and Carnahan used pneumatic nebulization in the study of metals in aqueous solution; detection limits were 0.1 to 0.5 ppm for Na, Cu, Cr, Pb, Mo, and Ca with a linear dynamic range covering three orders of magnitude.[114] Alkali metals in aqueous solution were also determined using pneumatic nebulization by Haas and Jamerson.[115] In their study, the Ar-MIP was compared to a commercial Ar-ICP with identical spectrometer, optics, and data acquisition. The Ar-MIP was found

Table 3: Analytical Figures of Merit for the MIP with Aqueous Sample Introduction

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD def'n	RSD (%)	LDR (μg/g)	Ref
Ag		A	Ar	36	120	2σ			111
Al		A	Ar	36	1400	2σ			111
B	249.7	C	Air	500	93000			100-1000	114
Ba		A	Ar	36	180	2σ			111
Br	478.6	D	He	500	3000	2σ		7.5-1000	117
	470.5	D	He	70	230		2.6		118
Ca		A	Ar	36	40	2σ			111
	393.4	C	Air	300	430			1-1000	114
Cl	479.5	B	He	480	7000	$2\sigma_{bkgd}$		70-21000	113
	479.5	D	He	500	400	2σ		1-1000	117
	479.5	D	He	70	120		1.7		118
Co		A	Ar	36	1800	2σ			111
Cr	357.9	C	Air	300	90			1-1000	114
		A	Ar	36	8000	2σ			111
	425.4	B	Ar	110	62	3σ	2	> 3 orders	112
Cu	324.8	C	Air	400	89			1-1000	114
Cs	455.5	C	Ar	450	170	$3\sigma_{bkgd}$			115
Fe		A	Ar	36	650	2σ			111
	372.0	C	Air	400	1400			3-1000	114
Fl	685.6	D	He	500	4000	$2\sigma_{bkgd}$		- 1000	119
I	206.2	D	He	500	800	2σ		2-1000	117
	206.2	D	He	70	60		3.8		118
In	451.1	B	Ar	110	18	3σ	2	> 3 orders	112
K		A	Ar	36	24	2σ			111
	766.5	C	Ar	450	2.0	$3\sigma_{bkgd}$			115
Li		A	Ar	36	43	2σ			111
	670.8	C	Ar	450	0.24	$3\sigma_{bkgd}$			115
Mg		A	Ar	36	63	2σ			111
Mn	403.1	B	Ar	110	18	3σ	2	> 3 orders	112
		A	Ar	36	6900	2σ			111
Mo	379.8	C	Air	350	420			1-1000	114
Na	589.0	C	Air	500	82			1-1000	114
		A	Ar	36	2	2σ			111
	589.0	C	Ar	450	1.3	$3\sigma_{bkgd}$			115
P	213.6	D	He	70	4.5		3.5		118
Pb	405.8	B	Ar	110	139	3σ	2	> 3 orders	112
	368.3	C	Air	300	590			1-1000	114
Rb	420.2	C	Ar	450	77	$3\sigma_{bkgd}$			115
Sr	460.7	B	Ar	110	13	3σ	2	> 3 orders	112
		A	Ar	36	25	2σ			111
V	437.9	B	Ar	110	91	3σ	2	> 3 orders	112
Zn		A	Ar	36	420	2σ			111
Zr	360.1	B	Ar	110	3945	3σ	2	> 3 orders	112

* A: Glass nebulizer, Scott-type spray chamber; B: MAK nebulizer; C: Pneumatic nebulizer; D: Ultrasonic nebulizer

to have better detection limits and sensitivities improved by ten to several hundred times. Pneumatic nebulization into an Ar-MIP has also been investigated by Zyrnicki, who measured rotational and vibrational spectra of NO, N2, and OH.[116] Pneumatic and ultrasonic nebulization methods were compared for the halides in a study by Michlewicz and Carnahan;[117] for the MAK pneumatic system without desolvation, detection limits were 2 mg l^{-1} for Cl, 60 mg l^{-1} for Br, and 7 mg l^{-1} for I compared with ultrasonic nebulization with desolvation of 0.4 mg l^{-1} for Cl, 3 mg l^{-1} for Br, and 0.8 mg l^{-1} for I. This study also found moderate interference effects for selected metals for the pneumatic system and significant effects for the ultrasonic system. Ultrasonic nebulization for halide determination was also used by Jin and coworkers with resulting detection limits of 0.0045, 0.12, 0.23, and 0.06 μg ml^{-1} for P, Cl, Br, and I, respectively.[118] In the determination of fluoride, Gehlhausen and Carnahan found a significant improvement in the limit of detection for ultrasonic versus pneumatic nebulization.[119] However, memory effects from the fluoride were significant and so flow injection analysis was employed, allowing discrete sample amounts to be ultrasonically nebulized into the plasma in order to minimize memory effects.

G. Solid and Slurry Analysis

Measuring atomic concentrations in solid samples has been among the greatest challenges posed to the analytical chemist. Analytical figures of merit for the analysis of solids with the MIP are provided in Table 4. One of the most common methods for analysis of solid samples is laser-ablation (LA) followed by plasma AES.

Uebbing, Ciocan, and Niemax investigated LA-MIP-OES using a pulsed Nd:YAG for the analysis solid samples.[120] Several optimization studies were performed for parameters such as delay time, argon pressure and flow rate, and microwave power. This same group also determined detection limits for various elements and investigated matrix effects in steel, copper, aluminum, and borax glass.[121] They found single shot detection limits on the order of those obtained with laser-induced fluorescence and were able to perform matrix-independent analysis through use of internal standards. In later papers, Niemax and others performed simultaneous multielement analysis of solid samples through use of an echelle polychromator and gateable optical multichannel detector.[122,123] In microbulk steel and aluminum samples, RSDs for silicon, nickel, and iron were approximately 10 to 31%. For quartz samples, concentrations as low as 0.6 ppm Na and 0.4 ppm Li were detected, but the RSDs were considerably worse at 60% and 75%, respectively. A novel spark ablation cell has also been developed by Uchida and coworkers in which aerosol from a solid sample was swept from the spark ablation cell into a pulsed MIP.[124] Detection limits based on the signal to background ratio and relative standard deviation of the background signal (the method used by Boumans and Vrakking[125]) were in the ppm range with precisions of only a few percent for Ni, Cr, and Mn. A more energetic spark source was proposed as a possible improvement.

Broekaert and Leis analyzed mg amounts of biological matrices by heating the solids directly in a graphite furnace and sweeping the vapor into an MIP;[126] detection limits were in the sub ppm range for Cu, Fe, and Mn, and the analysis of several biological NBS reference materials for manganese were within the range

Table 4: Analytical Figures of Merit for MIP Solids Analysis

Element	λ (nm)	Matrix	Intro*	Gas	Power (W)	LOD (μg/g)	LOD def'n	RSD (%)	Ref
Al	396.2	Copper	LA	Ar	50-150	5.1	$3(2\sigma)^{0.5}$		121
Be	313.0	Copper	LA	Ar	50-150	2.4	$3(2\sigma)^{0.5}$		121
Cd	228.8	Copper	LA	Ar	50-150	79	$3(2\sigma)^{0.5}$		121
	228.8	Slurry	Neb	Ar	210	0.28[a,b]		4.4	130
Cr	425.4	Copper	LA	Ar	50-150	20	$3(2\sigma)^{0.5}$		121
	425.4		SpA	Ar	50	100		3	124
Cu	324.7	Slurry	Neb	Ar	210	4.13[a,b]		3.5	130
	324.8		ETV	Ar	50	0.07		3	126
Fe	238.2	Copper	LA	Ar	50-150	120	$3(2\sigma)^{0.5}$		121
	260.6		ETV	Ar	50	0.5			126
	248.3	Slurry	Neb	Ar	210	1.90[a,b]			130
Li	670.8	Quartz	LA	Ar	100	0.4[b]		75	122
	670.8	Quartz	LA	Ar		0.070	3 σ	75	123
Mg	279.6	Copper	LA	Ar	50-150	0.32	$3(2\sigma)^{0.5}$		121
Mn	257.6	Copper	LA	Ar	50-150	3.5	$3(2\sigma)^{0.5}$		121
	403.3		SpA	Ar	50	62		2	124
	257.6		ETV	Ar	50	0.2			126
Na	588.9	Quartz	LA	Ar	100	0.6[b]		60	122
	588.9	Quartz	LA	Ar		0.035	3 σ	60	123
Ni	301.2		SpA	Ar	50	60		3	124
Pb	405.8	Copper	LA	Ar	50-150	340	$3(2\sigma)^{0.5}$		121

Table 4: Analytical Figures of Merit for MIP Solids Analysis

Element	λ (nm)	Matrix	Intro*	Gas	Power (W)	LOD (μg/g)	LOD def'n	RSD (%)	Ref
Sn	284.0	Copper	LA	Ar	50-150	180	$3(2\sigma)^{0.5}$		121
Zn	213.8	Slurry	Neb	Ar	210	1.80[a,b]		4.6	130
Zr	357.3	Copper	LA	Ar	50-150	28	$3(2\sigma)^{0.5}$		121

* LA: Laser ablation; Neb: V-groove Babington type nebulizer; ETV: Electrothermal vaporization; S
Spark Ablation
a: Slurry sample detection limits are μg/ml
b: levels given are the lowest which were analyzed

of the certified values. Similarly, nonmetal analyte studies conducted by Webster and Carnahan utilized the solid sample's inherent vapor pressure at room temperature and a sweeping stream of helium into the MIP.[127] Milligram amounts of solid particulate coal have been analyzed by direct injection into a 500 W helium MIP by Gehlhausen and Carnahan.[128] Accurate C/H mass ratios were obtained using simultaneous spectroscopic determinations with a polychromator and photomultiplier tubes. However, it was not possible to accurately determine S and Cl in the coal samples. Solid particulate samples have also been analyzed both for particle size distribution and elemental content in a novel approach by Frame, Takamatsu, and Suzuki.[129] Particles from 1 to 20 μm were captured on a polycarbonate filter and then aspirated into the plasma with a nozzle which scanned the filter. The emission spectra provided information about the particle size, particle counts, and speciation. Finally, Matusiewicz and Sturgeon introduced powdered slurry samples into an MIP via a V-groove Babington nebulizer.[130]

H. Gas Chromatography

Gas chromatography (GC) coupled with MIP-AES is the most common hyphenated microwave plasma technique. By employing a separation technique prior to atomic emission, valuable speciation information can be gained. Analytical figures of merit for the separation and analysis of compounds with GC-MIP are given in Table 5. A review on directly coupled gas chromatography - atomic spectroscopy is given by Ebdon, Hill, and Ward,[131] as well as a review by Uden on element-specific chromatographic detection by AAS, plasma AES, and plasma MS.[33] A review of the MIP for element-specific gas, liquid, and supercritical fluid chromatographies is provided by Long et al.[132] Several parameter studies for GC-MIP-AES systems have been performed. Goode and Kimbrough investigated the influence of the optical viewing axis and found axial (end-on) viewing provided greater sensitivity while lateral (side-on) viewing provided enhanced selectivity.[133] In another paper the same authors investigated signal-to-noise ratios.[134] Andersson and Schmid studied the performance of their system with respect to the chemical form of the analyte, limit of detection, selectivity, and variation of the flow rate of the make-up gas.[135] The elemental response and the effect of compound structure was examined by Yieru et al.[136] and also by Jelink and Venema.[137] Solvent venting techniques and interfaces have also been discussed.[138,139]

GC-MIP-AES has been used as an element-selective detector for a variety of elements,[140–142] including some simultaneous multielement applications.[143–145] Separation and identification of oxygen-containing compounds has been investigated.[146–152] Organic compounds such as organofluorines,[153] organosilicates,[154] organometallics,[155–157] and hydrogen containing organic compounds[158] have been separated and analyzed. Chelate[159,160] and speciation[161–163] studies have also been performed. In addition to the volatile organics mentioned here, gas mixtures have also been examined.[164–167]

GC-MIP-AES has become particularly popular for the analysis of environmental samples. Environmental waters have been examined for organolead and organotin.[168–173] Wines have also been analyzed for organotin content.[174] Mercury speciation has been investigated.[170,175,176] Selenium,[177] fluorine,[178] and trace beryllium[179]

Table 5: Figures of Merit for GC-MIP

Element	Form	λ (nm)	Gas	LOD (pg/s)	LOD (pg)	LOD (pg/ml)	LOD def'n	RSD (%)	LDR	Ref
As	marine sediments & coals	189	He		3		S/N=3		3.4 decades	183
	dimethylarsenic acid	228.8	He		80	20000				156
Br	4-bromodiphenyl ether	478	He		75		S/N=3			135
	insecticides	478.6	He	75*			S/N=2			187
	1,4-dibromobutane	470.5	He	3000	10000		A			143
		478	He	13*						142
Be		313.0	He			0.3	$3\sigma_{bl}$	4.1		179
C		247.9	He	15			S/N=3			133
	benzothiophene	193	He		10		S/N=3			135
	marine sediments & coals	193	He		0.2		S/N=3		3.2 decades	183
	insecticides	193.1	He	0.5*			S/N=2			187
	insecticides	247.9	He	2.6*			S/N=2			187
	dioxins	247.9	He	76				3	10-1000 ng	189
	decane	247.9	He	3000	10000		A			143
	methane	247.8	He		10		2σ			166
Cl	p-dichlorobenzene	479.5	He	400			S/N=3			133
	Cl_4,Cl_5,Cl_6-benzene	479	He		79		S/N=3			135
	insecticides	479.5	He	39*			S/N=2			187
	dioxins	479.5	He	120				6.7	10-1000 ng	189
	1,3,5-trichlorobenzene	479.5	He	500	2000		A			143
		479	He	20*						142
F	TMFS	685.6	He			20000		3	3.3 decades	178
	insecticides	685.6	He	40*			S/N=2			187
	hexafluorobenzene	685.6	He	4.8*						153
H	insecticides	486.1	He	2.2*			S/N=2			187
	organic solvents	656.2	He		5000				15-800 ng	158
	H_2	656.2	He		2		2σ			166

Hg	diphenylmercury	254	He		1.4		S/N=3			135
	methylated	253.7	He			0.60				170
	insecticides	184.9	He	0.1*			S/N=2			187
	Et_2Hg	253.6	He		10			4-5	0.04-12 pg	182
I	iodobenzene	206.2	He	40			S/N=3			133
N	marine sediments & coals	174.2	He		20		S/N=3		3.5 decades	183
	insecticides	174.2	He	7.0*			S/N=2			187
O	dimethylphthalate	777.2	He		1320		S/N=3			135
	marine sediments & coals	777.2	He		300		S/N=3		3.5 decades	183
	insecticides	777.2	He	75*			S/N=2			187
	alcohols	777.2	Ar	1000			3 σ_{bkgd}			152
P	marine sediments & coals	186	He		17		S/N=3		3 decades	183
	insecticides	177.5	He	1.5*			S/N=2			187
Pb	Me_3Br^+	405.8	He			1	3 σ	5		169
	methylated	261.4	He			0.20		2		170
Pd	chelated	340.4	He		50					159
S	benzothiophene	180.7	He		5.2		S/N=3			135
	marine sediments & coals	180.7	He		10		S/N=3		3 decades	183
	insecticides	180.7	He	1.7*			S/N=2			187
Se	dimethylselenide	196.0	He			2	3 σ	2-12		177
	marine sediments & coals	196.0	He		4		S/N=3		>2.5 decades	183
Si	insecticides	251.6	He	7.0*			S/N=2			187
		251.6	He		4.5					154
Sn	methylated	270.7	He			0.15		2.5		170

* Minimum Detectable Level

A: 2 times the peak to peak noise divided by the full width at half maximum of the peak

have also been determined in environmental waters.

Sediments, soils, and oils have been analyzed by GC-MIP-AES. Clean-up (such as enzymatic hydrolysis for the decomposition of organic matter) and extraction (such as supercritical fluid or Soxhlet extraction) steps are usually required before a sample can be injected into a gas chromatograph. Soils and sediments have been analyzed for organotin,[172,180] butylin compounds,[181] mercury,[182] and a variety of elements.[183] Oils and gasolines have also been analyzed for metals[184] and such compounds as thiophenes,185 metalloporphyrins.[186]

Other environmental samples have been analyzed with GC-MIP-AES. Pesticide residues on foods have been determined.[187,188] Dioxins and related compounds have also been studied by this method.[189-191] Biotic matrices have been analyzed for mercury[192] and other metals,[193] as well as polychlorinated biphenyls.[194]

GC-MIP-AES has also been used as a tool in the determination of empirical and molecular formulae. The validity of empirical formulae obtained by this technique and also methods for formula calculations are given by Valente and Uden.195 H/C molar ratios and multielement information on hydrocarbon mixtures were studied by Buteyn and Kosman[196] using capillary column simulated distillation. Uden and coworkers have determined formulae for polymer pyrolyzates with <2% relative error[197] and also for hydrocarbons and chlorinated organic compounds.[198] Empirical formulae for a wide variety of organic compounds were also determined by Yu.[199] Finally, Hooker and DeZwaan combined MIP-AES and mass spectral data in molecular formula determinations of large molecules (GMW 200-400).[200]

I. Liquid Chromatography Techniques

Liquid chromatography (LC) techniques, though generally not as popular as GC, have been investigated for separation of sample components prior to excitation in an MIP. Supercritical fluid (SFC), high performance (HPLC), replacement ion (RIC) chromatographies, as well as capillary zone electrophoresis (CZE) have been investigated as separation techniques coupled to the MIP.

In supercritical fluid chromatography, the microwave-induced plasma has been used as an element-selective detector. The effects of CO_2 on excitation temperature, electron number density, and analyte emission signals in a packed column SFC- Ar MIP system were investigated by Motley et al.[201] Plasma excitation temperature and organometallic analyte emission were found to decrease with increased amount of CO_2 introduced into the plasma, while electron density initially decreased and then leveled off. Motley and Long also investigated central versus sidearm sample introduction into a helium highly efficient microwave-induced plasma (He HEMIP) from the packed column SFC.[202] Sidearm sample introduction of several organometallic compounds was found to be superior to central introduction in terms of repeatability, linear dynamic range, and minimum detectable quantity. In addition, Motley and Long found minimum detectable quantities for Cl, S, and P in the subnanogram level for the SFC-HEMIP system.[203] They also reported that the helium plasma, unlike the argon plasma, was unaffected by the introduction of CO_2. Webster and Carnahan reported on a He MIP which could be coupled with packed column SFC for the determination of

nonmetals without detectable changes in plasma cavity tuning, peak area response, or electron number density.[204] They found low nanogram detection limits for sulfur, chlorine, and hydrogen.[205] Capillary SFC-He MIP was investigated by Webster and Carnahan, who reported plasma spectral characteristics for nonmetals under simulated SFC conditions.[206] Carnahan and coworkers used capillary SFC- He MIP for chlorine-selective detection with three orders of magnitude calibration range and a detection limit of 40 pg s^{-1}.[207]

HPLC coupled with MIP detection has been investigated, but has not found much promise due to incompatibilities between HPLC flow requirements and the extinguishing of the MIP.[208] Limentani and Uden analyzed organoarsenic compounds using HPLC-MIP.[209] Carnahan and coworkers explored use of a moving band interface to separate HPLC solvent from the analyte before injection into the MIP.[210] With this method, they found detection limits for chlorinated organic compounds in the low ng range (Cl), which approached the detection limits found with GC-MIP systems. Heltai et al. used hydraulic high pressure nebulization of the HPLC effluent into an MIP; nanogram amounts of metals and nonmetals could be detected.[211] Traditional liquid chromatography has also been investigated for separation prior to the MIP. Michlewicz and Carnahan characterized several halides and oxohalogen salts which were separated on an ion exchange column and then ultrasonically nebulized into a large volume MIP.[212] Detection limits were 1.5 to 6 mg, which were limited by background noise. Replacement ion chromatography effluent was introduced into the MIP using pneumatic nebulization by Hieftje et al.[213] Detection limits were 30 to 300 ng for anions and 100 to 500 ng for cations; the system was limited both in detectability of the ions and precision by multiplicative noise sources. Finally, a unique interface between a liquid chromatograph and an MIP was developed by Zhang and Carnahan.[214] Halides and oxohalogens separated by LC were nebulized and directed to a moving wheel interface, which evaporated the solvent and directed the dry vapor to the plasma. Detection limits were 0.4 to 20 μg for the halogens.

A unique system which coupled thin layer chromatography (TLC) and the MIP was developed by Jansen and coworkers.[215] This system created the plasma directly on the TLC plate by connecting the inner conductor of the coaxial cable to a stainless steel capillary tube through which the helium support gas flowed. The impedance of this plasma electrode was matched simply by controlling the distance between the capillary tubing and the grounded metal plate below the TLC silica support. 660 pg of mercury in a 1 μl spot on the TLC plate could be detected; irregularities in the sorbent surface and irregular positioning of the plate relative to the source led to irreproducibilities in the signal and background. Finally, capillary zone electrophoresis coupled with a helium MIP was investigated by Liu and Lopez-Avila.[216] The electrophoresis separation capillary was interfaced to the MIP through an ion exchange interfacing capillary, which was also used as the electrical junction connector to complete the electrophoresis circuit outside the detector. The detection limit for trimethyltin chloride using this system was 1 mg ml^{-1}; this poor detection limit was attributed to operation of the plasma while not under optimal conditions and inadequate cavity and plasma temperatures.

J. Near Infrared Detection

Freeman and Hieftje describe the analytical characteristics of near-infrared (NIR) nonmetal emission from a helium MIP.[217] Sulfur showed the greatest advantage in the NIR in terms of signal-to-background, while the carbon signal-to-background was considerably worse. In addition, they found that most of the best nonmetal emission lines fell within a narrow window which could be scanned using a photodiode array. Freeman and Hieftje also investigated nonmetal element ratio determinations in organic compounds with their system, but found that intensity ratios varied significantly with changes in plasma conditions and needed frequent calibration with reference compounds.[218] Finally, they used interferometric detection in the NIR for detection of C, N, and O and found the background to be simple and unstructured.[219] Fry et al. also investigated interferometric NIR detection of eleven nonmetals excited in an MIP, and published an extensive table of all observed lines and relative intensities for the MIP-excited elements.[220] Lastly, Hubert et al. detected NIR nonmetal emission with a Fourier transform spectrometer, which provided adequate resolution (1 cm^{-1}) and high wavelength accuracy.[221]

IV. CAPACITIVELY COUPLED MICROWAVE PLASMAS (CMP)

A. Introduction

The capacitively coupled microwave plasma was developed by Murayama, Matsuno, and Yamamoto at the Hitachi Central Research Center in 1968.[23] A common CMP design is shown in Figure 6. The CMP is generated by transmitting microwaves from the magnetron through a rectangular waveguide to an electrode. The waveguide supports a standing wave. Maximum coupling of the power from the magnetron to the electrode is accomplished by positioning the magnetron probe at $\lambda_g/4$ (where λ_g is the wavelength in the waveguide) or an odd multiple of $\lambda_g/4$ from the rear end of the waveguide and the electrode at $\lambda_g/4$ from the opposite end of the waveguide.[222] The microwaves are guided to the tip of the electrode using a coaxial waveguide which is positioned perpendicularly to the rectangular waveguide. The electrode is contained within a discharge tube and the plasma forms at the tip of the electrode around which the plasma gas flows.

The CMP offers several advantages, including robustness (easily accommodating both gaseous and liquid sample introduction) and operation at high powers. In addition, the CMP has demonstrated promising results in the direct analysis of solid samples. However, the CMP tends to be slightly less precise and suffers from a higher background than the MIP.[32] Analytical figures of merit for analysis of liquids by the CMP are given in Table 6.

B. Diagnostics and Characteristics

Temperature and electron number density measurements for the CMP have been investigated; several values are summarized in Table 1. Winefordner et al. examined spectroscopic plasma temperatures in a high flow rate (> 6 L min^{-1}) helium CMP and found little difference in temperatures for aqueous versus organic solutions.[223]

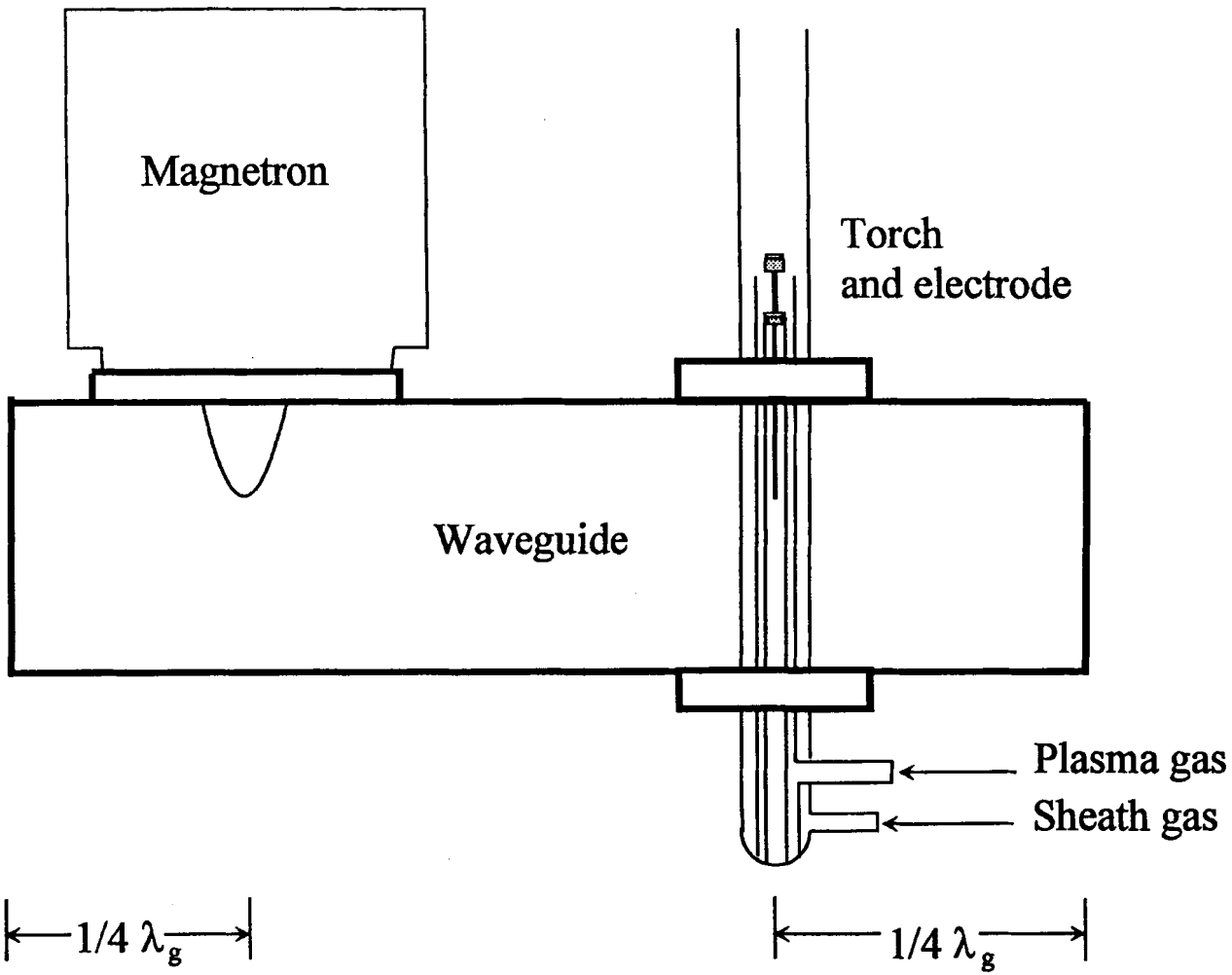

FIGURE 6. Capacitively coupled microwave plasma.

Table 6: Analytical Figures of Merit for the CMP

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD (pg)	LOD def'n	RSD (%)	LDR	Ref
Ag	328.1	A	N_2	325	470		3 σ_{bkgd}	1.6	2-100 μg/ml	232
	328.1	E	N_2-He	1000		210	3 σ	12	3.1	236
	328.1	E	He-H_2	135		12	3 σ_{bl}	5	4.0	237
Al	396.2	A	N_2	325	500		3 σ_{bkgd}	1.1	3-500 μg/ml	232
	396.1	A	He	900	3		3 σ_{bl}		≥ 2 orders	233
Ba	553.6	A	N_2	325	3100		3 σ_{bkgd}	2.0	10-100 μg/ml	232
	553.5	E	N_2-He	1000		50	3 σ	12	3.7	236
	553.5	E	He-H_2	135		104	3 σ_{bl}	8	> 2.3	237
Ca	422.7	A	N_2	325	650		3 σ_{bkgd}	6.5	2-200 μg/ml	232
	422.7	A	He	900	2		3 σ_{bl}		≥ 2 orders	233
Cd	228.8	A	N_2	325	620		3 σ_{bkgd}	1.2	4-250 μg/ml	232
	228.8	A	He	900	6		3 σ_{bl}		≥ 2 orders	233
	228.8	E	N_2-He	1000		30	3 σ	8	> 3.3	236
	228.8	E	He-H_2	135		4	3 σ_{bl}	6	> 3.0	237
Cl	837.6	B	He	850	400		3 σ			234
Cr	425.4	A	N_2	325	260		3 σ_{bkgd}	1.7	1-200 μg/ml	232
	427.5	A	He	900	9		3 σ_{bl}		≥ 2 orders	233
Cs	852.1	A	N_2	325	4000		3 σ_{bkgd}	2.8	10-100 μg/ml	232
Cu	324.8	A	N_2	325	90		3 σ_{bkgd}	6.0	0.5-200 μg/ml	232
	324.8	E	N_2-He	1000		15	3 σ	8	4.3	236
	324.8	E	He-H_2	135		7	3 σ_{bl}	6	4.1	237
F	685.6	B	He	850	1000		3 σ			234
Fe	371.9	A	He	900	12		3 σ_{bl}		≥ 2 orders	233
Ga	294.4	E	N_2-He	1000		45	3 σ	11	> 3.5	236
	294.4	E	He-H_2	135		28	3 σ_{bl}	9	> 3.0	237
Ge	265.1	E	N_2-He	1000		100	3 σ	12	> 3.0	236
	265.1	E	He-H_2	135		66	3 σ_{bl}	5	> 2.8	237
In	303.9	E	N_2-He	1000		65	3 σ	7	> 3.2	236
	303.9	E	He-H_2	135		44	3 σ_{bl}	7	> 3.0	237

K	766.5	A	N_2	325	260		3 σ_{bkgd}	3.5	2-500 μg/ml	232
Li	670.8	A	N_2	325	5		3 σ_{bkgd}	1.7	0.03-20 μg/ml	232
	670.8	E	N_2-He	1000		10	3 σ	10	4.0	236
	670.8	E	He-H_2	135		4	3 σ_{bl}	9	3.6	237
Mg	285.2	A	He	900	2		3 σ_{bl}		≥ 2 orders	233
	279.5	E	N_2-He	1000		15	3 σ	7	3.8	236
	279.5	E	He-H_2	135		1	3 σ_{bl}	7	> 3.5	237
Mn	257.6	D	Ar	500	8		3 σ_{bkgd}	1.8		235
	257.6	E	N_2-He	1000		85	3 σ	10	3.1	236
	257.6	E	He-H_2	135		16	3 σ_{bl}	9	> 3.6	237
Na	589.0	A	N_2	325	10		3 σ_{bkgd}	1.8	0.05-15 μg/ml	232
	589.6	A	He	900	0.05		3 σ_{bl}		≥ 2 orders	233
Ni	341.7	A	He	900	0.7		3 σ_{bl}		≥ 2 orders	233
Pb	405.8	A	N_2	325	2900		3 σ_{bkgd}	1.0	20-1000 μg/ml	232
	405.8	A	He	900	10		3 σ_{bl}		≥ 2 orders	233
Pd	342.1	A	N_2	325	2100		3 σ_{bkgd}	2.1	10-200 μg/ml	232
Rb	780.1	E	N_2-He	1000		30	3 σ	12	> 3.5	236
	780.1	E	He-H_2	135		12	3 σ_{bl}	10	3.2	237
Sn	235.5	C	He	320		1000	S/N=3	5.5		228
	317.5	A	He	900	10		3 σ_{bl}		≥ 2 orders	233
Sr	460.7	A	N_2	325	10		3 σ_{bkgd}	1.9	0.05-100 μg/ml	232
Ti	334.9	A	He	900	4		3 σ_{bl}		≥ 2 orders	233
Zn	213.9	E	N_2-He	1000		654	3 σ	9	> 3.7	236
	213.9	E	He-H_2	135		5	3 σ_{bl}	7	3.7	237
	213.9	A	N_2	325	5000		3 σ_{bkgd}	4.3	10-100 μg/ml	232

* A: Meinhard nebulization; B: Pneumatic nebulization; C: Hydride generation; D: Concentric nebulization; E: Thermal vaporization

Temperatures and electron number density as a function of power, observation position, and solution uptake and carrier gas flow rates were investigated for a helium/hydrogen CMP by Winefordner et al.[224] Hydrogen in the plasma gas provided slight increases in the rotational and excitation temperature, but reduced emission signals for elements introduced into the plasma by solution nebulization.[225] Bings and Broekaert found that the N2 CMP provided lower detection limits for several metals compared to Ar and air CMPs; however, these detection limits were still one order of magnitude worse than those obtained with ICP-OES.[226] Finally, analytical performances were compared for a Pt-clad W-rod electrode and a tubular tantalum electrode plasma torch by Winefordner and coworkers.[227] The tubular tantalum electrode was found to have improved signal-to-background, signal-to-noise and precision, as well as improved detection limits over the tungsten rod electrode.

C. Gas Introduction

The CMP has been used in conjunction with GC separation for detection of organic and inorganic compounds. Winefordner and coworkers used GC-CMP-AES for the determination of butyltin compounds with nanogram detection limits.[228] In the same study, organic and inorganic tin were determined using hydride generation and collection in a cold trap prior to introduction into the CMP. Nanogram detection limits were also found for nonmetals in organic compounds by Winefordner et al.[229] Huang and Blades found detection limits in the sub ng s^{-1} range for a variety of organotin compounds separated by GC.[230] Finally, the detection of trace levels of water in solid samples by evolved gas analysis was studied by Winefordner et al.[231] Absorbed water and chemically bound water in a variety of solid samples could be distinguished and quantified; however, the method proved less accurate than conventional methods and calibration curves needed to be prepared on a daily basis.

D. Liquid Introduction

Solution nebulization sample introduction was investigated by Winefordner and coworkers for the tubular electrode torch mentioned above.[232] Detection limits for a variety of elements were in the low and sub-μg ml^{-1} range with precisions of generally 1 to 2%. Parts per billion detection limits were also found by Winefordner et al. for a high power (up to 1600 W) helium CMP.[233] This system contained a graphite tube or rod as the electrode, which exhibited lower emission background and no significant contamination as compared to the metal rod electrode previously used. Aqueous and organic fluorine and chlorine were also determined by the He-CMP.[234] LODs for organic fluorine and chlorine were 1 and 0.4 μg ml^{-1}, respectively, while fluorine was undetected and chlorine was only weakly observed for the aqueous solutions. A highly efficient desolvation system was developed with pneumatic nebulization into a CMP by Winefordner and coworkers.[235] Sensitivity and detection limits for manganese were improved over CMP and ICP with conventional pneumatic nebulization.

Microsampling in a graphite cup contained at the top of the electrode was investigated by Ali, Ng, and Winefordner.[236]

Plasma heating of the electrode vaporized the sample with detection limits from 10 to 210 pg for a variety of elements and precision better than 12%. Microsampling was also achieved using a tungsten filament electrode, onto which samples could be injected before rapid vaporization and excitation in the plasma.[237] Detection limits for 12 elements were below 100 pg, with a linear dynamic range of 3 to 4 orders of magnitude and precision better than 10%. A tungsten cup electrode was also studied for the analysis of metals in microsamples.[238] Detection limits for Cd, Zn, and Pb were in the low pg range for 10 µl samples with less than 10% RSD.

Finally, whole blood samples have been analyzed by the Winefordner group using CMP-AES.[239-241] The detection limit for lead in a 2 µl blood sample was 30 ng ml^{-1} with precision better than 10%.

E. Solid Introduction

Hanamura, Wang, and Winefordner analyzed hydrogen and oxygen in metals by heating 1 to 2 g samples in a furnace under pressure and extracting the vapor in helium gas, which was carried to the CMP.[242] Steel samples were analyzed directly by Winefordner et al. by placing the sample in a cup cut into the top of the graphite electrode.[243] Limits of detection indicated a usefulness of this technique in the range of sub-µg g^{-1} to the percent range for solid steels. Tomato Leaves (SRM 1573a) and Coal Fly Ash (SRM 1633a) Standard Reference Materials were analyzed directly by Ali, Ng, and Winefordner[244] using CMP-AES with 20% N2/80% He as the plasma gas. Detection limits were reported in the nanogram and subnanogram range for a variety of elements. The precision was 12 to 18% for 5 to 10 mg samples. Finally, Winefordner et al. determined Cd in solid samples with picogram detection limits and relative standard deviations of less than 20%.[245] Montana Soil (SRM 2711), Tomato Leaves (SRM 1573a), and Bovine Liver (SRM 1577b) were all analyzed and the measured Cd concentrations compared well with certified values. Analytical figures of merit for the analysis of solids by the CMP are provided in Table 7.

V. SURFACE-WAVE/SURFATRON PLASMAS

A. Introduction

A microwave plasma obtained through surface wave propagation was reported by Hubert, Moisan, and Ricard in 1975[246] and developed as a source for optical spectroscopy.[247] Surface-wave, surfatron, or surfaguide microwave plasmas rely on propagation of microwaves along the boundary of a medium. If the surface-waves in a gaseous medium are adequately energetic, a plasma can form and the surface-waves then propagate and sustain the plasma simultaneously. An illustration of a surfatron is given in Figure 7. The surfatron, which is responsible for launching the surface waves which create plasma columns many times longer than the excitation structure (tens of centimeters), is composed of two main parts. The first part is the coupler which transfers the microwave energy from the coaxial cable to the plasma. The coupler can be moved vertically, which in turn moves the end plate that controls the coupling of the energy to the plasma. The second part is the excitation structure, which acts as an extension

Table 7: Analytical Figures of Merit for Solid Samples with Thermal Vaporization in a CMP

Element	λ (nm)	Matrix	Gas	Power (W)	LOD (μg/g)	LOD (ng)	LOD def'n	RSD (%)	LDR	Ref
Cd	228.8	TL*	He-N_2	400		0.3	3 σ_{bkgd}			244
	228.8		He-H_2	828	70000	0.040	3 σ_{bl}/m	< 20	40-4000 pg	245
	228.8		He-H_2	525		0.008	3 σ_{bl}	< 10		238
Cu	324.8	TL*	He-N_2	400		8	3 σ_{bkgd}			244
Fe	258.6	TL*	He-N_2	400		134	3 σ_{bkgd}			244
Mn	403.1	TL*	He-N_2	400		69	3 σ_{bkgd}			244
Mg	285.2	TL*	He-N_2	400		1	3 σ_{bkgd}			244
	285.2		He-H_2	639		0.037	3 σ_{bl}	< 10		238
Pb	283.3	TL*	He-N_2	400		2	3 σ_{bkgd}			244
	283.3	steel	He-H_2	450	0.08					243
Rb	780.0	TL*	He-N_2	400		4	3 σ_{bkgd}			244
Sn	189.9	steel	He-H_2	450	5			> 20		243
Sr	460.7	TL*	He-N_2	400		14	3 σ_{bkgd}			244
Zn	213.9		He-H_2	476		0.020	3 σ_{bl}	< 10		238
	213.9	TL*	He-N_2	400		30	3 σ_{bkgd}			244

* Tomato Leaves, NIST 1573a

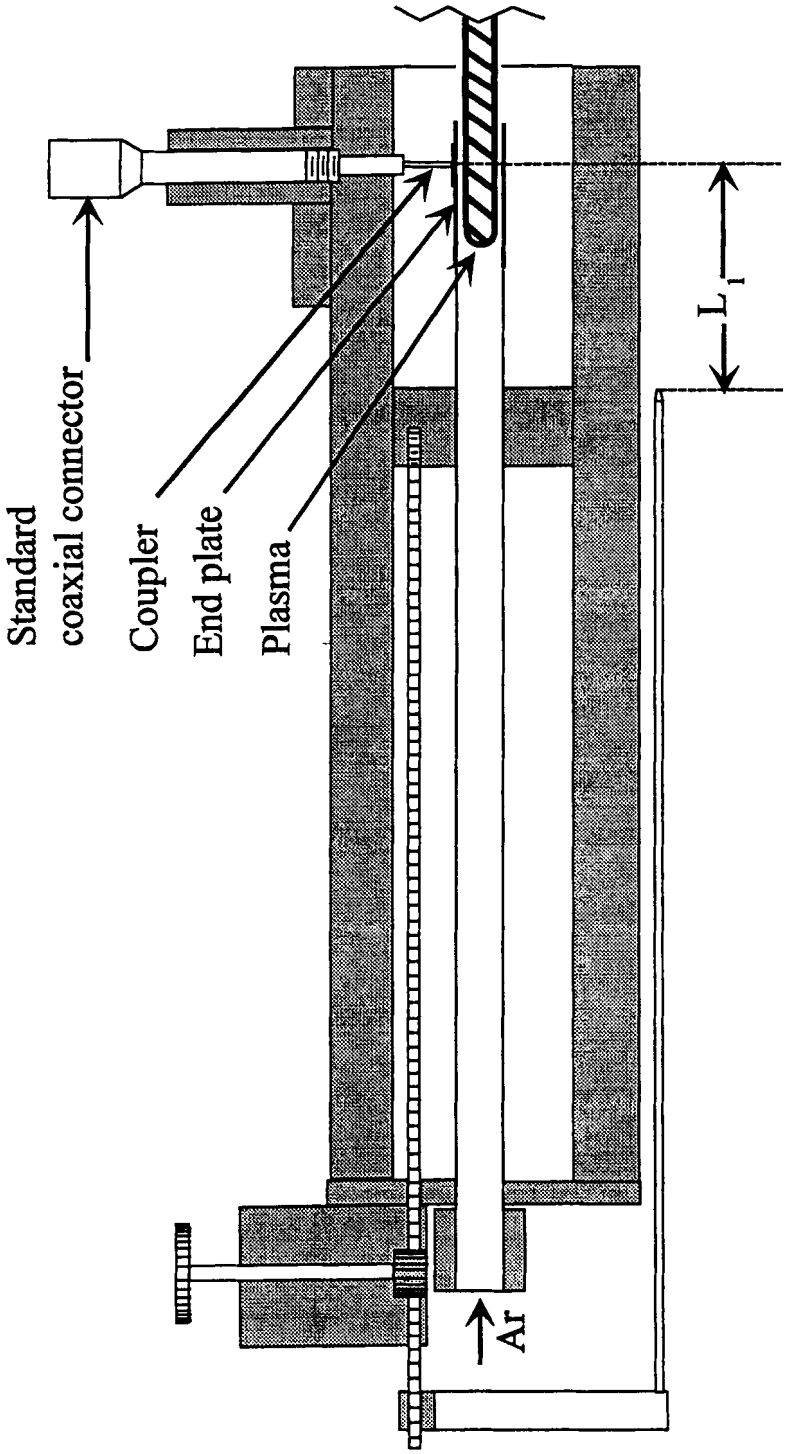

FIGURE 7. Surfatron. (Adapted from Reference 246.)

of the coaxial transmission line and extends into a Faraday cage. The length of the excitation structure, L1, is varied using a toothed rack and a pinion. A certain frequency bandwidth (in terms of a maximum admissible reflected power) is associated with any length L1. For a desired frequency, the length L1 is set to an approximate value before igniting the plasma with a Tesla coil. The depth of the coupler is then adjusted for minimum reflected power (which is also the maximum plasma length). The length L1 can then be adjusted so that the impedance is matched to the characteristic impedance of the transmission line, for a resulting reflected power of zero. Thus, no tuning stubs are needed and the resulting plasma is azimuthally symmetrical.

Because the coaxial cable of this design is limited to about 1 kW at 915 MHz for safe operation, the surfaguide was developed to permit use of higher microwave powers.[248] For a surfaguide launcher, the power which can be applied is only limited by how efficiently the plasma tube can be cooled. The surfaguide design is illustrated in Figure 8. Power is transmitted from the microwave generator to the plasma through a tapered waveguide. A moveable plunger located at the opposite end of the input power acts as a short circuit; tuning is accomplished by positioning the plunger so that there is a minimum reflected power on the reflectometer. A Tesla coil is used to ignite the plasma. A 1991 review of the design and physical principles of surface-wave plasma sources was given by Moisan and Zakrzewski.[249]

Surface-wave microwave plasmas have the advantage of operation over a wide range of parameters, including frequency, power, and flow rates.247 However, like the MIP, this plasma cannot accommodate liquid introduction at low power. Table 8 summarizes analytical figures of merit for analysis of liquids with surfatron microwave plasmas.

B. Diagnostics

Diagnostic values for several surfatron microwave plasmas are included in Table 1. Wave propagation and diagnostics of argon surface-wave microwave plasmas is given by Granier and coworkers.[250,251] Their studies include finding the axial density profile ne and collisional frequency within the plasma, as well as characteristics such as electron number density, maintaining electric field, and collision frequency. A collisional-radiative model for helium surface-wave plasmas at low and intermediate pressures has been given by Ferreira et al.[252] Noise characterization in the surfatron MIP with Fourier transform detection was examined by Sing and Hubert.[253] Flicker noise (1/f) was found to dominate below 1 Hz, with white noise dominating at higher frequencies and interferences at 60 and 120 Hz from the microwave power supply. These noise characteristics were similar to those found in resonant cavity microwave plasmas. Microwave and RF surface-wave discharges were also investigated by Moisan et al. as sources for plasma chemistry and plasma processing.[254] They found that surface wave plasmas possessed several inherent advantages over other plasmas, including that they require no internal electrodes and can be applied over a wide range of pressures and frequencies. In another study, Moisan and coworkers determined fundamental properties such as spectroscopic temperatures and electron number densities for argon versus helium plasmas produced in a surface-wave plasma.[255] Helium was found to have a higher excitation temperature than argon (3000 K versus 2400 K), with rota-

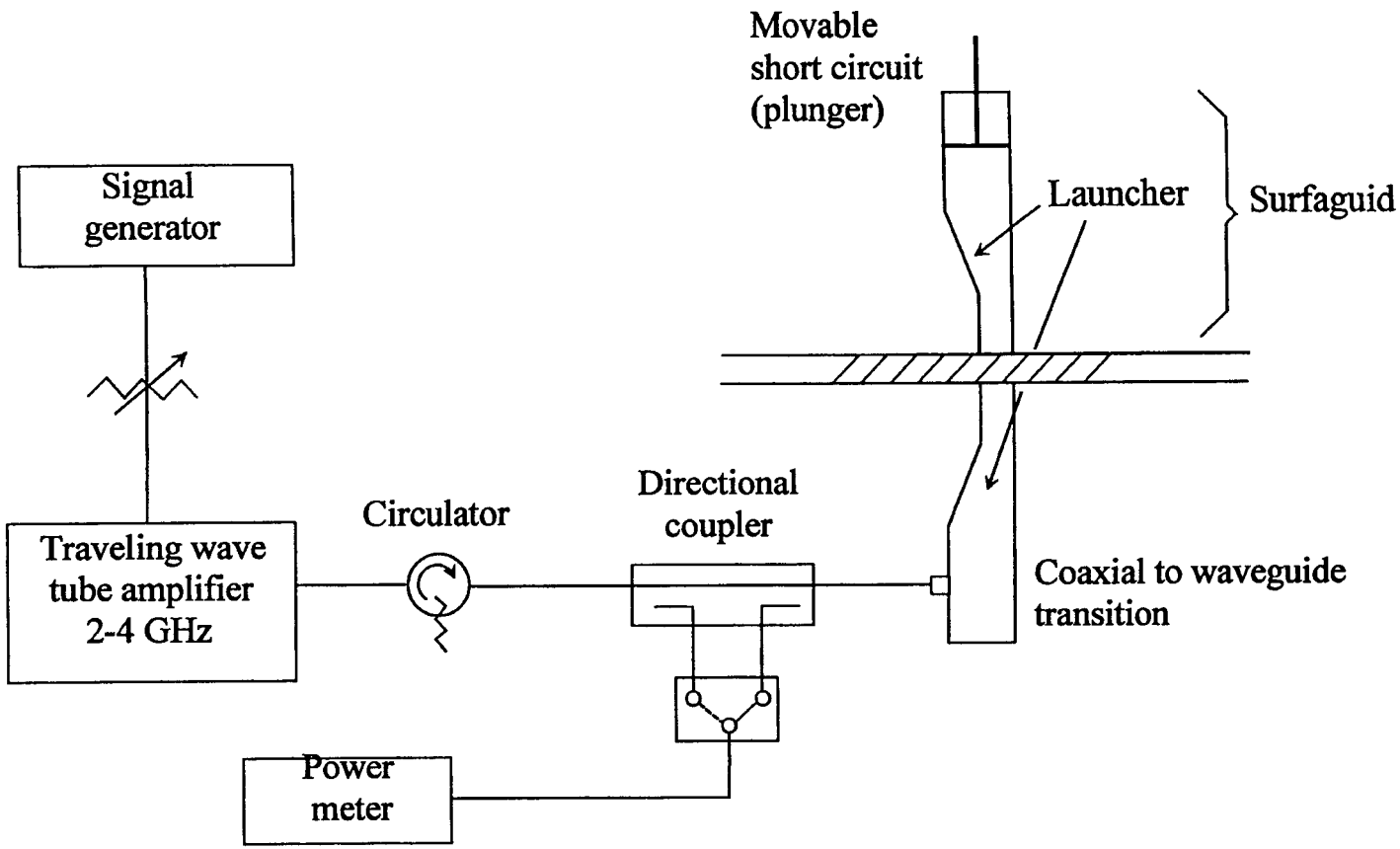

FIGURE 8. Surfaguide. (Adapted from Reference 247.)

Table 8: Figures of Merit for Surfatron Plasmas

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD def'n	RSD (%)	LDR	Ref
As	228.8	A	Ar	120	50	3 σ_{bl}	5	- 400 μg/ml	268
	197.2	A	Ar	160	1.4	3 σ			269
	228.8	I	Ar	75	1	3 σ	2.8		282
Br	827.2	D	Ar	100	2	3 σ	0.7	2-20000 ng/ml	265
	827.2	D	Ar	100	50		1.0	0.30-35 μg/ml	267
	889.7	G	He	100	0.017[a]	3 σ_{bl}/m			278
Cd	228.8	F	Ar	130	20	3 σ	3-5	> 3 orders	274
Cl	837.6	D	Ar	100	50		2.5	0.25-25 μg/ml	267
	912.1	G	He	100	0.005[a]	3 σ_{bl}/m			278
Cu	324.8	F	Ar	130	10	3 σ	3-5	3 orders	274
Hg	253.7	B	Ar	50	0.9	3 σ	1.7	3 orders	292
	253.7	E	Ar	60	0.0007	3 σ	1.0	- 0.2 μg/ml	272
	253.6	J	Ar	115	0.15	3 σ	6.7		282
I	206.1	D	Ar	150	20		0.75	50-20000 ng/ml	266
	804.4	D	Ar	100	200		2.2	0.70-75 μg/ml	267
	905.8	G	He	100	0.110[a]	3 σ_{bl}/m			278
	206.2	H	He	150	1600	S/N=2	10-13	100-10000 μg/ml	282
N	821.6	C	Ar	150	50	3 σ_{bkgd}	0.5	0-33 μg/ml	264
P	213.6	H	He	150	370	S/N=2	10-13	10-5000 μg/ml	281
S	921.3	G	He	100	0.016[a]	3 σ_{bl}/m			278
	921.3	K	He	125	0.025[a]	S/N=2	1-5	3 orders	284
Sb	206.8	A	Ar	160	0.39	3 σ			269
Se	196.0	A	Ar	160	1.2	3 σ			269

* A: Hydride generation (HG); B: Ultrasonic nebulization; C: Gas introduction; D: Chemical generation; E: Cold vapor generation (CV); F: Electrothermal vaporization; G: gas chromatography intro; H: Glass frit nebulization; I: HPLC-HG; J: HPLC-CV; K: Supercritical fluid intro

a: chromatography detection limits are in units of ng/s

tional temperatures for the plasmas being lower (2000 K). Electron densities were 3 to 4 $\times 1014$ cm^{-3} for argon and about three times lower for helium. In addition, frequency was found to have little or no effect on the fundamental properties of the two plasmas. Spectroscopic determinations of fundamental properties were also reported by Cotrino et al., who characterized the departure from local thermal equilibrium in the plasma,[256] and by Mermet et al., who investigated CO_2 and He-CO_2 plasmas.[257] An a.c. modulated surfatron plasma was also studied by Mermet and coworkers.[258] Analytical performance of the plasma at intermediate and high (>100 Torr) pressure was found to be sensitive to the composition of the discharge and inter-element effects were found to be concentration and pressure dependent. This plasma was used with GC separation for the determination of sulfur, with detection limits in the picogram range. Spatial emission properties of the surfatron microwave plasma sustained in argon have been investigated by Moussounda, Ranson, and Mermet.[259] Spectroscopic temperatures, electron and metastable number densities, and absolute values of the continuum emission constant were determined for the inner diameter of the discharge. Unlike ICPs and DCPs, the continuum in the visible region of the spectrum could not be explained simply be radiative recombination. Spatial resolution of emission properties were also determined in a helium surfatron microwave plasma by Hieftje and coworkers.[260] The helium plasma was found to be shaped similarly to the "doughnut" argon ICP, with maximum metallic analyte emission localized along the central axis and helium atom line, molecular band, background continuum, and difficult-to-excite nonmetallic transmissions restricted to the annulus of the plasma. In addition, Moussounda and Ranson found that broadening of argon lines in a surfatron microwave plasma could be attributed to collisions between neutral atoms.[261] Finally, a spatial investigation of a large diameter microwave plasma sustained with surface waves was reported by Marec and coworkers.[262]

C. Gas Introduction

Surface-wave plasmas can be operated at very low power. When low power is employed, these plasmas are less useful for the analysis of liquid samples. Gas samples can be easily analyzed at low power and a variety of pressures using the surface-wave plasma. Granier et al. studied the effect of pressure on CH emission from methane introduced into the argon plasma; the emission maximum was found to be at 100 Torr rather than atmospheric pressure.[263] Nitrogen determination in argon was investigated by Hubert and coworkers.[264] The detection limit was 0.4 ppm using a CCD detector and 0.05 ppm using a photodiode array.

The halogens have also been investigated using a surface-wave microwave plasma. Bromide was determined after continuous generation into an argon plasma by Sanz-Medel et al. with a detection limit of 2 $\mu g\ L^{-1}$ and 0.7% RSD.[265] They also determined iodine using continuous generation with a detection limit of 20 $\mu g\ L^{-1}$ and 0.75% RSD.[266] Chlorine, bromine, and iodine were determined by Calzada and coworkers with detection limits of 50, 50, and 200 ng ml^{-1}, respectively.[267]

Hydride generation has been used for the determination of arsenic in a surfatron microwave plasma by Luge and Broekaert.[268] Arsenic was generated by two methods. The first involved solid NaBH4 onto which 10 µl of acidified arsenic solu-

tion was injected, and the second method involved hydride generation using a 5% (w/w) NaBH4 solution with a continuous liquid removal flow cell. Detection limits for As were 1.0 μg ml^{-1} (10 ng) for the former and 50 ng ml^{-1} for the latter method. Continuous hydride generation was also used for arsenic, antimony, and selenium determination for both helium and argon surface-wave plasmas by Broekaert et al.[269] Detection limits were 1, 0.4, and 1 ng ml^{-1} in the argon plasma and 2, 0.3, and 6 ng ml^{-1} in the helium plasma for As, Sb, and Se, respectively. Similar improvements in the argon plasma for these elements were also observed by Sanz-Medel et al.[270] Arsenic has also been analyzed in biological tissue samples by Broekaert et al.[271]

The effect of plasma pressure upon online continuous cold mercury generation was investigated by Sanz-Medel and coworkers.[272] Low pressure argon plasmas provided lower detection limits than helium plasmas. The detection limits were 0.7 pg ml^{-1} at 40 Torr and 8 pg ml^{-1} at atmospheric pressure for argon, and 3 pg ml^{-1} at 40 Torr and 4 pg ml^{-1} at atmospheric pressure for helium. MONES-surfatron MIP and FANES were used in the determination of nitrogen and oxygen through monitoring of NH and OH radical emission by Mermet et al.[273] Absolute detection limits were found in the sub-nanogram range, with MONES-surfatron MIP being more amenable to gaseous samples and FANES to liquids. Finally, a comparison study of ETV from a tungsten coil with the Beenakker cavity versus the surfatron was conducted by Broekaert and coworkers.[274] Detection limits for Cu and Cd were lower for the surfatron (10 to 20 ng ml^{-1}) than the Beenakker cavity, and the linear dynamic range was greater (over three decades). Interferences from EIEs such as Na were also reduced in the surfatron system.

D. Gas Chromatography

Gas chromatography has been used in conjunction with the surface-wave microwave plasma. The effect of discharge-tube cooling on the performance of a GC-surface-wave MIP-AES system was investigated by Hubert and coworkers.[275] Water cooling of the discharge tube allowed dimensions of 2 mm i.d. and a 0.1 mm wall thickness to sustain a 500 W plasma for extended periods without severe harm to the cavity. A factorial analysis and response surface technique was used for the system optimization of a GC-surface-wave plasma by Caetano, Golding, and Key.[276] Forward power and flow rate were determined to be the most influential parameters for the performance of the system. Detection limits for chlorine and bromine were monitored as the system was optimized and then compared to work done by others using the "one variable at a time" method. Although the final detection limits were similar for both optimization methods, the factorial analysis and response surface method proved to be a faster and more reliable method. A photodiode array was used as a detection device for capillary GC-surfatron MIP by Hubert et al.[277] A variety of organic compounds were separated and detected by carbon, chlorine, and bromine emission in the near infrared, which reduced interferences by helium and air. Multi-wavelength detection using a Fourier transform spectrometer with GC-surfatron MIP was also investigated by Hubert et al.[278] Good linearity and correlation coefficients were obtained for both single line and multi-wavelength emission calibration curves of Cl, Br, I, and S. However, limits of detection were poorer than those obtained with a dispersive single channel detector. Investigation into the use of dopants to reduce refrac-

tory oxides in tin analysis was performed by Besner and Hubert.[279] Sulfur hexafluoride reduced tin oxide formation most significantly, allowing for organotin detection limits in the low pg s^{-1} range. Finally, pesticides were separated and analyzed with GC-surfatron MIP by Mermet and coworkers.[280] Detection limits for P, S, Cl, Br, and C in pesticides were in the low pg s^{-1} range.

E. Liquid Introduction, HPLC, and SFC

A low-power, low He flow rate surfatron with a gas-frit nebulizer and desolvation system was used for the analysis of nonmetals in aqueous solution by Hieftje and coworkers.[281] Detection limits for P, I, S, Cl, Br, and C were in the low and sub-ppm range with <5% RSD. Addition of EIEs improved nonmetal emission by as much as 30%.

Sanz-Medel et al. investigated HPLC coupled with cold vapor or hydride generation with a surfatron at reduced pressure in the analysis of mercury and arsenic species.[282] Detection limits were 1 to 6 ng ml^{-1} for the toxic arsenic species, 0.15 ng ml^{-1} Hg in inorganic mercury, and 0.35 ng ml^{-1} Hg for methylmercury. In addition, arsenic and mercury speciation was successfully performed in natural waters and human urine.

Supercritical fluid chromatography has also been coupled with the surfatron MIP. Hieftje et al. characterized the helium surfatron-MIP as a detector for SFC.[283] Optimization of viewing position, helium flow rate, microwave power, and the effects of CO_2 and N2O SFC mobile phases were discussed. A helpful table of major sources of interfering band emission was also included. Hieftje et al. also examined a capillary SFC- surfatron MIP system for the analysis of sulfur-containing polycycles.[284] The detection limit for sulfur was 25 pg s^{-1} for thiophene and the calibration curve was linear for three orders of magnitude. Luffer and Novotny investigated near infrared detection of sulfur and the sensitivities of several elements with CO_2 versus N2O SFC mobile phases.[285] NIR detection with the SFC-surfatron MIP did not perform as well as expected, based on results for sulfur. In addition, detection limits were high, particularly for carbon with the N2O mobile phase. Luffer and Novotny later studied capillary SFC-surfatron MIP for the detection of cyclic boronate esters of hydroxy compounds.[286] Sensitivity for boron in catechol boronate was 25 pg s^{-1} with the molar selectivity ratio > 5000 for CO_2 and N2O SFC mobile phases.

VI. MICROWAVE PLASMA TORCH (MPT)

A. Introduction

The microwave plasma torch was developed at Jilin University in 1985 and improved by joint cooperation at Jilin University and Indiana University by Jin, Hieftje and others in 1991.[287,288] The MPT works differently from other microwave plasmas in that an argon plasma can be sustained at very low flow rate (10 ml min^{-1}) and forward power (40 to 500 W). Under slightly different conditions a He or N2 plasma can be formed. Unlike the Beenakker and surface-wave microwave plasmas, the MPT can more easily withstand liquid sample introduction. Sample aerosol can be introduced into this plasma with or without desolvation. Figure 9 il-

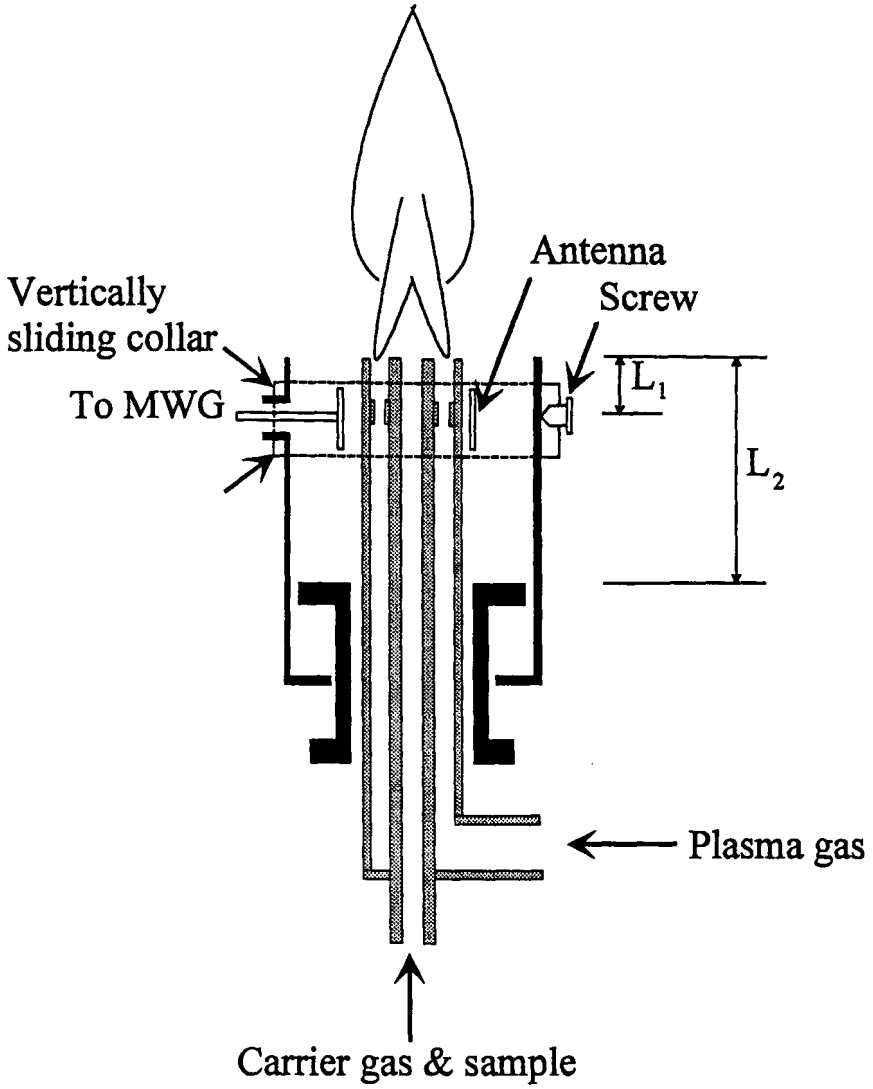

FIGURE 9. Microwave plasma torch. (Adapted from Reference 286.)

lustrates a microwave plasma torch. The torch is similar to the ICP torch, with three concentric metal tubes. The intermediate tube contains the plasma gas. The sample and carrier gas are introduced through the central channel of the torch and the sample is then vaporized and atomized in the plasma. The plasma does not come in contact with the tip of the electrode and therefore does not suffer from contamination from the electrode material. Microwave energy from the generator is coupled to the torch through a cylindrical antenna which surrounds the intermediate tube and is tuned by changing the distance from the top of the torch to the antenna (L1) and/or the short circuit (L2). Hieftje and coworkers have characterized the noise in an MPT, which was found to be dominated by white noise below 100 Hz with discrete noise peaks (presumably from argon flow fluctuations) in the region above 300 Hz.[289]

The MPT offers several advantages over other microwave plasma techniques such as operation at atmospheric pressure, low flow rates and forward power, ease of tunability, no contamination from electrode material, and most important of all reduced sensitivity to introduction of liquid aerosols. These attributes make the MPT a promising source in microwave plasma spectrochemical analysis.[288] Analytical figures of merit for the MPT are given in Table 9.

B. Gas and Liquid Introduction

Although most of the work performed with the MPT to date has been with aqueous samples, gas sample introduction is also possible with this plasma. Hydride generation directly coupled to the MPT for the analysis of arsenic, antimony, and tin was performed by Hieftje et al.[290] Several characteristics were studied including plasma stability, continuum background and noise and emission signal with addition of hydrogen to the plasma gas. Detection limits were 3.2, 5.9, and 2.5 ng ml^{-1} for arsenic, antimony, and tin, respectively. The MPT was also evaluated as an element-specific detector for both gas and capillary supercritical fluid chromatographies by Hieftje et al.[291] The MPT was found to have higher stability and sensitivity to SFC effluent than a surface-wave microwave plasma. Detection limits for chlorine in organic compounds were lower than the GC-MPT system; the detection limit for Fe in ferrocene was better than that achieved by Ar-ICP. The GC-MPT system had detection limits, selectivity, and dynamic range similar to other systems found in the literature.

A comparison study of the surfatron versus MPT in the determination of mercury was carried out by Duan, Du, and Jin.[292] In both systems, argon was used as the carrier gas and solutions were ultrasonically nebulized into the plasmas. Detection limits were 0.9 and 1.3 ng ml^{-1} for the surfatron and MPT, respectively. An inexpensive batch-type ultrasonic nebulizer based on a common room humidifier was developed by Hieftje and coworkers for the analysis of aqueous solutions.[293] Aerosol generation rate and hence detection capabilities were improved over pneumatic nebulization.

Flow injection (FI) sample introduction has been used with MPT-AES. Jin et al. used flow injection with pneumatic nebulization and desolvation for the analysis of several elements, with detection limits in the low ng ml^{-1} range and precisions of less than 5%.[294] Several standard reference materials of alloyed steel were dissolved in acid and analyzed; measured values compared well with certified values. Flow-injection with on-line column preconcentration has also been investigated by Jin and coworkers.[295] Analytes (Cd, Cu, Mn, and Zn) were preconcentrated in a thiol resin prior to pneumatic nebulization and desolvation into the MPT. Detection limits were improved over FI-MPT-AES without the preconcentration and precisions of 1.2% or better were achieved. Jin et al. also measured Fe, Zn, Cd, and Mo using on-line anion-exchange pre-separation and preconcentration prior to nebulization and desolvation into the MPT.[58] Detection limits were 6.5, 0.23, 2.9, and 7.2 ng ml^{-1} for Fe, Zn, Cd, and Mo, respectively. In addition, Jin et al. analyzed trace amounts of boron using on-line separation and preconcentration with detection limits of 0.0055 mg L^{-1} at 45 samples h^{-1} and 0.0018 mg L^{-1} at 20 samples h^{-1} with a precision of 4.2% at the 0.020 mg L^{-1} level of boron.[296] A new spray chamber for use with FI-MPT-AES was developed

Table 9: Analytical Figures of Merit for the MPT

Element	λ (nm)	Intro*	Gas	Power (W)	LOD (ng/ml)	LOD def'n	RSD (%)	LDR	Ref
Ag	328.1	B	Ar	150	3				293
	328.1	B	Ar	200	3	S/N=3	2.5	1-20 μg/ml	297
Al	396.2	C	Ar	60	24	3 σ	4.22	≥ 3 orders	294
	396.2	B	Ar	150	14				293
As	228.8	A	He	200	3.2	3 σ			290
B	249.7	C	Ar	60	1.8	3 σ	0.15	20-40000 ng/ml	296
Ba	455.4	C	Ar	60	16	3 σ	3.84	≥ 3 orders	294
	455.5	B	Ar	200	6.8	S/N=3	2.5	1-20 μg/ml	297
Ca	422.7	B	Ar	150	0.24				293
	422.7	B	Ar	200	0.24	S/N=3	2.5	1-20 μg/ml	297
Cd	228.8	C	Ar	60	10	3 σ	3.45	≥ 3 orders	294
	228.8	B	Ar	150	18				293
	228.8	B	Ar	200	18	S/N=3	2.5	1-20 μg/ml	297
	228.8	D	Ar	60	3.6	3 σ	0.69	0.01-20 μg/ml	295
	228.8	E	Ar	60	2.9		3.2	0.02-100 μg/ml	58
Cr	357.9	C	Ar	60	10	3 σ	3.00	≥ 3 orders	294
	429.0	B	Ar	150	9.2				293
Cu	324.7	C	Ar	60	9.3	3 σ	3.02	≥ 3 orders	294
	324.8	B	Ar	150	1.7				293
	324.8	B	Ar	200	1.7	S/N=3	2.5	1-20 μg/ml	297
	324.7	D	Ar	60	2.2	3 σ	1.1	0.01-20 μg/ml	295
Fe	259.9	C	Ar	60	12	3 σ	3.51	≥ 3 orders	294
	248.3	B	Ar	200	38	S/N=3	2.5	1-20 μg/ml	297
	259.9	E	Ar	60	6.5		3.7	0.05-100 μg/ml	58
Hg	253.7	B	Ar	50	1.3	3 σ	1.4	0.013-50 μg/ml	292
Li	670.8	B	Ar	150	0.99				293
Mg	279.6	C	Ar	60	5.8	3 σ	4.47	≥ 3 orders	294

Mn	257.6	C	Ar	60	9.1	3 σ	2.76	≥ 3 orders	294
	279.5	B	Ar	200	8	S/N=3	2.5	1-20 μg/ml	297
	257.6	D	Ar	60	3.1	3 σ	0.76	0.01-20 μg/ml	295
Mo	379.8	C	Ar	60	37	3 σ	4.10	≥ 3 orders	294
	379.8	E	Ar	60	7.2		3.5	0.08-500 μg/ml	58
Ni	232.0	C	Ar	60	39	3 σ	5.00	≥ 3 orders	294
Pb	405.8	C	Ar	60	103	3 σ	3.90	≥ 3 orders	294
	405.8	B	Ar	150	27				293
	405.8	B	Ar	200	27	S/N=3	2.5	1-20 μg/ml	297
Sb	252.8	A	He	200	2.5	3 σ			290
Sn	190.0	A	He	200	5.9	3 σ			290
Sr	407.8	C	Ar	60	5.0	3 σ	4.44	≥ 3 orders	294
V	437.9	C	Ar	60	20	3 σ	2.44	≥ 3 orders	294
Zn	213.9	C	Ar	60	7.8	3 σ	2.40	≥ 3 orders	294
	213.9	B	Ar	150	14				293
	213.4	D	Ar	60	1.8	3 σ	1.2	0.01-20 μg/ml	295
	213.9	E	Ar	60	0.23		5.6	0.002-100 μg/ml	58
Zr	343.8	C	Ar	60	17	3 σ	1.30	≥ 3 orders	294

* A: Hydride generation; B: Ultrasonic nebulization; C: Flow injection - pneumatic nebulization; D: Flow injection - concentric nebulization; E: Pneumatic nebulization

by Hieftje and coworkers.[297] This vertical rotary spray chamber significantly decreased memory effects (sample washout time) and increased transport efficiency (3.1% over the 1.9 % obtained with the conventional Scott-type spray chamber). Noise above 40 Hz was also lower for the new vertical rotary spray chamber than for the Scott-type.

VII. UNIQUE DESIGNS

A. Introduction

Other microwave plasma systems exist which are variations on the systems discussed above. This section will review several of these variant systems which have appeared in the literature.

B. Kilowatt-Plus Microwave-Induced Plasma (KiP-MIP)

The kilowatt-plus microwave-induced plasma differs from a conventional MIP in that higher powers (up to 3 kW) are transferred to the plasma. This higher power allows for a more energetic plasma, thus enhancing the emission of nonmetals over the traditional MIP. The KiP-MIP system also differs from the traditional MIP in energy coupling. The energy from the microwave generator is transferred to the plasma through a waveguide and then adapted to a coaxial cable, which is in turn connected to the coupling loop in a modified Beenakker cavity.

Cull and Carnahan describe the design and characterization of a pulsed KiP-MIP composed of nitrogen or helium.[298] The microwave energy of this system was capable of provided up to 3 kW of 120 pulse-per-second power to the plasma without damage to the resonator cavity. Bromine and chlorine were easily excited in this high-powered plasma. Wu and Carnahan later evaluated the KiP-MIP system using a redesigned plasma torch with the original 2 and 3 cm depth TM010 resonator cavities.[299] This design modification provided enhanced plasma energy coupling and excitation characteristics, and improved the detection limit of aqueous chloride by two orders of magnitude. Carnahan et al. also compared ETV and ultrasonic nebulization as sample introduction methods for the KiP-MIP in the determination of inorganic and organic sulfur.[300] Limits of detection were 3 to 5 ppm using ETV introduction, which was a tenfold improvement over ultrasonic nebulization. Carnahan and coworkers also used the KiP-MIP in the determination of aqueous carbon, phosphorus, and sulfur with ultrasonic nebulization,[301] and in the determination of metals, nonmetals, and metalloids in the vacuum ultraviolet region of the spectrum.[302]

C. Stabilized Capacitive Plasma (SCP)

The stabilized capacitive plasma transfers energy from the microwave generator directly to the annular electrodes which power the plasma. However, rather than being in contact with electrodes, the plasma is contained in a liquid-cooled fused silica tube surrounded by two annular electrodes. The SCP was used by Knapp and coworkers as an atomic emission source for gas chromatographic detection.[303] The effects of introducing small quantities of various

gases into the helium plasma gas was investigated. Knapp et al. also investigated the graphite furnace as a sample introduction technique for the SCP in the determination of chlorine in aqueous solution and in organic compounds in methanol.[304] The detection limit of chlorine using this method was 5 ng, with 3.2% RSD at the 25 $\mu g\ ml^{-1}$ level. In addition, Broekaert et al. investigated hydride generation, ETV, and pneumatic nebulization with desolvation as sample introduction techniques with the SCP.[305] Detection limits were 5 ng for arsenic using hydride generation, in the ng ml^{-1} range (~100 pg) for Cu, Cd, Ca, and Mg using ETV, and 10 to 100 ng ml^{-1} for Cu, Cd, Fe, Mn, Ca, Mg, and Sr using ultrasonic nebulization.

D. Other Designs

Variations of the microwave plasma systems described previously can differ in microwave power input, cavity, and torch designs. For a variation on power input, a pulse-operated MIP which required no cooling system was developed to overcome difficulties due to Joule heating.[306]

Most modifications to microwave plasma designs occur in the cavity design. The stripline source used a central strip as a waveguide to distribute the microwave energy; the strip was coupled by an antenna plate and a capacitive tuning screw.[307,308] The high-efficiency helium microwave-induced plasma (He-HEMIP) used a capacitor antenna probe for coupling resulting in a power transfer efficiency of greater than 90%.[309] In addition, an electrodeless plasma could be formed at high pressures using a cylindrical discharge cavity.[310] A reentrant resonator cavity with a reflecting structure produced a plasma at low power with high electric field strengths.[311] Finally, an integrated microwave generator/cavity combination by Matusiewicz allowed for the direct introduction of wet aerosols without extinguishing of the plasma.[312]

Torch modifications can also make a microwave plasma system unique. An MIP with a special torch design was developed by Michlewicz, Urh, and Carnahan which contained six plasma gas flow streams which were directed tangentially within the quartz tube.[306] A "torche á injection axiale" was developed by van der Mullen and coworkers which exhibited much higher electron temperatures (25,000 K in a helium plasma) than those found in the MPT. Lastly, a dual microwave plasma system was developed by Ng and Chen which used one plasma to desolvate and vaporize liquid samples and a second for atomization and excitation.[313]

VIII. SUMMARY

Microwave plasmas provide a less expensive alternative to the ICP in terms of both initial and operational costs. Although still approaching the precision and detection limits of the ICP, microwave plasma systems are continually being improved in terms of power handling capabilities, efficiency of coupling, and in the analysis of solid, liquid, and gas samples. The MIP offers the best analytical capabilities in terms of detection limits and precision in the analysis of gas samples, where it has served particularly well as an element-selective detector for gas chromatography. The surfatron has also performed well under a wide variety of operating conditions. The CMP has proven to be a robust atomization source which can handle all

forms of sample introduction. The MPT, while a relatively new source, is making great progress in the area of liquid sample analysis. As these systems continue to become more refined, the microwave plasma will play a more prominent role in commercial atomic emission spectroscopy.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (STTR), the Engineering Research Center (ERC) for Particle Science and Technology at the University of Florida (National Science Foundation Grant No. EEC-94-02989), the Industrial Partners of the ERC, and the Thermo-Jarrell Ash Corporation.

REFERENCES

1. **Littlejohn, D., Jowitt, R., Sparkes, S. T., Thorne, A. P., and Walton, S. J.,** *Journal of Analytical Atomic Spectrometry,* 6, 137R, 1991.

2. **Sharp, B. L., Jowitt, R., Sparkes, S. T., Thorne, A. P., and Walton, S. J.,** *Journal of Analytical Atomic Spectrometry,* 7, 155R, 1992.

3. **Sharp, B. L., Chenery, S., Jowitt, R., Sparkes, S. T., and Fisher, A.,** *Journal of Analytical Atomic Spectrometry,* 8, 151R, 1993.

4. **Sharp, B. L., Chenery, S., Jowitt, R., Sparkes, S. T., and Fisher, A.,** *Journal of Analytical Atomic Spectrometry,* 9, 171R, 1994.

5. **Sharp, B. L., Chenery, S., Jowitt, R., Fisher, A., and Sparkes, S. T.,** *Journal of Analytical Atomic Spectrometry,* 10, 139R, 1995.

6. **Marshall, J., Fisher, A., Chenery, S., and Sparkes, S. T.,** *Journal of Analytical Atomic Spectrometry,* 11, 213R, 1996.

7. **Beauchemin, D., Blanc, J. C. Y. L., Peters, G. R., and Craig, J. M.,** *Analytical Chemistry,* 64, 442R, 1992.

8. **Keliher, P. N., Boyko, W. J., Clifford, R. H., Snyder, J. L., and Zhu, S. F.,** *Analytical Chemistry,* 58, 335R, 1986.

9. **Keliher, P. N., Ibrahim, H., and Gerth, D. J.,** *Analytical Chemistry,* 62, 184R, 1990.

10. **Dahmen, J.,** *ICP Information Newsletter,* 11, 71, 1985.

11. **Dahmen, J.,** *ICP Information Newsletter,* 12, 7, 1986.

12. **Dahmen, J.,** *ICP Information Newsletter,* 13, 77, 1987.

13. **Dahmen, F.-J.,** *ICP Information Newsletter,* 14, 195, 1988.

14. **Dahmen, J.,** *ICP Information Newsletter,* 15, 249, 1989.

15. **Dahmen, J.,** ICP Information Newsletter, 15, 94, 1989.

16. **Dahmen, J.,** *ICP Information Newsletter,* 16, 321, 1990.

17. **Greenfield, S., McGeachin, H. M., and Smith, P. B.,** *Talanta,* 22, 553, 1975.

18. **McGregor, D. A., Cull, K. B., Gehlhausen, J. M., Viscomi, A. S., Wu, M., Zhang, L., and Carnahan, J. W.,** *Analytical Chemistry,* 60, 1089A, 1988.

19. **Zander, A. T.,** *Analytical Chemistry,* 58, 1139A, 1986.

20. **Broekaert, J. A. C.,** *Analytica Chimica Acta,* 196, 1, 1987.

21. **Forbes, K. A., Reszke, E. E., Uden, P. C., and Barnes, R. M.,** *Journal of Analytical Atomic Spectrometry,* 6, 57, 1991.

22. **Carr, J. A.,** *Elements of Microwave Electronics Technology,* Harcourt Brace Jovanovich, Inc., San Diego, 1989.

23. **Murayama, S., Matsuno, H., and Yamamoto, M.,** *Spectrochimica Acta B,* 23B, 513, 1968.

24. **Beenakker, C. I. M.,** *Spectrochimica Acta B,* 31B, 483, 1976.

25. **Laverghetta, T. S.,** *Practical Microwaves,* Prentice Hall, Inc., Englewood Cliffs, NJ, 1996.

26. **Scott, A. W.,** *Understanding Microwaves,* John Wiley & Sons, Inc., New York, 1993.

27. **Lieberman, M. A. and Lichtenberg, A. J.,** *Principles of Plasma Discharges and Materials Processing,* John Wiley & Sons, Inc., New York, 1994.

28. **Matousek, J. P., Orr, B. J., and Selby, M.,** *Progress in Analytical Atomic Spectroscopy,* 7, 275, 1984.

29. **Beenakker, C. I. M.,** *Spectrochimica Acta B,* 32B, 173, 1977.

30. **Broekaert, J. A. C.,** *Journal of the Chinese Optical Society,* 37, 1, 1990.

31. **Culp, R. C. and Ng, K. C.,** *Advances in Atomic Spectrometry,* 2, 215, 1995.

32. **Winefordner, J. D., II, E. P. W., and Smith, B. W.,** *Journal of Analytical Atomic Spectrometry,* 11, 689, 1996.

33. **Uden, P. C.,** *Journal of Chromatography A,* 703, 393, 1995.

34. **Alandari, J., Diamy, A. M., Guillerme, J. M., Legrand, J. C., and Ben-aim, R. I.,** *Applied Spectroscopy,* 43, 681, 1989.

35. **Brown, P. G., Workman, J. M., Haas, D. L., Fleitz, P. A., Miller, D. C., Seliskar, C. J., and Caruso, J. A.,** *Applied Spectroscopy,* 40, 477, 1986.

36. **Workman, J. M., Fleitz, P. A., Fannin, H. B., Caruso, J. A., and Seliskar, C. J.,** *Applied Spectroscopy,* 42, 96, 1988.

37. **Workman, J. M., Brown, P. G., Miller, D. C., Seliskar, C. J., and Caruso, J. A.,** *Applied Spectroscopy,* 40, 857, 1986.

38. **Brown, P. C., Brotherton, T. J., Workman, J. M., and Caruso, J. A.,** *Applied Spectroscopy,* 41, 774, 1987.

39. **Workman, J. M., Fannin, H. B., Brown, P. G., and Caruso, J. A.,** *Applied Spectroscopy,* 43, 621, 1989.

40. **Goode, S. R., Buddin, N. P., Chambers, B., Baughman, K. W., and Deavor, J. P.,** *Spectrochimica Acta B,* 40B, 317, 1985.

41. Goode, S. R. and Emily, J. N., Spectrochimica Acta B, 49B, 31, 1994.

42. **Pak, Y.-N. and Koirtyohann, S. R.,** *Applied Spectroscopy,* 45, 1132, 1991.

43. **Wu, M., Gehlhausen, J. M., and Carnahan, J. W.,** *Journal of Chemical Education,* 69, 757, 1992.

44. **Clay, J. T. and Neimczyk, T. M.,** *Spectrochimica Acta B,* 47B, 835, 1992.

45. **Matousek, J. P., Orr, B. J., and Selby, M.,** *Applied Spectroscopy,* 43, 573, 1989.

46. **Selby, M., Rezaaiyaan, R., and Hieftje, G. M.,** *Applied Spectroscopy,* 41, 761, 1987.

47. **Huang, M.,** *Microchemical Journal,* 53, 79, 1996.

48. **Huang, M., Hanselman, D. S., Jin, Q., and Hieftje, G. M.,** *Spectrochimica Acta B,* 45B, 1339, 1990.

49. **Urh, J. J. and Carnahan, J. W.,** *Applied Spectroscopy,* 40, 877, 1986.

50. **Deutsch, R. D. and Hieftje, G. M.,** *Applied Spectroscopy,* 39, 214, 1985.

51. **Deutsch, R. D., Keilsohn, J. P., and Hieftje, G. M.,** *Applied Spectroscopy,* 39, 531, 1985.

52. **Deutsch, R. D. and Hieftje, G. M.,** *Applied Spectroscopy,* 39, 19, 1985.

53. **Aguilar, J. F. C., Garcia, R. P., Uría, J. E. S., and Medel, A. S.,** *Spectrochimica Acta B,* 49B, 545, 1994.

54. **Chambers, D. M., Carnahan, J. W., Jin, Q., and Hieftje, G. M.,** *Spectrochimica Acta B,* 46B, 1745, 1991.

55. **Hubert, J., Moisan, M., and Zakrzewski, Z.,** *Spectrochimica Acta B,* 41B, 205, 1986.

56. **Borer, M. W., Ensman, R. E., Madrid, Y., and Hieftje, G. M.,** *Applied Spectroscopy,* 46, 1162, 1992.

57. **Brandl, P. G., Arnow, C. L., Caldwell, C. L., and Carnahan, J. W.,** *Applied Spectroscopy,* 51, 280, 1997.

58. **Jin, Q., Zhang, H., Duan, Y., Yu, A., Ren, Y., Zhang, X., Lu, H., and Yu, S.,** *Microchemical Journal,* 44, 153, 1991.

59. **Matousek, J. P., Orr, B. J., and Selby, M.,** *Spectrochimica Acta B,* 41B, 415, 1986.

60. **Ducatte, G. R. and Long, G. L.,** *Applied Spectroscopy,* 48, 493, 1994.

61. **Brown, P. G., Haas, D. L., Workman, J. M., and Caruso, J. A.,** *Analytical Chemistry,* 59, 1433, 1987.

62. **Michlewicz, K. G., Urh, J. J., and Carnahan, J. W.,** *Spectrochimica Acta B,* 40B, 493, 1985.

63. **Goode, S. R., Chambers, B., and Buddin, N. P.,** *Spectrochimica Acta B,* 40B, 329, 1985.

64. **McCleary, K. A., Ducatte, G. R., Renfro, D. H., and Long, G. L.,** *Applied Spectroscopy,* 47, 994, 1993.

65. **Sobering, G. S., Bailey, T. D., and Farrar, T. C.,** *Applied Spectroscopy,* 42, 1023, 1988.

66. **Fielden, P. R., Jiang, M., and Snook, R. D.,** *Applied Spectroscopy,* 43, 1444, 1989.

67. **Bruce, M. L., Workman, J. M., Caruso, J. A., and Lahti, D. J.,** *Applied Spectroscopy,* 39, 935, 1985.

68. **Bolainez, R. M. A., Dziewatkoski, M. P., and Boss, C. B.,** *Analytical Chemistry,* 64, 1992.

69. **Matusiewicz, H. and Sturgeon, R. E.,** *Spectrochimica Acta B,* 48B, 515, 1993.

70. **Mierzwa, J., Brandt, R., Broekaert, J. A. C., Tschöpel, P., and Tölg, G.,** *Spectrochimica Acta B,* 51B, 117, 1996.

71. **Rodero, A., Quintero, M. C., Sola, A., and Gamero, A.,** *Spectrochimica Acta B,* 51B, 467, 1996.

72. **Barnett, N. W.,** *Journal of Analytical Atomic Spectrometry,* 3, 969, 1988.

73. **Ng, K. C., Xu, X.-x., and Brechmann, M. J.,** *Spectroscopy Letters,* 22, 1251, 1989.

74. **Barnett, N. W.,** *Spectrochimica Acta B,* 42B, 859, 1987.

75. **Matusiewicz, H., Sturgeon, R. E., and Berman, S. S.,** *Spectrochimica Acta B,* 45B, 209, 1990.

76. **Camuña, F., Uria, J. E. S., and Medel, A. S.,** *Spectrochimica Acta B,* 48B, 1115, 1993.

77. **Michlewicz, K. G. and Carnahan, J. W.,** *Analytica Chimica Acta,* 183, 275, 1986.

78. **Nakahara, T., Yamada, S., and Wasa, T.,** *Applied Spectroscopy,* 44, 1673, 1990.

79. **Nakahara, T., Yamada, S., and Wasa, T.,** *Applied Spectroscopy,* 45, 1561, 1991.

80. **Nakahara, T., Morimoto, S., and Wasa, T.,** *Journal of Analytical Atomic Spectrometry,* 7, 211, 1992.

81. **Abdillahi, M. M., Tschanen, W., and Snook, R. D.,** *Analytica Chimica Acta,* 172, 139, 1985.

82. **Abdillahi, M. M. and Snook, R. D.,** *Analyst,* 111, 265, 1986.

83. **Matusiewicz, H.,** *Spectrochimica Acta Reviews,* 13, 47, 1990.

84. **Carey, J. M. and Caruso, J. A.,** *Critical Reviews in Analytical Chemistry,* 23, 397, 1992.

85. **Ng, K. C. and Caruso, J. A.,** *Applied Spectroscopy,* 39, 719, 1985.

86. **Matusiewicz, H.,** *Advances in Atomic Spectroscopy,* 2, 63, 1995.

87. **Brooks, E. I. and Timmons, K. J.,** *Analyst,* 110, 557, 1985.

88. **Evans, E. H., Caruso, J. A., and Satzger, R. D.,** *Applied Spectroscopy,* 45, 1478, 1991.

89. **Abdillahi, M. M.,** *Applied Spectroscopy,* 47, 366, 1993.

90. **Matusiewicz, H., Brovko, I. A., Sturgeon, R. E., and Luong, V. T.,** *Applied Spectroscopy,* 44, 736, 1990.

91. **Barnett, N. W. and Kirkbright, G. F.,** *Journal of Analytical Atomic Spectrometry,* 1, 337, 1986.

92. **Wu, M. and Carnahan, J. W.,** *Applied Spectroscopy,* 44, 673, 1990.

93. **Dittrich, K., Fuchs, H., Berndt, H., Broekaert, J. A. C., and Schaldach, G.,** *Fresenius' Journal of Analytical Chemistry,* 336, 303, 1990.

94. **Matusiewicz, H. and Sturgeon, R. E.,** *Spectrochimica Acta B,* 51B, 377, 1996.

95. **Matousek, J. P., Orr, B. J., and Selby, M.,** *Talanta,* 33, 875, 1986.

96. **Yang, J., Zhang, J., Schickling, C., and Broekaert, J. A. C.,** *Spectochimica Acta B,* 51B, 551, 1996.

97. **Heltai, G., Broekaert, J. A. C., Leis, F., and Tölg, G.,** *Spectrochimica Acta B,* 45B, 301, 1990.

98. **Heltai, G., Broekaert, J. A. C., Burba, P., Leis, F., Tschöpel, P., and Tölg, G.,** *Spectrochimica Acta B,* 45B, 857, 1990.

99. **Bulska, E., Tschöpel, P., Broekaert, J. A. C., and Tölg, G.,** *Analytica Chimica Acta,* 271, 171, 1993.

100. **Nakahara, T., Nakanishi, K., and Wasa, T.,** *Chemistry Express,* 1, 149, 1986.

101. **Snell, J. P., Frech, W., and Thomassen, Y.,** *Analyst,* 121, 1055, 1996.

102. **Natarajan, S.,** *Atomic Spectroscopy,* 9, 59, 1988.

103. **Nojiri, Y., Otsuki, A., and Fuwa, K.,** *Analytical Chemistry,* 58, 544, 1986.

104. **Okumura, M., Fukushi, K., Willie, S. N., and Sturgeon, R. E.,** *Fresenius' Journal of Analytical Chemistry,* 345, 570, 1993.

105. **Nakahara, T. and Wasa, T.,** *Microchemical Journal,* 41, 148, 1990.

106. **Alvardo, J. S. and Carnahan, J. W.,** *Analytical Chemistry,* 65, 3295, 1993.

107. **Nakahara, T., Mori, T., Morimoto, S., and Ishikawa, H.,** *Spectrochimica Acta B,* 50B, 393, 1995.

108. **Denkhaus, E., Golloch, A., and Kub, H.-M.,** *Fresenius' Journal of Analytical Chemistry,* 353, 156, 1995.

109. **Vermaak, H., Kujirai, O., Hanamura, S., and Winefordner, J. D.,** *Canadian Journal of Spectroscopy,* 31, 95, 1986.

110. **Matusiewicz, H.,** *Journal of Analytical Atomic Spectrometry,* 8, 961, 1993.

111. **Long, G. L. and Perkins, L. D.,** *Applied Spectrometry,* 41, 980, 1987.

112. **Ng, K. C. and Shen, W.-L.,** *Analytical Chemistry,* 58, 2084, 1986.

113. **Michlewicz, K. G. and Carnahan, J. W.,** *Analytical Chemistry,* 57, 1092, 1985.

114. **Urh, J. J. and Carnahan, J. W.,** *Analytical Chemistry,* 57, 1253, 1985.

115. **Haas, D. L. and Jamerson, J. D.,** *Spectrochimica Acta B,* 42B, 299, 1987.

116. **Zyrnicki, W.,** *Microchemical Journal,* 46, 346, 1992.

117. **Michlewicz, K. G. and Carnahan, J. W.,** *Analytical Chemistry,* 58, 3122, 1986.

118. **Jin, Q., Zhang, H., Ye, D., and Zhang, J.,** *Microchemical Journal,* 47, 278, 1993.

119. **Gehlhausen, J. M. and Carnahan, J. W.,** *Analytical Chemistry,* 61, 674, 1989.

120. **Uebbing, J., Ciocan, A., and Niemax, K.,** *Spectrochimica Acta B,* 47B, 601, 1992.

121. **Ciocan, A., Uebbing, J., and Niemax, K.,** *Spectrochimica Acta B,* 47B, 611, 1992.

122. **Ciocan, A., Uebbing, J., Hiddemann, L., and Niemax, K.,** *Proceedings SPIE - International Society of Optical Engineers,* 2461, 166, 1995.

123. **Hiddemann, L., Uebbing, J., Ciocan, A., Dessenne, O., and Niemax, K.,** *Analytica Chimica Acta,* 283, 152, 1993.

124. **Mohamed, M. M., Uchida, T., and Minami, S.,** *Applied Spectroscopy,* 43, 794, 1989.

125. **Boumans, P. W. J. M. and Vrakking, J. J. A. M.,** *Spectrochimica Acta B,* 42B, 553, 1987.

126. **Broekaert, J. A. C. and Leis, F.,** *Mikrochimica Acta, II,* 261, 1985.

127. **Webster, G. K. and Carnahan, J. W.,** *Analytical Chemistry,* 61, 790, 1989.

128. **Gehlhausen, J. M. and Carnahan, J. W.,** *Analytical Chemistry,* 63, 2430, 1991.

129. **Frame, E. M. S., Takamatsu, Y., and Suzuki, T.,** *Spectroscopy,* 11, 17, 1996.

130. **Matusiewicz, H. and Sturgeon, R. E.,** *Spectrochimica Acta,* 48B, 723, 1993.

131. **Ebdon, L., Hill, S., and Ward, R. W.,** *Analyst,* 111, 1113, 1986.

132. **Long, G. L., Ducatte, G. R., and Lancaster, E. D.,** *Spectrochimica Acta B,* 49B, 75, 1994.

133. **Goode, S. R. and Kimbrough, L. K.,** *Applied Spectroscopy,* 42, 1011, 1988.

134. **Goode, S. R. and Kimbrough, L. K.,** *Spectrochimica Acta B,* 42B, 309, 1987.

135. **Andersson, J. T. and Schmid, B.,** *Fresenius' Journal of Analytical Chemistry,* 346, 403, 1993.

136. **Yieru, H., Qingyu, O., and Weile, Y.,** *Journal of Chromatographic Science,* 28, 584, 1990.

137. **Jelink, J. T. and Venema, A.,** *Journal of High Resolution Chromatography,* 13, 447, 1990.

138. **Birch, M. E.,** *Analytica Chimica Acta,* 282, 451, 1993.

139. **Zhang, L., Carnahan, J. W., Winans, R. E., and Neill, P. H.,** *Analytica Chimica Acta,* 233, 149, 1990.

140. **Quimby, B. D. and Sullivan, J. J.,** *Analytical Chemistry,* 62, 1027, 1990.

141. **Kovacic, N. and Ramus, T. L.,** *Journal of Analytical Atomic Spectrometry,* 7, 999, 1992.

142. **Sullivan, J. J. and Quimby, B. D.,** *Analytical Chemistry,* 62, 1034, 1990.

143. **Müller, H. and Cammann, K.,** *Journal of Analytical Atomic Spectrometry,* 3, 907, 1988.

144. **Evans, J. C., Olsen, K. B., and Sklarew, D. S.,** *Analytica Chimica Acta,* 194, 247, 1987.

145. **Pivonka, D. E., Fateley, W. G., and Fry, R. C.,** *Applied Spectroscopy,* 40, 291, 1986.

146. **Goode, S. R. and Thomas, C. L.,** *Journal of Analytical Atomic Spectrometry,* 9, 965, 1994.

147. **Bradley, C. and Carnahan, J. W.,** *Analytical Chemistry,* 60, 858, 1988.

148. **Goode, S. R. and Thomas, C. L.,** *Journal of Analytical Atomic Spectrometry,* 9, 73, 1994.

149. **Slowick, J. J. and Uden, P. C.,** *Journal of Analytical Atomic Spectrometry,* 951, 1994.

150. **Webster, C. and Cooke, M.,** *Analytical Proceedings Including Analytical Communications,* 31, 237, 1994.

151. **Slatkavitz, K. J., Uden, P. C., and Barnes, R. M.,** *Journal of Chromatography,* 355, 117, 1986.

152. **Goode, S. R. and Kimbrough, L. K.,** *Journal of Analytical Atomic Spectrometry,* 3, 915, 1988.

153. **Brill, J. H., Narayanan, B. A., Doom, J. P., and McCormick, J. P.,** *Journal of High Resolution Chromatography,* 11, 368, 1988.

154. **Slatkavitz, K. J., Hoey, L. D., Uden, P. C., and Barnes, R. M.,** *Analytical Chemistry,* 57, 1848, 1985.

155. **Greenway, G. M. and Barnett, N. W.,** *Journal of Analytical Atomic Spectrometry,* 4, 783, 1989.

156. **Haraguchi, H. and Takatsu, A.,** *Spectrochimica Acta B,* 42B, 235, 1987.

157. **Olsen, K. B., Sklarew, D. S., and Evans, J. C.,** *Spectrochimica Acta B,* 40B, 357, 1985.

158. **Stilkenböhmer, P. and Cammann, K.,** *Fresenius' Journal of Analytical Chemistry,* 335, 764, 1989.

159. **Khuhawar, M. Y., Sarafraz-Yazdi, S., Zeng, Y., and Uden, P. C.,** *Chemia Analityczna (Warsaw),* 40, 271, 1995.

160. **Uden, P. C. and Wang, T.,** *Journal of Analytical Atomic Spectrometry,* 3, 919, 1988.

161. **Hill, S. J.,** *Analytical Proceedings,* 29, 399, 1992.

162. **Bulska, E.,** *Journal of Analytical Atomic Spectrometry,* 7, 201, 1992.

163. **Lobinski, R. and Adams, F. C.,** *Trends in analytical Chemistry,* 12, 41, 1993.

164. **Goode, S. R., Gemmill, J. J., and Watt, B. E.,** *Journal of Analytical Atomic Spectrometry,* 5, 483, 1990.

165. **McKenna, M., Marr, I. L., Cresser, M. S., and Lam, E.,** *Spectrochimica Acta B,* 41B, 669, 1986.

166. **George, M. A., Hessler, J. P., and Carnahan, J. W.,** *Journal of Analytical Atomic Spectrometry,* 4, 51, 1989.

167. **Baumann, H. and Heumann, K. G.,** *Fresenius' Journal of Analytical Chemistry,* 327, 186, 1987.

168. **Lobinski, R. and Adams, F. C.,** *Anlaytica Chimica Acta,* 262, 285, 1992.

169. **Lobinski, R. and Adams, F. C.,** *Journal of Analytical Atomic Spectrometry,* 7, 987, 1992.

170. **Ceulemans, M. and Adams, F. C.,** *Journal of Analytical Atomic Spectrometry,* 11, 201, 1996.

171. **Sadiki, A.-i. and Williams, D. T.,** *Chemosphere,* 32, 1983, 1996.

172. **Dirkx, W. M. R., Lobinski, R., and Adams, F. C.,** *Analytica Chimica Acta,* 286, 309, 1994.

173. **Lobinski, R., Boutron, C. F., Candelone, J.-P., Hong, S., Szpunar-Lobinska, J., and Adams, F. C.,** *Analytical Chemistry,* 65, 2510, 1993.

174. **Lobinski, R., Szpunar-Lobinska, J., Adams, F. C., Teissedre, P.-L., and Cabanis, J.-C.,** *Journal of AOAC International,* 76, 1262, 1993.

175. **Emteborg, H., Baxter, D. C., and Frech, W.,** *Analyst,* 118, 1007, 1993.

176. **Mena, M. L., McLoed, C. W., Jones, P., Withers, A., Minganti, V., Capelli, R., and Quevauviller, P.,** *Fresenius' Journal of Analytical Chemistry,* 351, 456, 1995.

177. **Guntiñas, M. B. d. l. C., Ceulemans, M., Witte, C., Lobinski, R., and Adams, F. C.,** *Mikrochimica Acta,* 120, 73, 1995.

178. **Haraguchi, H.,** *Studies in Environmental Science,* 27, 31, 1988.

179. **Tao, H., Miyazaki, A., and Bansho, K.,** *Analytical Sciences,* 4, 299, 1988.

180. **Liu, Y., Lopez-Avila, V., Alcaraz, M., and Beckert, W. F.,** *Analytical Chemistry,* 66, 3788, 1994.

181. **Szpunar, J., Schmitt, V. O., Lobinski, R., and Monod, J.-L.,** *Journal of Analytical Atomic Spectrometry,* 11, 193, 1996.

182. **Bettmer, J., Bradter, M., Buscher, W., Erber, D., Rieping, D., and Cammann, K.,** *Applied Organometallic Chemistry,* 9, 541, 1995.

183. **Seeley, J. A., Zeng, Y., Uden, P. C., Eglinton, T. I., and Ericson, I.,** *Journal of Analytical Atomic Spectrometry,* 7, 979, 1992.

184. **Zeng, Y., Seeley, J. A., Dowling, T. M., Uden, P. C., and Khuhawar, M. Y.,** *Journal of High Resolution Chromatography,* 15, 669, 1992.

185. **Sklarew, D. S., Olsen, K. B., and Evans, J. C.,** *Chromatographia,* 27, 44, 1989.

186. **Zeng, Y. and Uden, P. C.,** *Journal of High Resolution Chromatography,* 17, 217, 1994.

187. **Wylie, P. L. and Oguchi, R.,** *Journal of Chromatography,* 517, 131, 1990.

188. **Ting, K.-C. and Kho, P.,** *Journal of the Association of Official Analytical Chemistry,* 74, 991, 1991.

189. **Haas, D. L. and Caruso, J. A.,** *Analytical Chemistry,* 57, 846, 1985.

190. **Bruce, M. L. and Caruso, J. A.,** *Applied Spectroscopy,* 39, 942, 1985.

191. **Mohamed, A. H., Zerezghi, M., and Caruso, J. A.,** *Analytical Chemistry,* 58, 469, 1986.

192. **Bulska, E., Emteborg, H., Baxter, D. C., Frech, W., Ellingsen, D., and Thomassen, Y.,** *Analyst,* 117, 657, 1992.

193. **Mingani, V., Capelli, R., and Pellegrini, R. D.,** *Fresenius' Journal of Analytical Chemistry,* 351, 471, 1995.

194. **Hajslova, J., Cuhra, P., Kempny, M., Poustka, J., Holadova, K., and Kocourek, V.,** *Journal of Chromatography A,* 699, 231, 1995.

195. **Valente, A. L. P. and Uden, P. C.,** *Analyst,* 115, 525, 1990.

196. **Buteyn, J. L. and Kosman, J. J.,** *Journal of Chromatographic Science,* 28, 19, 1990.

197. **Perpall, H. J. and Uden, P. C.,** *Spectrochimica Acta B,* 42B, 243, 1987.

198. **Uden, P. C., Slatkavitz, K. J., and Barnes, R. M.,** *Analytica Chimica Acta,* 180, 401, 1986.

199. **Yu, W.-L.,** *Journal of Analytical Atomic Spectrometry,* 3, 893, 1988.

200. **Hooker, D. B. and DeZwann, J.,** *Analytical Chemistry,* 61, 2207, 1989.

201. **Motley, C. B., Ashraf-Khorassani, M., and Long, G. L.,** *Applied Spectroscopy,* 43, 737, 1989.

202. **Motley, C. B. and Long, G. L.,** *Applied Spectroscopy,* 44, 667, 1990.

203. **Motley, C. B. and Long, G. L.,** *Journal of Analytical Atomic Spectrometry,* 5, 477, 1990.

204. **Webster, G. K. and Carnahan, J. W.,** *Applied Spectroscopy,* 45, 1285, 1991.

205. **Webster, G. K. and Carnahan, J. W.,** *Analytical Chemistry,* 64, 50, 1992.

206. **Webster, G. K. and Carnahan, J. W.,** *Applied Spectroscopy,* 44, 1020, 1990.

207. **Zhang, L., Carnahan, J. W., Winans, R. E., and Neill, P. H.,** *Analytical Chemistry,* 63, 212, 1991.

208. **Krull, I. S.,** *ACS Symposium Series,* 297, 137, 1986.

209. **Limentani, G. B. and Uden, P. C.,** *Journal of Chromatography,* 325, 53, 1985.

210. **Mason, P. B., Zhang, L., Carnahan, J. W., and Winans, R. E.,** *Analytical Chemistry,* 65, 2596, 1993.

211. **Heltai, G., Jósza, J., and Percsich, K.,** *Fresenius' Journal of Analytical Chemistry,* 355, 638, 1996.

212. **Michlewicz, K. G. and Carnahan, J. W.,** *Analytical Letters,* 20, 1193, 1987.

213. **Galante, L. J., Wilson, D. A., and Hieftje, G. M.,** *Analytica Chimica Acta,* 215, 99, 1988.

214. **Zhang, L., Carnahan, J. W., Winans, R. E., and Neill, P. H.,** *Analytical Chemistry,* 61, 895, 1989.

215. **Jansen, G. W., Huf, F. A., and Jong, H. J. D.,** *Spectrochimica Acta B,* 40B, 307, 1985.

216. **Liu, Y. and Lopez-Avila, V.,** *Journal of High Resolution Chromatography,* 16, 717, 1993.

217. **Freeman, J. E. and Hieftje, G. M.,** *Spectrochimica Acta B,* 40B, 475, 1985.

218. **Freeman, J. E. and Hieftje, G. M.,** *Spectrochimica Acta B,* 40B, 653, 1985.

219. **Freeman, J. E. and Hieftje, G. M.,** *Applied Spectroscopy,* 39, 211, 1985.

220. **Pivonka, D. E., Schleisman, A. J. J., Fateley, W. G., and Fry, R. C.,** *Applied Spectroscopy,* 40, 766, 1986.

221. **Hubert, J., Tra, H. V., Tran, K. C., and Baudais, F. L.,** *Applied Spectroscopy,* 40, 759, 1986.

222. **Laio, S. Y.,** *Microwave Devices and Circuits,* Prentice Hall, Englewood Cliffs, NJ, 1980.

223. **Spencer, B. M., Smith, B. W., and Winefordner, J. D.,** *Applied Spectroscopy,* 48, 289, 1994.

224. **Masamba, W. R. L., Ali, A. H., and Winefordner, J. D.,** *Spectrochimica Acta B,* 47B, 481, 1992.

225. **Masamba, W. R. L. and Winefordner, J. D.,** *Spectrochimica Acta B,* 48B, 521, 1993.

226. **Bings, N. H. and Broekaert, J. A. C.,** *Fresenius' Journal of Analytical Chemistry,* 355, 242, 1996.

227. **Patel, B. M., Heithmar, E., and Winefordner, J. D.,** *Analytical Chemistry,* 59, 2374, 1987.

228. **Uchida, H., Johnson, P. A., and Winefordner, J. D.,** *Journal of Analytical Atomic Spectrometry,* 5, 81, 1990.

229. **Uchida, H., Berthod, A., and Winefordner, J. D.,** *Analyst,* 115, 933, 1990.

230. **Huang, D. and Blades, M. W.,** *Journal of Analytical Atomic Spectrometry,* 6, 215, 1991.

231. **Hanamura, S., Kirsch, B., and Winefordner, J. D.,** *Analytical Chemistry,* 57, 9, 1985.

232. **Patel, B. M., Deavor, J. P., and Winefordner, J. D.,** *Talanta,* 35, 641, 1988.

233. **Hwang, J. D., Masamba, W., Smith, B. W., and Winefordner, J. D.,** *Canadian Journal of Spectroscopy,* 33, 156, 1988.

234. **Spencer, B. M., Raghani, A. R., and Winefordner, J. D.,** *Applied Spectroscopy,* 48, 643, 1994.

235. **Uchida, H., Masamba, W. R., Uchida, T., Smith, B. W., and Winefordner, J. D.,** *Applied Spectroscopy,* 43, 425, 1989.

236. **Ali, A. H., Ng, K. C., and Winefordner, J. D.,** *Spectrochimica Acta B,* 46B, 1207, 1991.

237. **Ali, A. H. and Winefordner, J. D.,** *Analytica Chimica Acta,* 264, 327, 1992.

238. **Pless, A. M., Smith, B. W., Bolshov, M. A., and Winefordner, J. D.,** *Spectrochimica Acta B,* 51B, 55, 1996.

239. **Wensing, M. W., Liu, D.-Y., Smith, B. W., and Winefordner, J. D.,** *Analytica Chimica Acta,* 299, 1, 1994.

240. **Wensing, M. W., Smith, B. W., and Winefordner, J. D.,** *Analytical Chemistry,* 66, 531, 1994.

241. **Besteman, A. D., Lau, N., Liu, D.-Y., Smith, B. W., and Winefordner, J. D.,** *Journal of Analytical Atomic Spectrometry,* 11, 479, 1996.

242. **Hanamura, S., Wang, W.-J., and Winefordner, J. D.,** *Canadian Journal of Spectroscopy,* 30, 46, 1985.

243. **Masamba, W. R. L., Smith, B. W., and Winefordner, J. D.,** *Applied Spectroscopy,* 46, 1741, 1992.

244. **Ali, A. H., Ng, K. C., and Winefordner, J. D.,** *Journal of Analytical Atomic Spectrometry,* 6, 211, 1991.

245. **Pless, A. M., Croslyn, A., Gordon, M. J., Smith, B. W., and Winefordner, J. D.,** *Talanta,* 44, 39, 1997.

246. **Moisan, M., Beaudry, C., and Leprince, P.,** *IEEE Transactions on Plasma Science,* PS–3, 55, 1974.

247. **Hubert, J., Moisan, M., and Ricard, A.,** *Spectrochimica Acta B,* 33B, 1, 1979.

248. **Moisan, M., Zakrzewski, Z., Pantel, R., and Leprince, P.,** *IEEE Transactions on Plasma Science,* PS–12, 203, 1984.

249. **Moisan, M. and Zakrzewski, Z.,** *Journal of Physics D,* 1025, 1991.

250. **Granier, A., Boisse-Laporte, C., Leprince, P., Marec, J., and Nghiem, P.,** 204, 1987.

251. **Boisse-Laporte, C., Granier, A., Dervisevic, E., Leprince, P., and Marec, J.,** *Journal of Physics D,* 197, 1987.

252. **Alves, L. L., Gousset, G., and Ferreira, C. M.,** *Journal of Physics D,* 25, 1713, 1992.

253. **Sing, R. A. and Hubert, J.,** *Applied Spectroscopy,* 44, 1605, 1990.

254. **Chaker, M., Moisan, M., and Zakrzewski, Z.,** *Plasma Chemistry and Plasma Processing,* 6, 79, 1986.

255. **Besner, A., Moisan, M., and Hubert, J.,** *Journal of Analytical Atomic Spectrometry,* 3, 863, 1988.

256. **Cotrino, J., Saez, M., Quintero, M. C., Menendez, A., Uria, E. S., and Medel, A. S.,** *Spectrochimica Acta B,* 47B, 425, 1992.

257. **Riviére, B., Mermet, J.-M., and Deruaz, D.,** *Journal of Analytical Atomic Spectrometry,* 3, 551, 1988.

258. **Riviére, B., Mermet, J.-M., and Deruaz, D.,** *Journal of Analytical Atomic Spectrometry,* 4, 519, 1989.

259. **Moussounda, P. S., Ranson, P., and Mermet, J. M.,** *Spectrochimica Acta B,* 40B, 641, 1985.

260. **Selby, M., Rezaaiyaan, R., and Hieftje, G. M.,** *Applied Spectroscopy,* 41, 749, 1987.

261. **Moussounda, P. S. and Ranson, P.,** *Journal of Physics B,* 20, 949, 1987.

262. **Bluem, E., Béchu, S., Boisse-Laporte, C., Leprince, P., and Marec, J.,** *Journal of Physics D,* 28, 1529, 1995.

263. **Granier, A., Bloyet, E., Leprince, P., and Marec, J.,** *Spectrochimica Acta B,* 43B, 963, 1988.

264. **Boudreau, D., Laverdure, C., and Hubert, J.,** *Applied Spectroscopy,* 43, 456, 1989.

265. **Calzada, M. D., Quintero, M. C., Gamero, A., and Cotrino, J.,** *Talanta,* 39, 341, 1992.

266. Ortega, M. C. Q., Bautista, J. C., Saez, M., Garcia, A. M., **Uria, J. E. S., and Medel, A. S.,** *Spectrochimica Acta B,* 47B, 79, 1992.

267. **Calzada, M. D., Quintero, M. C., Gamero, A., and Gallego, M.,** *Analytical Chemistry,* 64, 1374, 1992.

268. **Luge, S. and Broekaert, J. A. C.,** *Mikrochimica Acta,* 113, 277, 1994.

269. **Yang, J., Schicking, C., Broekaert, J. A. C., Tschöpel, P., and Tölg, G.,** *Spectrochimica Acta B,* 50B, 1351, 1995.

270. **Lunzer, F., Pereiro-García, R., Bordel-García, N., and Sanz-Medel, A.,** *Journal of Analytical Atomic Spectrometry,* 10, 311, 1995.

271. **Schickling, C., Yang, J., and Broekaert, J. A. C.,** *Journal of Analytical Atomic Spectrometry, 11, 739, 1996.*

272. **Costa-Fernández, J. M., Pereiro-García, R., and Sanz-Medel, A.,** *Journal of Analytical Atomic Spectrometry,* 10, 649, 1995.

273. **Dittrich, K., Fuchs, H., Mermet, J.-M., and Riviére, B.,** *Journal of Analytical Atomic Spectrometry,* 6, 313, 1991.

274. **Richts, U., Broekaert, J. A. C., Tschöpel, P., and Tölg, G.,** *Talanta,* 38, 863, 1991.

275. **Sing, R. L., Lauzon, C., Tran, K. C., and Hubert, J.,** *Applied Spectroscopy,* 46, 430, 1992.

276. **Caetano, M., Golding, R. E., and Key, E. A.,** *Journal of Analytical Atomic Spectrometry,* 7, 1007, 1992.

277. **Takigawa, Y., Hanai, T., and Hubert, J.,** *Journal of High Resolution Chromatography and Chromatography Communications,* 9, 698, 1986.

278. **Lauzon, C., Tran, K. C., and Hubert, J.,** *Journal of Analytical Atomic Spectrometry,* 3, 901, 1988.

279. **Besner, A. and Hubert, J.,** *Journal of Analytical Atomic Spectrometry,* 3, 381, 1988.

280. **Riviére, B. and Mermet, J.-M.,** *Journal of Analytical Atomic Spectrometry,* 2, 705, 1987.

281. **Galante, L. J., Selby, M., and Hieftje, G. M.,** *Applied Spectroscopy,* 42, 559, 1988.

282. **Costa-Fernández, J. M., Lunzer, F., Pereiro-García, R., Sanz-Medel, A., and Bordel-García, N.,** *Journal of Analytical Atomic Spectrometry,* 10, 1019, 1995.

283. **Galante, L. J., Selby, M., Luffer, D. R., Hieftje, G. M., and Novotny, M.,** *Analytical Chemistry,* 60, 1370, 1988.

284. **Luffer, D. R., Galante, L. J., David, P. A., Novotny, M., and Hieftje, G. M.,** *Analytical Chemistry,* 60, 1365, 1988.

285. **Luffer, D. R. and Novotny, M.,** *Journal of Chromatography,* 517, 477, 1990.

286. **Luffer, D. R. and Novotny, M. V.,** *Journal of Microcolumn Separations,* 3, 39, 1991.

287. **Jin, Q., Zhang, H., Yu, A., Duan, Y., Liu, X., and Yang, F.,** *Analytical Sciences,* 7, 559, 1991.

288. **Jin, Q., Zhu, C., Borer, M. W., and Hieftje, G. M.,** *Spectrochimica Acta B,* 46B, 417, 1991.

289. **Madrid, Y., Borer, M. W., Zhu, C., Jin, Q., and Hieftje, G. M.,** *Applied Spectroscopy,* 48, 994, 1994.

290. **Pereiro, R., Wu, M., Broekaert, J. A. C., and Hieftje, G. M.,** *Spectrochimica Acta B,* 49B, 59, 1994.

291. **Jin, Q., Wang, F., Zhu, C., Chambers, D. M., and Hieftje, G. M.,** *Journal of Analytical Atomic Spectrometry,* 5, 487, 1990.

292. **Duan, Y., Du, X., and Jin, Q.,** *Journal of Analytical Atomic Spectrometry,* 9, 629, 1994.

293. **Jin, Q., Zhu, C., Brushwyler, K., and Hieftje, G. M.,** *Applied Spectroscopy,* 44, 183, 1990.

294. **Zhang, H., Ye, D., Zhao, J., Yu, J., Men, R., Jin, Q., and Dong, D.,** *Microchemical Journal,* 53, 69, 1996.

295. **Ye, D., Zhang, H., and Jin, Q.,** *Talanta,* 43, 535, 1996.

296. **Jin, Q., Zhang, H., Liang, F., Yang, W., and Jin, Q.,** *Journal of Analytical Atomic Spectrometry,* 11, 331, 1996.

297. **Wu, M., Madrid, Y., Auxier, J. A., and Hieftje, G. M.,** *Analytical Chimica Acta,* 286, 155, 1994.

298. **Cull, K. B. and Carnahan, J. W.,** *Applied Spectroscopy,* 42, 1061, 1988.

299. **Wu, M. and Carnahan, J. W.,** *Applied Spectroscopy,* 46, 163, 1992.

300. **Alvardo, J., Wu, M., and Carnahan, J. W.,** *Journal of Analytical Atomic Spectrometry,* 7, 1253, 1992.

301. **Wu, M. and Carnahan, J. W.,** *Journal of Analytical Atomic Spectrometry,* 7, 1249, 1992.

302. **Alvardo, J. and Carnahan, J. W.,** *Applied Spectroscopy,* 47, 2036, 1993.

303. **Gross, R., Platzer, B., Leitner, E., Schalk, A., Sinabell, H., Zach, H., and Knapp, G.,** *Spectrochimica Acta B,* 47B, 95, 1992.

304. **Katshcthaler, C., Quan, X., Krizová, H., Gross, R., and Knapp, G.,** *Spectrochimica Acta B,* 50B, 453, 1995.

305. **Luge, S., Broekaert, J. A. C., Schalk, A., and Zach, H.,** *Spectrochimica Acta B,* 50B, 441, 1995.

306. **Mohamed, M. M., Uchida, T., and Minami, S.,** *Applied Spectroscopy,* 43, 129, 1989.

307. **Argentine, M. D. and Barnes, R. M.,** *Journal of Analytical Atomic Spectrometry,* 7, 1013, 1992.

308. **Barnes, R. M. and Reszke, E. E.,** *Analytical Chemistry,* 62, 2650, 1990.

309. **Perkins, L. D. and Long, G. L.,** *Applied Spectroscopy,* 43, 499, 1989.

310. **Offermanns, S.,** *Jounal of Applied Physics,* 67, 115, 1990.

311. **Brown, M. R., Sheridan, T. E., and Hayes, M. A.,** *Review of Scientific Instrumentation,* 57, 2957, 1986.

312. **Matusiewicz, H.,** *Spectrochimica Acta B,* 47B, 1221, 1992.

313. **Ng, K. C. and Chen, S.,** *Microchemical Journal,* 48, 383, 1993.