Recent Advances in Analytical Atomic Radiofrequency Emission Spectroscopy [and Discussion]

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Recent advances in analytical atomic radiofrequency emission spectroscopy

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Four major development topics highlight present inductively coupled plasma (i.c.p.) activities: (*a*) i.c.p. spectrum characterization, diagnostics and interpretations; (*b*) i.c.p. discharge and analyte properties within the discharge; (*c*) sample introduction, and (*d*) extended use of the i.c.p. discharge as in atomic fluorescence and mass spectrometry. The background, status and prospects of i.c.p. spectroscopy with particular emphasis on these development areas are examined.

INTRODUCTION

This review will highlight recent advances in atomic emission spectroscopy by use of an inductively coupled plasma (i.c.p.) discharge source. While the concept of the induction discharge supplied by a radiofrequency source dates to before World War II, the practical i.c.p. discharge is now only 20 years old (Barnes 1978*b*; Fassel 1979; Greenfield 1980). First described as a device for the high-temperature growth of crystals (Reed 1961), the i.c.p. has been developed into a practical analytical tool for the spectrochemical determination of metals and non-metals that compares favourably with the flame and electrical furnaces. In fact, practical development and fundamental inquiries have stimulated uses of the i.c.p. discharge extended beyond emission spectroscopy (e.s.) to absorption (a.a.s.), fluorescence (a.f.s.), and mass (m.s.) spectroscopies. The attributes of the modern i.c.p. discharge that make it a popular source for emission spectroscopy (Fassel 1977, 1979; Greenfield 1980) also match the needs of a light or ion *source* in atomic absorption, atomic and molecular fluorescence, and mass spectroscopies as well as an analyte atom *reservoir* in atomic absorption and fluorescence spectroscopies. In spite of the repeated successful evaluations of the i.c.p. as an a.a.s. atom reservoir, the advantages of simultaneous or rapid sequential multi-element determinations provided by atomic emission or fluorescence measurements account for their predominance over i.c.p.–a.a.s. Only recently has a commercial i.c.p. instrument employing a.f.s. become available (Demers & Allemand 1981), whereas the number of i.c.p.–a.e.s. instruments probably exceeds 1000. Furthermore, the recent implementation of the i.c.p. as an ion source for mass spectrometry combines two powerful technologies to yield a unique result (Date & Gray 1981, 1982; Douglas *et al.* 1982; Gray & Date 1981; Houk *et al.* 1980, 1981).

All in all, the title 'I.c.p.: the universal spectrochemical source?' might be considered as more appropriate than that published. 'Universal' denotes 'unlimited', 'present everywhere', 'embracing a wide range', 'used for or among all', and 'adaptable to various uses', all of which apply to i.c.p. spectroscopy. While not unlimited in its applications and capabilities, the i.c.p., when applied in emission spectroscopy, fulfils the requirements of an ideal multi-element analytical system (Fassel 1977, 1979) at least as well as the other analytical approaches. As its popularity has grown, the commercial i.c.p. emission system is found in large and small laboratories throughout the world, where it is applied to a diversity of samples for the determination of practically all elements over wide concentration ranges (Barnes 1978*b*; Fassel

Table 1. Chronology of i.c.p. spectroscopy (Barnes 1978)

1942	stationary induction plasma described
1961	flowing induction plasma described
1964–5	i.c.p.–a.e.s. spectrochemical analyses reported
	graphite yarn thermal atomizer invented
	hydride generation applied to i.c.p.
	d.c. arc-produced aerosol sampled by i.c.p.
1966	atomic absorption in i.c.p. discharge described
	ultrasonic nebulizer described
1967	powder analysis performed
1968	molten metal aerosol and metals analysed in oils
1969	nanogram per litre detection limits reported
	rare earth elements determined
1972	nanogram per litre detection limits verified
	S, P, As, Se, I determined
	microlitre sample methods described
1973	temperature distribution measured
1974	commercial i.c.p.–a.e.s. instrument introduced
	tantalum filament vaporizer employed
	interelement effects described
1975	*ICP Information Newsletter* published
	geochemical analysis performed
	i.c.p. computer simulations described
	steel, plant materials analysed
	compromise operating conditions confirmed
	electron density and temperature distributions measured
1976	computerized programmable monochromator operated
	stray light effects described
	atomic fluorescence measured in i.c.p.
	spark sampling employed for i.c.p.
1977	improved ultrasonic nebulizer developed
	effect of easily ionizable elements measured
	photodiode array profiles presented
	low-gas consumption torch designed
	non-thermal excitation mechanisms proposed
	ammonium nitrogen determination developed
	water analysis demonstrated
1978	analysis accuracy for biologicals and soils established
	photodiode array i.c.p. spectrometer designed
	Jarrell–Ash Plasma Newsletter published
	advanced computer simulation employed
	gas hydride introduction refined
	laser vaporization applied for particulate samples
	graphite electrothermal vaporizer refined
	high-solids nebulizers designed
	quantitative survey analysis proposed
1979	stray light reduction achieved
	laser-excited atomic fluorescence demonstrated
	i.c.p. source employed for atomic and molecular flourescence
	small-diameter, water-cooled torches designed
	prominent wavelength tables compiled
	commercial sequential i.c.p.–a.e.s. instruments produced
	i.c.p.–g.c. and i.c.p.–h.p.l.c. detectors designed
	E.P.A. i.c.p.–a.e.s. waste water method proposed
	solution and powder injection methods refined
	recombination, broadening background documented
1980	International Winter Conference held
	commercial i.c.p.–a.e.s./a.a.s. instrument introduced
	spectral interference wavelength tables published
	new nebulizers and aerosol characterization described
	simplex optimized operating conditions demonstrated
	O, N, F spectra characterized
	HF-resistant nebulizers and torches designed
	air, nitrogen and oxygen i.c.p. discharges produced
	noise power spectrum analysis performed
	commercial spark sampling i.c.p.–a.e.s. instrument introduced
	research i.c.p.–mass spectrometry demonstrated
	non-l.t.e. calculations performed for i.c.p.
	seawater analysed
	E.P.A. i.c.p.–a.e.s. air particulate method proposed
	s.i.t.–i.c.p. spectrometer evaluated
	Atomic Spectroscopy published
	i.c.p. nomenclature system proposed
1981	spectral interference wavelength computer programs described
	commercial i.c.p.–a.f.s. spectrometer introduced
	argon metastable spatial distributions measured
	emission and matrix effect profiles interpreted
	i.c.p.–flow injection analysis introduced
	i.c.p. isotopic abundance determinations performed
	generalized standard addition method applied in i.c.p.–a.e.s.

1977, 1979; Greenfield 1980). Not only chemists but others from agronomists to zoologists apply data obtained by i.c.p.–a.e.s. (Barnes 1978*a*, *b*, 1979, 1981*a*). Adaption in a.a.s., a.f.s. and m.s.–i.c.p. illustrate the various uses of the i.c.p. discharge. Thus, among spectrochemical sources the i.c.p. discharge has become universal like the combustion flame in its application, characterization and utilization (Fassel 1982). Also, like the flame, it may become one of the first totally diagnosed and theoretically predictable spectrochemical sources.

The qualitative operating principles as well as analytical advantages and limitations of i.c.p.–a.e.s. have been described previously (Barnes 1978*b*, 1979; Fassel 1978, 1979), but a brief chronology of developments in i.c.p. spectroscopy is summarized in table 1. Four major development topics highlight present i.c.p. activities: (*a*) i.c.p. spectrum characterization, diagnostics and interpretations; (*b*) i.c.p. discharge and analyte properties within the discharge; (*c*) sample introduction, and (*d*) extended utilization of the i.c.p. discharge, as in atomic fluorescence and mass spectrometry. These topics will be examined in the next sections.

Spectrum characterization

Among the major growth steps in i.c.p. spectroscopy have been the characterization, diagnostics and interpretation of the i.c.p. emission spectrum. Although this process began as early as 1962 in England and America with the evaluation of the first i.c.p. source for spectrochemistry (Fassel 1979), the i.c.p. spectrum is sufficiently novel and complex for work to continue today to identify new spectra and to systematize for spectrochemical applications the spectral emissions identified. Initial efforts were directed to the identification of experimental conditions for multi-element analysis under which the discharge should be operated to obtain those excellent spectrochemical analysis properties (e.g. low interelement effects, high power of detection, excellent accuracy and precision) that account for its present popularity (Boumans & de Boer 1975, 1977; Scott *et al.* 1974). Compromise conditions that provide good sensitivity and minimal concomitant interferences for multi-element emission analysis are well established today, and the optimization of operating parameters and conditions for new samples or in non-routine applications are efficient and rapid, especially with computer-controlled instrumentation and Simplex procedures (Ebdon *et al.* 1980; Cave *et al.* 1982; Terblanche *et al.* 1981).

As pioneer workers evaluated the emission spectra from the i.c.p. discharge, they discovered that spectral intensities of tabulated wavelengths often deviated significantly from values previously documented for arc, flame, spark and low-pressure discharges (Boumans *et al.* 1978). This resulted in the compilation and publication in 1979 of two experimentally determined wavelength tables for about 70 metals, which provided wavelengths and limits of detection estimates for all prominent i.c.p. emission lines (Boumans & Bosveld 1979; Winge *et al.* 1979). These tables have been widely used by practising analysts in method development. During the past few years, i.c.p. emission spectra of O, N, C, S, Cl, Br and F were reported in the near infrared and vacuum ultraviolet regions (Fry *et al.* 1980; Heine *et al.* 1980; Hughes & Fry 1981*a*, *b*; Northway *et al.* 1980; Northway & Fry 1980). These later studies reflect a desire to characterize the i.c.p. spectrum as well as to improve the detection capabilities of the i.c.p. for non-metals.

The identification of instrumental stray light and plasma background emission and line-broadening phenomena resulted as practical samples containing substantial concentrations of aluminium, calcium and magnesium were analysed (Fassel 1979; Larson *et al.* 1976, 1979;

Mermet 1979). Sample-dependent background emission studies have led to improvements in instrument and optical design to reduce stray light effects and to the introduction of computer-controlled background measurement and correction instrumentation (Sobel & Dahlquist 1981). In addition, ion-recombination continuum spectra have been characterized and applied as a semi-quantitative tool for estimating electron number densities in the i.c.p. (Montaser *et al.* 1981). The contributions from radiative recombination and Bremsstrahlung were recently evaluated for the argon discharge continuum (Batal *et al.* 1981), and the influence of line broadening resulting from collisions between atoms or ions of analyte elements and neutral atoms of argon has been theoretically and experimentally examined (Batal & Mermet 1981; Mermet & Trassy 1981) during the past year. The contribution of line broadening in the i.c.p. discharge to spectral overlap of an analyte line by the wing of an interfering line is now established as the limiting spectral feature for selecting high-resolution instruments (Mermet 1979).

Since spectral line intensities emitted by the i.c.p. do not correspond to those reported in standard wavelength tabulations, the evaluation of spectral interferences in i.c.p.–a.e.s. could have been a major limitation to the rapid selection of appropriate conditions for each sample arriving in the i.c.p. laboratory. Recognizing this potential problem, at least three groups described line coincidence tables for i.c.p.–a.e.s. during 1980 (Boumans 1980*a*, *b*, 1981*a*; Parson *et al.* 1980; Winge *et al.* 1981). Both experimental data and appropriate modification of tabulated arc intensities have been employed, although not yet in a single compilation. In the most quantitative of these tables, a line coincidence is expressed as the ratio of concentrations of interferent and analyte lines for seven values of spectral bandpass (Boumans 1980*a*, *b*, 1981*a*). An important consideration in the application of these line coincidence tabulations is that all of the data are available in a computer format so as to enable the convenient and rapid dissemination of the tables. Furthermore, the application of computer-based i.c.p. systems equipped with a quantitative line coincidence table can substantially reduce the time and difficulty in i.c.p. method development (Floyd *et al.* 1980). This results from the use of computer programs to search and cross-check line coincidences based upon estimates of the general sample composition provided by the analyst (Boumans 1981*b*). Combined with commercial computer-controlled sequential spectrometers, these programs and data should speed the development of i.c.p.–a.e.s. methods. While this approach is progressing in research laboratories, computer-controlled spectrometers and advanced software allow the i.c.p. operator rapid access and display of experimental spectra so as to select appropriate analysis wavelengths or background and spectral interference correction procedures, or both (Sobel & Dahlquist 1981). Using a multivariate standard addition method, Kalivas & Kowalski (1981) demonstrated a computer correction procedure for interferences and matrix effects in i.c.p.–a.e.s. without preliminary examination of the sample matrix spectrum.

Thus the prospect is excellent within the next few years for an automated i.c.p. analyser that minimizes the analyst's development effort and maximizes the instrument use. The major problems that exist are those of appropriate sample preparation and introduction to the discharge.

Discharge and analyte properties

Although systematic optimization of i.c.p. operating conditions leads to reliable spectrochemical results, only recently have the properties of the i.c.p. discharge and spatial emission and absorption characteristics of analyte species been closely scrutinized. The consequence of studies during the past 2 years is an emerging description of the i.c.p. source spatial properties and a growing recognition of the complexities of the discharge.

Spatial excitation temperature and velocity distribution in argon i.c.p. discharges without analyte compared well with model calculations in the induction energy addition region but deviated above the discharge (Barnes & Genna 1981; Barnes & Schleicher 1981). Complete spatial maps of the discharge temperatures, number densities, velocity and magnetic fields with sufficient accuracy to compare with computer model predictions are still needed.

Meanwhile, the spatial properties of argon i.c.p. discharges as typically applied for spectrochemical analysis are being measured, and a qualitative picture of the spatial zones and their unique properties began to emerge only recently (Blades & Horlick 1981*a*, *b*; Goldbart & Lorber 1981; Kawaguchi *et al.* 1981; Koirtyohann *et al.* 1980, 1981; Savage & Hieftje 1980).

The induction region is probably the most complex portion of the i.c.p. discharge because it serves as the energy input volume of the discharge. Although detected only by mass spectroscopy (Houk *et al.* 1981), argon ions dominate the induction zone and contribute to the significant continuum background. Ambipolar diffusion from the induction annulus to the central channel (Aeschbach 1980; Eckert 1981*a*, *b*) and other surrounding areas has been proposed to elevate electron concentrations in this interfacial region as well as in the central channel. Both additional computation and experimental effort will be required before accounting for these phenomena.

Along the central channel the sample, introduced with a carrier gas flow, undergoes desolvation, decomposition and analyte excitation and ionization. The spatial separation of the analyte emission from the argon discharge continuum is unique to the i.c.p. discharge. Spatial distributions of atom, ion and continuum emission in low-power argon i.c.p. discharges have been documented recently (Blades & Horlick 1981*a*, *b*; Goldbart & Lorber 1981; Kawaguchi *et al.* 1981; Koirtyohann *et al.* 1980, 1981; Savage & Hieftje 1980). A small region exists along the discharge axis sometimes called the 'initial radiation zone' (Goldbart & Lorber 1981; Koirtyohann *et al.* 1980), which appears to be characterized by low-energy, mostly atomic, excitation and emission, the spatial position of which corresponds to the normal temperature of the axial channel (Blades & Horlick 1981*b*; Kawaguchi *et al.* 1981; Koirtyohann *et al.* 1981). Some consider this region to be thermally dominated by electron collisions and 'soft line' behaviour (Goldbart & Lorber 1981; Blades & Horlick 1981*a*). The addition of easily ionizable elements enhances emission from both atoms and ions (Blades & Horlick 1981*b*; Koirtyohann *et al.* 1981; Savage & Hieftje 1980), and a low-argon metastable population has been measured (Uchida *et al.* 1980, 1981). The region commonly employed for spectrochemical analysis, sometimes called the 'normal analytical zone', is separated from the induction coil by 15–20 mm in a region of high signal:background ratio (Goldbart & Lorber 1981; Koirtyohann *et al.* 1980). Strong emission is observed for ions, the spatial distribution of which is insensitive to operating variables and normal temperatures. High-energy excitation of 'hard lines', specifically ions, and atoms with high excitation energies, occurs along with a high population of argon metastable levels in this region (Uchida *et al.* 1980, 1981). Departures from local thermodynamic equilibrium in this zone provide enhanced ion line emission signals and minimum influence from easily ionized elements. In this non-thermal analytical zone, the addition of easily ionized elements often depresses emission intensities (Blades & Horlick 1981*a*), and at least a compromise location can be found for most elements for which the enhancement and depression balance.

The role played by energetic argon species is unclear now, although Penning processes involving both radiating and non-radiating argon excited levels between 11.5 and 11.8 eV appear to be contributing (Blades *et al.* 1981). These recent findings have stimulated considerable activity during the past year to document population densities of argon excited levels, and a number of mechanisms are being evaluated. Conventional as well as novel plasma diagnostics are being applied, and the number of scientists undertaking these studies has increased during the past year.

These basic studies have also helped to reduce analysis costs, without degrading analysis performance, by the exploitation of low argon consumption i.c.p. torch configurations especially when operated at low power (Kawaguchi *et al.* 1980; Weiss *et al.* 1981). Discharges in low-cost gases, such as air, nitrogen and oxygen, or mixtures with argon (Montaser *et al.* 1981), have also been examined recently (Barnes & Meyer 1980; Meyer & Barnes 1981). The generation and operation of an air i.c.p. discharge with a compressed air laboratory supply provides a novel and inexpensive spectrochemical source. The introduction of airborne aerosols into an air i.c.p. discharge allows analytical possibilities, such as real-time airborne particulate analysis, not readily available with conventional argon i.c.p. discharges. The evaluation of these molecular gas discharge plasmas and their analytical properties is now under way, and preliminary results indicate high decomposition rates of sample aerosols and powders, central channel temperature exceeding 6000 K, and acceptable signal:background ratios for selected wavelengths. The generation of an analytical i.c.p. discharge in helium appears to be less successful (Robin 1981).

SAMPLE INTRODUCTION

All steps in an analysis related to the sample have or will receive the bulk of the analyst's attention in i.c.p. spectroscopy. The precision, reliability, sensitivity and speed of i.c.p.–a.e.s. is more often than not limited by the technique employed for sample introduction or preparation. Because the investigation of sample preparation procedures is stimulated by the reliability of the i.c.p. result (Dahlquist & Knoll 1978), sample preparation methodology has been challenged, extended and refined. In routine analysis, an increase in sample throughput, extended analysis capabilities, and automated calibration and standardization are needed. Conventional solution introduction by pneumatic and ultrasonic nebulizers (Taylor & Floyd 1981) has been augmented by application of high solids and corrosion-resistant nebulizers (Barnes 1981*b*). Fundamental characteristics of nebulizer operation are being studied to improve i.c.p. analysis, and novel techniques for transporting powders and solid aerosols are under development (Salin & Horlick 1979; Sommer & Ohls 1980). Although these are currently in the research phase, practical implementations can be expected during the next few years.

The combination of i.c.p.–a.e.s. with proven sample introduction techniques appear effective without degrading plasma performance. For example, commercial and laboratory hydride generation systems, borrowed from a.a.s., conveniently extend detection capabilities for a group of important elements (As, Bi, Sb, Se, Sn and Te) that exhibit relatively poor sensitivity when analysed as nebulized solutions (Pahlavanpour *et al.* 1981; Wolnik *et al.* 1981). Although somewhat limited by the hydride-generating chemical reaction, this technique will shortly be as commonplace in i.c.p.–a.e.s. as it is in a.a.s. Similarly, the introduction of small volumes of liquid samples by either direct injection or by vaporization from an electrothermal heater (Camara Rica *et al.* 1981) has been tested successfully. A well engineered, commercial electrothermal vaporizer–i.c.p.–a.e.s. combination will stimulate this approach. Flow injection analysis combined with i.c.p.–a.e.s. offers a number of advantages, including increased sample throughput and the automation of standardization and calibration procedures (Greenfield 1981; Tyson & Idris 1981). At least one commercial i.c.p. manufacturer and a number of researchers are exploring f.i.a.–i.c.p., and the application of this combination is expected to increase during the next few years.

Solvent extraction, ion exchange separation and gas and liquid chromatography have been employed to improve the selectivity and sensitivity of i.c.p. analyses. These and other chemical or separation techniques will extend the i.c.p.–a.e.s. capability to low concentration levels or to the identification of chemical species.

Fluorescence and mass spectrometry applications

The universal nature of the i.c.p. discharge extends its applications to atomic absorption, atomic and molecular fluorescence, and mass spectrometry. The commercial availability of an a.f.s.–i.c.p. instrument (Demers & Allemand 1981) has stimulated research and applications, although the values of a.f.s.–i.c.p. were reported earlier (Epstein *et al.* 1980*a*).

As a light source for a.a.s., a.f.s. (Epstein *et al.* 1980*b*) or molecular fluorescence (Tallant 1979), the i.c.p. remains underused because only a few research efforts have been reported. Next to i.c.p.–a.f.s., probably the largest application of the i.c.p. discharge exists as an ion source for mass spectrometry (Date & Gray 1981, 1982; Douglas *et al.* 1982; Houk *et al.* 1980, 1981). The difficulty of introducing solution samples into the ion source of conventional mass spectrometers and the utility derived from the reliable isotopic abundance analysis of the mass spectrometer have stimulated two research groups (Date & Gray 1981, 1982; Houk *et al.* 1980, 1981) and one commercial firm to evaluate i.c.p.–m.s. (Douglas *et al.* 1982). Encouraging results demonstrating improved performance and capabilities may justify the high equipment costs expected.

Future developments

The extension of present research and development in i.c.p. spectroscopy during the 1980s appears likely, especially as i.c.p. sources become widespread in academic and research laboratories. In the near future, problems associated with each of the previously mentioned development areas will be attacked. Engineering by i.c.p. manufacturers should produce optical arrangements with maximum light gathering and throughput to the detector (Boumans *et al.* 1981). Improved computer systems and advanced programming will emphasize user-oriented data base management and advanced signal treatment. A breakthrough is needed in generator design to make small, efficient solid-state generators available at moderate cost, and the optimum operating frequency for i.c.p. spectroscopy between 30 and 200 MHz remains undefined. By the end of the decade, smart i.c.p. instruments will prepare samples, select interference-free wavelengths, autocalibrate and standardize the source and spectrometer, transport and analyse the sample, and document, report and interpret the data for routine laboratory as well as process control applications.

Hybridization of the i.c.p. with flow-injection analysis, hydride and chemical vapour generation, chromatography, electrothermal vaporization, mass spectrometry and atomic fluorescence, and solid sample introduction will continue as refined commercial equipment becomes available.

Two other prospects, (*a*) to improve the data quality to 0.1–0.2% and (*b*) to understand quantitatively the mechanisms of the i.c.p. discharge, are distant objectives.

In conclusion, the i.c.p. discharge has become a commonplace analytical tool for emission spectroscopy. Its universal nature as a fluorescence atom reservoir or ion source for mass spectrometry is becoming recognized, and the extent to which the i.c.p. discharge serves as the primary discharge in these techniques will probably depend upon the success of commercial instrumentation. Furthermore, the details of transport and excitation processes occurring within the i.c.p. discharge under spectrochemical measuring conditions should become apparent as continued fundamental research studies are conducted. These processes might also be quantitatively predictable. New high-frequency plasma sources could be designed as a direct consequence. Finally, developments in i.c.p. spectroscopy will help to stimulate improvements in flame and furnace atomic spectroscopy.

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Discussion

J. D. R. Thomas (*Chemistry Department, U.W.I.S.T., Cardiff, U.K.*). Viscosity was mentioned as having a limiting effect on the application of i.c.p.; would this cause any further problems in adapting i.c.p. to flow injection analysis?

R. M. Barnes. Greenfield (1981) indicates that one of the major advantages of flow injection analysis is the reduced effect of viscosity on nebulization rate compared with direct nebulization of viscous solutions continuously.