

Quantitative Elemental Analyses by Plasma Emission Spectroscopy

Atomic spectra excited in inductively coupled plasmas
are used for simultaneous multielement analyses.

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From its early stages of development in the 1930's until the middle 1960's, atomic emission spectroscopy (AES) was often the method of choice for the simultaneous determination of major, minor, and trace constituents in virtually all sample types. Although arc-spark excitation AES has continued its primary role in routine compositional control in

tem, namely the component that has to vaporize the sample, dissociate the vapor, and excite and ionize the free atoms. This advance was the development of an inductively coupled plasma (ICP) source—an electrodeless argon plasma formed at atmospheric pressure and sustained by inductive coupling to high-frequency magnetic fields.

Summary. Argon-supported inductively coupled plasmas operated at atmospheric pressures are excellent vaporization-atomization-excitation-ionization sources for analytical atomic emission spectroscopy. When a polychromator is used for observing the emitted spectra, the metals and metalloids can be determined simultaneously at the ultratrace, trace, minor, and major concentration levels under one set of experimental parameters. Alternatively, programmable scanning spectrometers may be utilized for sequential determinations. The atomization-excitation process is remarkably free of interelement interactions, the powers of detection are in the part per billion range for most elements, and sample manipulation requirements prior to analyses are often minimal. The technique meets the requirements of an analytical system for the simultaneous or sequential determination of the elements at all concentration levels to an unusual high degree.

the metals industries, its use as a general analytical technique has gone through a period of decline during the past 15 years. The wide acceptance of atomic absorption spectroscopy (AAS) during this period was primarily responsible for this decline. But decline in usage does not imply stagnation in scientific development. There is now abundant evidence that AES is regaining its appeal.

One reason for this sharp upturn in the use of AES is that analytical chemists have been increasingly faced with the necessity of determining many elements at all concentration levels, and particularly at lower concentrations. Because of these needs, "one element at a time" procedures, such as classical chemical approaches or the various AAS methods, have lost some of their attractiveness. Another factor is a major advance in the heart of any AES analytical sys-

tem, namely the component that has to vaporize the sample, dissociate the vapor, and excite and ionize the free atoms. This advance was the development of an inductively coupled plasma (ICP) source—an electrodeless argon plasma formed at atmospheric pressure and sustained by inductive coupling to high-frequency magnetic fields. ICP's may be coupled with a multi-channel polychromator of the type shown in Fig. 1. In these instruments, precisely located exit slits isolate the spectral lines of interest from the dispersed spectrum formed by the diffraction grating. Each exit channel has its own photomultiplier detector and electronic channel. Up to 40 or 50 channels may be provided, allowing the simultaneous integration of up to that many analyte signals. Polychromators of this type lack flexibility because only the lines sampled by the exit slit array can be observed. To provide flexibility for the observation of other lines, it is advantageous to add a scanning monochromator, preferably of the slew-scanning type, to the facility. The polychromator may then be programmed for the 20 to 40 or more elements that are determined routinely, and the scanning instrument reserved for

the sequential determination of other elements, for observing other lines, and for diagnostic studies.

Historical Aspects

The development of ICP's began in 1942, when Babat (1) published his first paper on the properties of electrodeless discharges (2). The importance of Babat's papers are that they document the first successful operation of ICP's at atmospheric pressure. The next significant development in the evolution of ICP's occurred in the early 1960's, when Reed (3, 4) described his ingenious approach to the stabilization and thermal isolation of these plasmas. Reed's accounts called attention to three attractive properties possessed by these plasmas that should contribute to their usefulness as vaporization cells and free-atom reservoirs for analytical AES. These properties were (i) high gas temperatures, (ii) capability of being sustained in noble gas environments (important from free-atom lifetime considerations), and (iii) freedom from contamination from electrodes, since none were required.

Because these plasmas offered such promise, studies of their analytical performance were initiated in our laboratories in March 1962, and within a few weeks similar investigations were started at the laboratories of Albright and Wilson, Oldbury, England, by S. Greenfield and associates. The first independent publications from these groups appeared in late 1964 and early 1965 (5-7). Later significant contributions by other investigators have been reviewed (8-10). Specific goals of the early investigations were to study the behavior of these plasmas when aerosols of solutions were injected into them and to evaluate their analytical performance, particularly for trace element determinations. The initial results were disappointing (11), especially compared to the powers of detection of AAS, which was then beginning its phenomenal growth. Progressive refinements in (i) the reduction of radio-frequency interference with the recording electronics, (ii) impedance matching between the high-frequency generator and the plasma, (iii) forward power regulation, (iv) techniques for generating aerosols of solutions, and (v) the efficiency of injection of aerosols into properly shaped plasmas resulted in lowering the detection limits by approximately one order of magnitude every 2 years.

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Formation of Inductively Coupled

Plasmas

Plasmas are gases having a significant fraction of their atoms or molecules ionized. Magnetic fields readily interact with plasmas, and one of these interactions is an inductive coupling of time-varying magnetic fields with the plasma, analogous to the inductive heating of metal cylinders (12). To appreciate the course of events that lead to the formation of ICP's, it should be recalled that the high-frequency currents flowing in an induction coil generate oscillating magnetic fields whose lines of force are axially oriented inside the coil. The induced axial magnetic fields cause charged particles (electrons and ions) within the coil to flow in closed annular paths. The electrons (and ions) meet resistance to their flow, Joule or ohmic heating is a natural consequence, and additional ionization occurs. Electric field coupling is also involved in the early stages of formation of the plasma, but its role has been neglected in this simplified discussion. The steps discussed above may lead to the formation of a plasma of extended dimensions if argon flows of the proper configuration and magnitude pass through the coil, an adequate seed of electrons is initially provided, and the output impedance of the generator is properly matched to the plasma.

The overall plasma configurations are based on the concepts developed by Reed (3, 4). In the discussion that follows specific reference is made to the configuration and argon flow patterns

commonly used in present commercial instruments. As shown in Fig. 2, the plasma is formed and sustained at the open end of an assembly of quartz tubes, which fit into the coil space. The open end of the outermost tube is surrounded by the induction coil, which is connected to a high-frequency current generator. In our systems the latter provides a forward power of up to ≈ 3 kilowatts at a frequency of 27.12 megahertz. To form a stable plasma, a pattern of two or sometimes three argon flows is used, as shown in Fig. 2. When the flows are adjusted properly, the plasma is readily initiated by "tickling" the quartz tube inside the coil with a Tesla discharge.

Thermal Isolation and Stabilization of the Plasma

A plasma formed in this way attains gas temperatures of such magnitude (13, 14) that some thermal isolation from the quartz cylinder must be provided. This thermal isolation is achieved by Reed's vortex stabilization technique (3, 4), using a flow of argon that is introduced tangentially as shown in Fig. 2. The tangential flow of argon, which is typically 10 to 15 liters per minute for the apparatus shown, streams upward, cooling the inside walls of the outermost quartz tube and centering the plasma radially in the tube. It also serves as the primary sustaining flow. The plasma itself is anchored near the exit end of the concentric tube arrangement.

Another argon flow of approximately 1

to 1.5 liter/min transports the sample to the plasma either as an aerosol, a powder, or a thermally generated vapor. The total argon flow required is therefore 11 to 17 liter/min. The operating cost of these plasmas, exclusive of electrical power, is lower than the cost of the gases needed to operate the nitrous oxide-acetylene flame commonly used in AAS.

Preliminary Sample Preparation

Samples are most commonly introduced into plasmas as aerosols generated from aqueous or organic solutions either by pneumatic (15) or ultrasonic nebulization (16) techniques; typical systems are illustrated in Figs. 3 and 4. Samples in this form are most convenient for the direct examination of liquids, including process streams, edible oils, liquid fuels, and body fluids.

Solid samples may be dissolved by a variety of methods, but the direct sampling of solids without prior dissolution is clearly advantageous. The transformation of solid metal samples into aerosols that are subsequently injected into the plasma has been achieved in several ways. In one method, aerosols of solid metallic particles have been produced by ultrasonic nebulization of molten metals (17). In another, for which a hand-held device is now commercially available (18, 19), the cold cathode termination of a d-c arc in argon is utilized to generate the aerosol. The cathode spot (or spots) of the arc discharge moves rapidly over the surface of the sample, the sampling area being defined by a boron nitride insulator against which the sample is sealed. The ejected particulates, which are typically micrometers in diameter, are transported to the plasma by the same argon flow that ejects sample material into the axial channel of the discharge. The aerosol may be transported through flexible tubing over distances of 10 to 20 meters, thus allowing remote sampling.

Sample Injection into the Plasma

To be effectively atomized and excited, the sample aerosols should be injected into the plasma and remain in the interior high-temperature environment of the plasma as long as possible. Efficient sample injection has been difficult or impossible to attain in non-ICP plasma systems (8). The ICP poses problems as well, because the gases are heated internally and expand in a direction perpendicular to the exterior surface of the plasma. There is also an excess

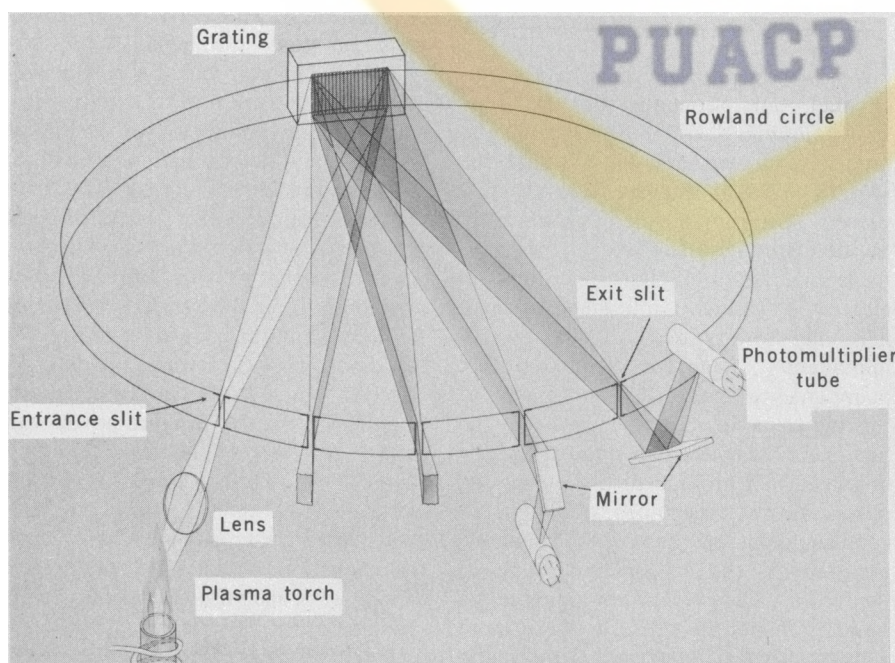


Fig. 1. Schematic diagram of a typical atomic emission polychromator (9).

magnetic pressure along the axial channel of the plasma (20) that causes axial flow of plasma toward the floor and tail flame. This magnetic pumping effect has been observed (21) and, along with the thermal expansion thrust, should oppose the entry of sample particles into the plasma.

Because of the skin depth of induction heating, most of the forward power into the plasma is dissipated near the surface of the plasma. ICP's therefore tend to assume a toroidal or annular shape in the energy input region. The degree to which the annular discharge is developed depends on the frequency of the current flow, the torch configuration, and the argon aerosol-carrier flow (22, 23). This flow must overcome the aerodynamic forces that oppose entry of sample material into the plasma. When the frequency of the current flow is increased from, say, 4 to 30 MHz, the annular discharge is more effectively punctured by low aerosol-carrier flow rates. At ~30 MHz, a carrier gas flow of ~1 liter/min ensures effective injection of sample into the plasma, if properly designed injection orifices are used (8, 22, 24).

Sample Vaporization, Dissociation, Excitation, and Ionization

Several physical properties of ICP's contribute to their remarkable success as vaporization-atomization-excitation sources for analytical spectroscopy. Aerosol droplets or finely divided powders introduced into the plasma are heated indirectly by radiation, convection, and conduction. Because there is very little interaction of the sample with the eddy currents that sustain the flow, changes in sample composition have an unusually small or negligible effect on the properties of the plasma, a situation that does not prevail in most other vaporization-atomization sources.

Temperatures measured above the coil region and estimated by extrapolation down into the induction region are shown in Fig. 5 (13, 14). By the time the sample species reach the observation height of 15 to 20 millimeters above the coil, they have had a residence time of ~2 milliseconds at temperatures ranging from ~8000 to ~5500 K. The residence times and temperatures experienced by the sample are approximately twice those found in nitrous oxide-acetylene flames—the hottest combustion flames commonly used in AAS. The combination of high temperature and relatively long interaction time should lead to an unusually high, if not total, degree of

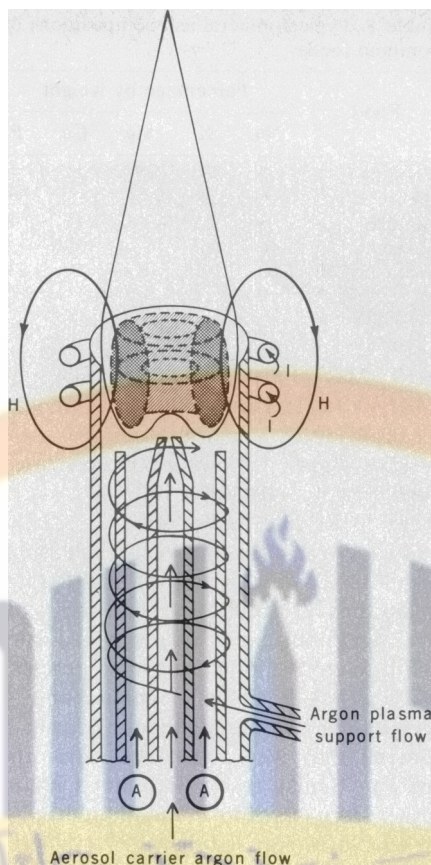


Fig. 2. Typical inductively coupled plasma configuration (11).

atomization of the analyte species, especially for the small aerosol particles resulting from solutions with total salt contents of 0.5 to 2 percent by weight. When atomization is essentially complete, dissociation equilibria play a less significant role and vaporization-atomization interference effects are unlikely to be a serious problem.

Ionization equilibria, however, might play an important role, especially if the analyte were ionized to a considerable degree in the absence of other easily ionizable elements. But under the plasma conditions now generally employed, ionization interference effects are surprisingly small. These results can be understood if the change in electron number density and excitation temperature on the introduction of high concentrations of easily ionizable elements is small (14). The question of why there is such a small change can be rationalized by assuming an unusually high, suprathermal electron number density in a "pure" argon plasma, so that the total is not significantly affected by the addition of easily ionizable elements. The search for a definitive answer to the unexpectedly low ionization interference effect in these plasmas has catalyzed extensive experimentation and speculation (13, 14, 25-29).

Freedom from Interelement Interactions or Interferences

One of the most important factors in the application of any analytical technique is the degree of freedom from interelement interactions or interferences (matrix effects). These interferences by concomitants (constituents in the sample other than the analyte) may be spectral or nonspectral in nature. The former arise from incomplete isolation of the radiation emitted by the analyte from other radiation detected by the instrument.

The analyte signal itself may be directly affected by nonspectral interferences. I have discussed above several physical properties of ICP's that should contribute to the reduction or elimination of many, if not most, of the interelement effects observed with conventional discharges. These expectations have been repeatedly confirmed. One of the classical interferences is the suppression of calcium free-atom formation in the presence of increasing concentrations of aluminum. This suppression has been attributed to formation of refractory compounds and occlusion of the Ca analyte in a refractory oxide matrix (30, 31) during the evaporation and dehydration of aqueous aerosols of solutions containing these elements. In flames and many arc discharges, the Ca emission is observed to decrease toward zero with increasing Al concentrations. The behavior in an ICP is shown in Fig. 6, bottom. The absence of any depression at low Al/Ca molar ratios verifies that there is no measurable interference with analyte vaporization, dissociation, and atomization. There is a gentle decrease in intensity up to a molar ratio of 100 (1350 micrograms of Al per milliliter); for the neutral atom line this depression is remarkably low (~2 percent). Thus, if analytical calibration curves established for the determination of Ca in "pure" water were applied directly to the determination of Ca in Al, an error of only ~2 percent of the amount present would be experienced if the Al sample concentration in solution was selected to be ≤ 0.14 percent by weight.

The behavior of calcium neutral atom and ion emission in the presence of increasing concentrations of sodium (Fig. 6, top) is typical of an ionization-type interference, but in comparison to the magnitude of line intensity changes in other atomization-excitation sources the effect in ICP's is also remarkably small. Thus, at a Na concentration of 0.2 percent by weight, which might typically be used for the determination of Ca in NaCl, simple aqueous reference calibration standards

would introduce only a 5 to 10 percent bias. It is quite certain that factors other than ionization effects play a role in the trends of the curves plotted in Fig. 6. A definitive interpretation of the interelement effect observed at higher concentrations of the concomitants will require a far more detailed knowledge than is now available of the spatial distribution of analyte free atoms and temperature, of the ionization equilibria, and of the role played by the argon sustaining gas (32). Nevertheless, the interelement interactions are small or insignificant for reasonable changes in the concentrations of concomitants under the experimental conditions that provide excellent powers of detection.

Because of the high degree of freedom from interelement effects, it is possible to establish a single set of calibration curves for the determination of analytes in a variety of sample matrices. For example, data reported by Boumans and De Boer (33) verify that the observed relative intensities of the analyte lines of Al, Ba, Ca, Cd, Cu, Li, Mg, Mn, V, and Zn rarely show a change significantly greater than the estimated experimental error of 3 to 4 percent when the matrix is changed from relatively pure water to a 0.1 percent solution of NH_4Cl , CsCl ,

Table 1. Typical mineral ash compositions of common foods.

Food	Percentage by weight				
	Na	K	Mg	Ca	P
Total diet	19	41	2	15	23
Steak	6	58	3	2	31
Lettuce	3	72		11	7
Carrots	10	70		10	9
White bread	63	13	3	10	11

KCl , MgCl_2 , CdCl_2 , AlCl_3 , FeCl_3 , or $(\text{NH}_4)_2\text{HPO}_4$. The same behavior has been observed in more direct analytical studies. Figure 7 shows sets of congruent analytical curves observed for pure, hard, and saline water (34).

In a recent study of foods, results such as those shown in Fig. 8 verified that the manganese concentrations in a variety of different foods could be determined from a single calibration curve when perchloric acid was the dominant component (50 percent by volume) of the food digest solutions that were introduced into the plasma. Similar results were obtained for other trace elements found in foods (35). It should be recalled that the "mineral" content (Ca, Mg, Na, K, and P) of foods can vary widely, as shown in Table 1. Thus the resulting solutions ranged wide-

ly in the concentrations of these constituents, yet no effect was observed on the analytical calibrations.

A third illustration is based on the demonstration by Butler *et al.* (36) that Al, Cr, Cu, Mn, and Ni could be determined accurately in low- and high-alloy steels by relating the analyte line intensities to analytical calibration curves that were based on reference solutions containing only iron and the analyte elements. No attempt was made to match the overall composition of the steel samples and the synthetic reference solutions employed for the calibration. The accuracy of the analysis was assessed by analyzing a series of National Bureau of Standards (NBS) reference samples. Three different ICP systems with different characteristics were used. The analytical results, summarized in Table 2, show excellent agreement with the NBS average and range values, even though the Fe content varied from > 99 (sample 19g) to < 1 (sample 169) percent by weight.

In all of the examples cited above, changes in the concentrations of the constituents not determined may have caused shifts in the background, for which proper baseline background corrections were made.

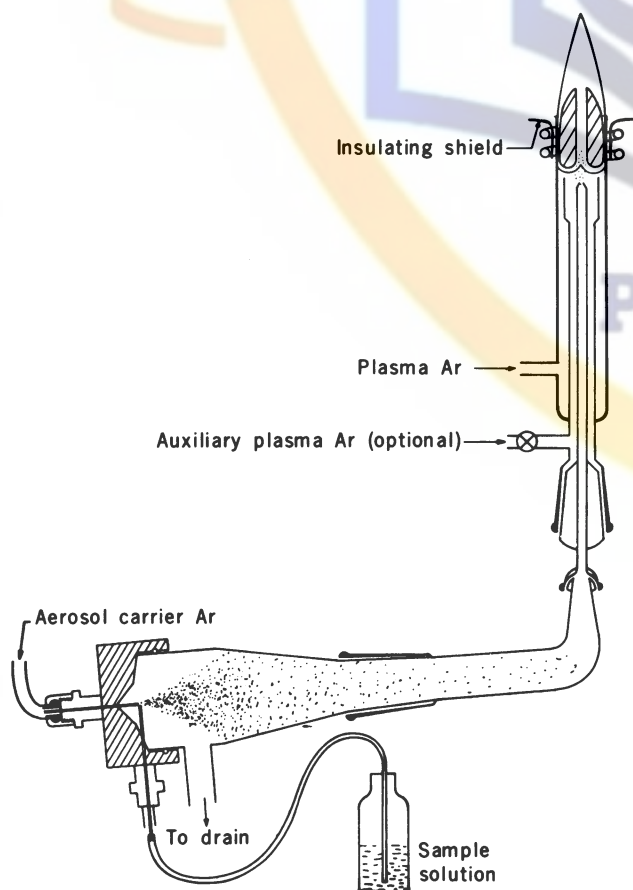


Fig. 3 (left). Typical pneumatic nebulization facility (11). The crossed-needle nebulizer is described in (15).

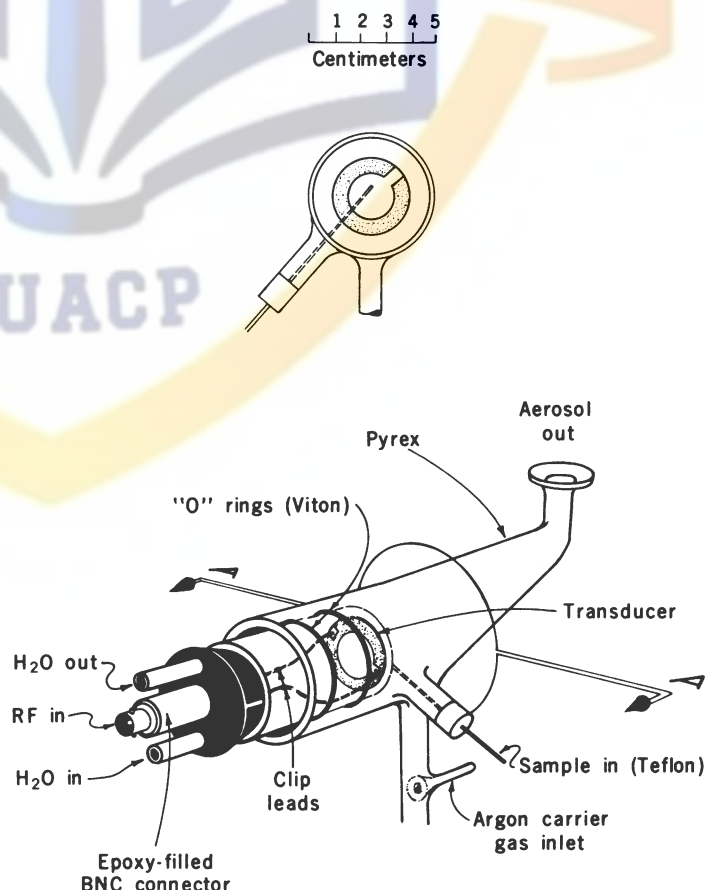


Fig. 4 (right). Ultrasonic nebulization facility (16).

Description of Spectra Emitted

The plasma has the overall appearance of a very intense, brilliant white, non-transparent core and a flamelike tail. The plasma core, which resides inside and extends a few millimeters above the induction coil region, emits an intense continuum in addition to a rather fully developed spectrum of neutral argon. The continuum presumably arises from ion recombination processes and Bremsstrahlung emission. The core fades into a second recognizable zone of the plasma which extends ~1 to 3 centimeters above the induction coil. This zone is also bright but slightly transparent. In the middle to upper regions of this zone, the continuum emission is sharply reduced by several orders of magnitude from the core emission. The tail flame or third zone of the plasma is barely visible when distilled water is nebulized but assumes typical flame colors when analytes are added to the plasma. The axial passage of the sample aerosol and its decomposition products through the plasma is clearly visible.

The radiation from the plasma core has little analytical utility. Because of the sharp reduction in background emission above the core, it is possible to separate spatially the high spectral background region, where the primary free-atom formation occurs, from the observation zone. This capability of observing the free atoms in a region of low background emission is an important factor in the observed excellent powers of detection.

Under optimal operating conditions, the background in the region of most of the sensitive lines of the elements is remarkably free of structure. As shown by the background spectrum in Fig. 9 (34), the only structural features detectable are the C lines at 193.1 and 247.9 nm, the weak OH emission at 281.1 and 306.4 nm, and the appearance of Ar lines above 320 nm. Most of the sensitive lines of the elements being analyzed fall between 190 and 300 nm. The fact that many of these sensitive lines originate from singly ionized species was suggested in some of the earlier data on detection limits, especially those of Souilart and Robin (37). Wavelength tables of the most sensitive lines observed in the plasma may be found in several publications (10, 37, 38).

Linear Dynamic Range

The tendency of the plasma to confine the free atoms and ions formed into a

narrow channel leads to another advantage. At the normal viewing height, the central axial channel not only is populated with a much higher free-atom and ion number density than the surrounding sheath but also exhibits a relatively uniform temperature profile (13, 14). Also, in contrast to conventional flames, arc and spark discharges, and other plasmas, the sheath that immediately surrounds the axial channel is sustained at a high temperature by the upflow of hot Ar from the high-temperature toroid. As a

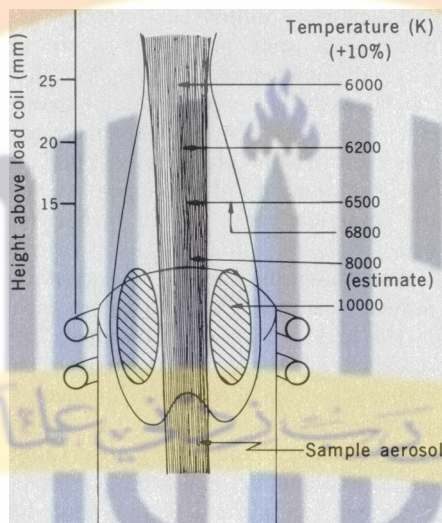


Fig. 5 (left). Schematic diagram of sample flow through the plasma and the temperatures experienced (11).

consequence, self-absorption and reversal effects, which often cause serious nonlinearity of the response when other atomization-excitation sources are employed, are usually not detected. In fact, for most analyte lines, the ICP acts as if it were an optically thin emitting source. If the intensity measurement system has an adequate linear dynamic range, calibration curves that are linear over a concentration range of five orders of magnitude are usually observed. The variable dilutions that are so often required in

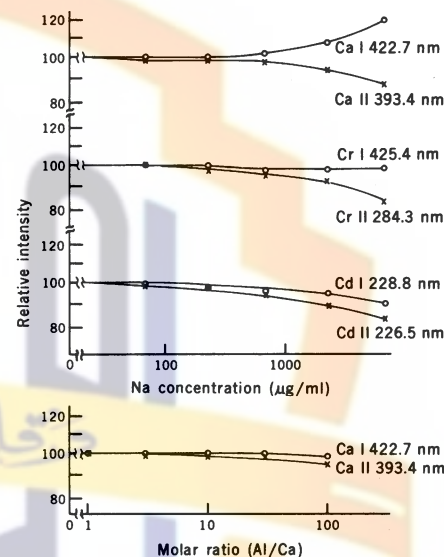


Fig. 6 (right). (Top) Effect of increasing concentrations of Na on the Ca, Cr, and Cd neutral atom and ion emission intensities. (Bottom) Effect of increasing concentrations of Al on Ca neutral atom and ion emission intensities (11).

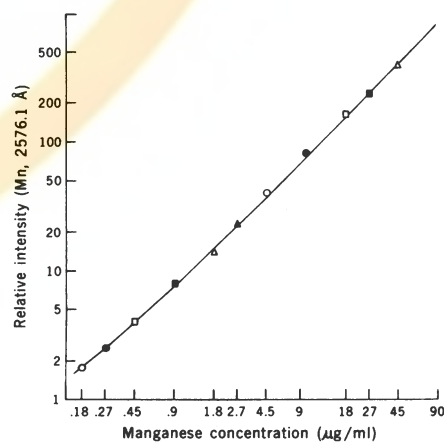
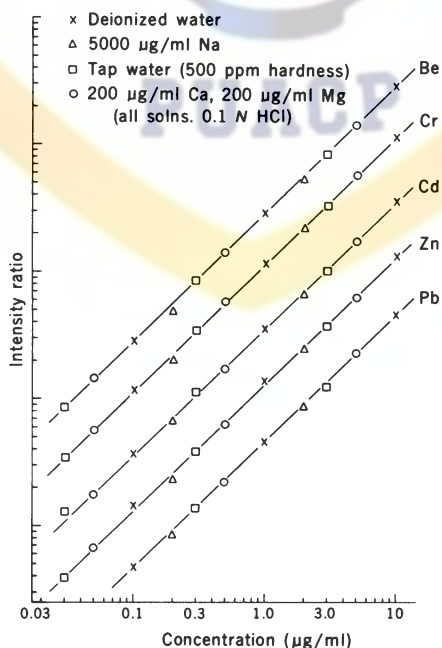


Fig. 7 (left). Analytical calibration curves for the determination of trace metal pollutants in pure, hard, and saline waters. The intensities of the analyte lines are relative to that of the yttrium 242.2-nanometer internal reference line. Fig. 8 (right). Analytical calibration curve for Mn in matrix compositions that are encountered in the analysis of foods; (○) 35 percent HClO₄, (●) steak, (□) lettuce, (■) carrots, (Δ) white bread, and (▲) common salt. The reference blank and calibrating solutions were based on 35 percent HClO₄ by weight in deionized distilled water; test solutions for the foods contained 0.1 percent food matrix in the same medium. The compositions of the test food matrices are given in Table 3.

AAS to achieve a similar range are therefore eliminated.

A striking example of the linearity of ICP-AES is shown by the data plotted in Fig. 10. It is appropriate to recall that rare earth mixtures cannot be analyzed by classical chemical methods, except in a few isolated cases where changes of oxidation state can be effected. For the analysis of rare earth mixtures as they are, physical measurements must be used. Figure 10 shows that both major and trace constituents can be determined simultaneously without changing experimental conditions.

Compromise Experimental Variables

The analytical performance of ICP's may be greatly affected by the choice of experimental parameters. If the assumption is made that the choice of frequency of the current flowing in the coil, the torch configuration, and the pattern of gas flows ensure effective injection of the sample, the remaining dominant experimental parameters are (i) the power input into the plasma, (ii) the flow rate of the argon carrier gas, and (iii) the observation height. The excellent powers of detection observed in our laboratory at fixed observation heights and gas flows and the general experience that improvement factors greater than 5 could be rarely achieved by optimizing these parameters support the use of a single "compromise" set of experimental parameters for all metals and metalloids (9, 24). Further evidence that compromise parameters can be identified has been provided by Boumans and de Boer (38).

Detection Limits

For the determination of trace constituents, detection limits are the primary figures of merit. Detection limits based on the signal-to-noise ratio may be used to compare analytical techniques and predict the lowest concentration at which quantitative determinations can be made. The values listed in Table 3 were obtained for samples that were ultrasonically nebulized (39). A range of values is shown because different spectrometers, analyte lines, and solution matrices were employed, although the plasma operating parameters were always at the compromise settings. Thus the values are readily transferable to other systems and to many other matrices. It is seen that the presence of 2 percent NaCl in solution did not appear to bias the detection limits toward higher values.

Also shown in Table 3 are values reported for atomic absorption spectroscopy (40) and for laser-excited atomic fluorescence (LEAF) (41). In these two techniques it is often necessary to change the primary sources and the flames, the stoichiometry, and the observation height to obtain optimal detection limits. A comparison of the detection limits for AAS and ICP in Table 3 shows that the latter are generally superior, even if it is taken into account that ultrasonic nebulization leads to an order of magnitude improvement in the ICP values.

The practical relevance of the data in Table 3 can be assessed by noting that the detection limits listed are the concentrations required to produce a net line signal that is three times greater than the

standard deviation of the background noise or scatter. Quantitative determinations with a coefficient of variation of 5 to 10 can usually be made at concentrations five times greater than the listed values.

Spectral and Background Interferences

Spectral line interferences are common in AES, and there are well-known approaches for eliminating or drastically reducing their effects on analytical results. Interferences can frequently be eliminated altogether by judicious selection of the lines to be used. Although this may require some compromise between optimum detecting power and least interference from major concomitants, such compromises are generally acceptable. The most definitive assessment of possible spectral line interferences is based on observations of spectra of pure reference samples free of the analyte species. The general unavailability of such reference samples remains a problem of ultratrace analysis by atomic spectroscopy. Weak spectral line interferences may not always be avoidable, and under these circumstances, correction schemes based on measurements of the concentrations of the interfering elements can be used (42). The latter approach is particularly appropriate when the concentrations of several elements are determined simultaneously with a polychromator.

When concentrations are near the detection limit, the spectral background will normally be a large fraction of the total measured signal and precise background corrections will be required for accurate analyses. Changes in the concentrations of concomitants may produce subtle changes in the background level. These background shifts may be caused by true spectral interference, as discussed above, or by stray light (43), or they may be true spectral background shifts arising from radiative recombination continuum emission or from line-broadening processes (44). The stray light contributions, other than the portion arising from far scatter, can usually be reduced by use of high-quality gratings, such as holographic gratings, and by proper design of the spectrometer. Residual far scatter, which may be considered a form of stray light, may often be rejected by mounting band-pass absorption or rejection filters immediately in front of the detector or the entrance slit of the spectrometer (43, 45).

True background shifts, if not mea-

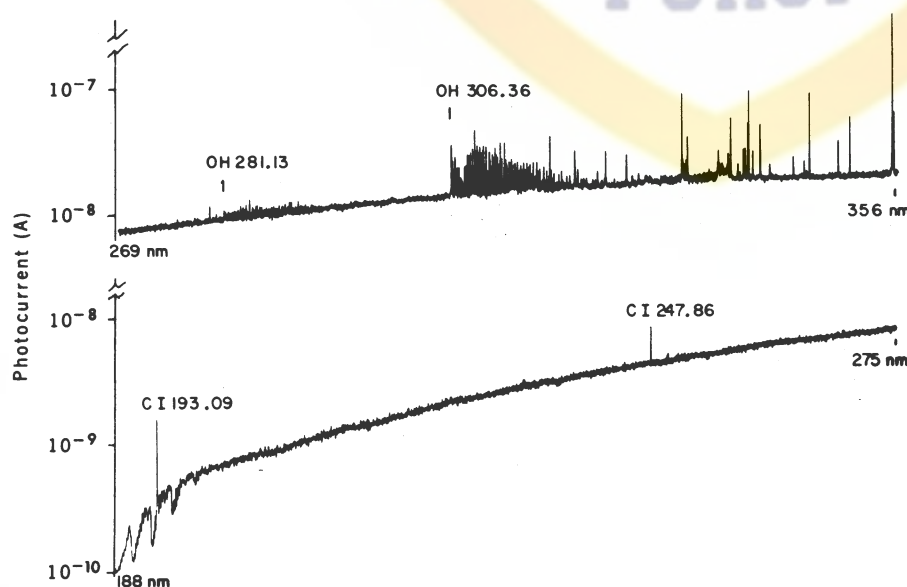


Fig. 9. Background spectrum of plasma.

When the angle of incidence of the plasma radiation falling on the grating is changed by moving the entrance slit of the polychromator a short distance along the focal curve, the wavelengths that are sampled by the fixed exit slits no longer coincide with the wavelengths of the lines selected for analysis, but instead coincide with wavelengths that are all slightly less or greater than those of the analysis lines. If the entrance slit is moved in a stepwise manner by a computer-actuated stepper motor through a range of positions that includes the normal analyte position and the adjoining regions of background emission, then time-averaged intensity measurements for each stepper motor position, performed simultaneously for all of the analyte lines, yield digital representations of the profiles of intensity versus wavelength. These profiles contain both analyte intensity and spectral background data for the sample. With this information, the proper wavelength or wavelengths at which background corrections should be measured for each analyte can be selected, and the value measured can be automatically subtracted. Evaluations to date have shown that this approach is sound and that the control operations and computer calculations are well within the capabilities of computer systems provided with commercially available ICP-AES systems.

One of the major challenges in analytical chemistry and spectroscopy has been to develop an analytical system that would allow the determination of all the elements, from the ultratrace to the major constituent level, in an acceptable manner. It is doubtful that a single analytical instrument or technique will ever fulfill all the requirements for such an ideal system. Because I implied that the ICP-AES approach met these requirements to an unusually high degree, I will

Determination of all the elements. Under the experimental conditions commonly employed, the plasma is observed in an air environment. Thus, the determination of O and N is usually not practical. When hydrogen-containing solvents are used, the determination of H is also precluded. The determination of Br, Cl,

Table 2. Accuracy data for steel analyses. Determined values are compared with National Bureau of Standards (NBS) values. Percentages are by weight.

Element	NBS sample	Matrix	Value determined (%)			NBS value (%)	
			System 1	System 2	System 3	Average	Range
Al	10g	Open hearth (0.2% C)	0.032	0.033	0.030	0.031	0.027–0.033
	33c	3 Ni	0.033	0.037	0.031	0.032	0.030–0.034
Cr	169	77Ni, 20 Cr	0.095	0.10	0.130	0.095	0.095–0.105
	19g	Open hearth (0.2% C)	0.37	0.37	0.36	0.374	0.369–0.380
	33c	3 Ni	0.055	0.052	0.051	0.052	0.049–0.056
Cu	129	Bessemer (0.1% C)	0.018	0.020	0.021	0.018	0.014–0.019
	160	19 Cr, 9 Ni, 3 Mo	0.051	0.05	0.048	0.053	0.047–0.06
	169	77 Ni, 20 Cr	0.014	0.014	0.015	0.015	0.013–0.02
Mn	341	20 Ni, 2 Cr	0.15	0.13	0.15	0.152	0.145–0.159
	19g	Open hearth (0.2% C)	0.56	0.59	0.57	0.55	0.55–0.559
	33c	3 Ni	0.73	0.73	0.78	0.73	0.73–0.735
Ni	73c	Stainless steel	0.33	0.31	0.28	0.33	0.325–0.34
	73c	Stainless steel, 13 Cr	0.24	0.23	0.220	0.246	0.241–0.255
	111b	1 Mn, 2 Ni	1.80	1.78	1.82	1.81	1.80–1.83



Simultaneous multielement determinations from major to ultratrace levels. It is important to distinguish between multielement and simultaneous multielement determinations. Many analytical techniques have been proposed for which multielement data can be provided in sequence. The sequence cycle may last from minutes to days in neutron activation analysis (NAA), up to hours in spark source mass spectroscopy (SSMS), and from tens of minutes to hours in x-ray fluorescence (XRF), especially when trace constituents are determined. In addition, to cover a broad range of elements and concentration ranges, NAA, XRF, and AAS require changes in operating and observing conditions. To a higher degree than any other analytical technique, ICP-AES can simultaneously determine the elements, at major, minor, trace, and ultratrace levels, without changing any experimental parameters.

Absence of interelement effects. Interelement interaction effects in the ICP are small if proper background corrections are applied; they are far smaller than the matrix effects observed in AAS, XRF, and SSMS. The residual interelement effects that have been observed have often arisen from the fact that nebulization and aerosol transport are affected when the total composition of a sample changes markedly (32, 42, 49). These effects can be compensated internally by adding a constant amount of a reference element to each solution and relating intensity ratios to concentrations. This requirement is satisfied to an unusually high degree by ICP-AES systems.

Applicability to microliter and microgram samples. This capability has been reviewed (50) for samples presented to the plasma in solution form. Techniques based on electrothermal vaporization and atomization (ESVA) combined with AAS have a lower absolute detection limit for microliter volumes of solutions than does ICP-AES. However, ESVA-AAS techniques are very sensitive to interelement interferences and can provide only limited multielement coverage. If at least 0.5 to 1 ml of sample is available, the relative powers of detection of the ICP-AES and ESVA-AAS techniques are comparable (50).

Direct analysis of solids, liquids, and gases with minimal sample preparation or manipulation. This capability has been demonstrated for a variety of sample types, including solid metal specimens (18, 19), organic liquids and oils (51), gas chromatographic effluents (52), and even liquid metals (17). A practical solution to the problem of injecting pow-

dered samples, such as powdered ores and minerals, into the plasma has not been developed (11); however, such samples have been analyzed after dissolution. This requirement is fulfilled to an unusually high degree.

Capability of performing rapid analyses. The time required for the simultaneous determination of 40 or even more elements with commercial instruments is approximately 2 to 3 minutes for the complete cycle, assuming that preliminary sample preparation, if required, has been completed. This requirement is therefore fulfilled.

Acceptable precision and accuracy. The ICP-AES literature shows that with proper functioning of the instrumentation and adequate calibration, this requirement is fulfilled. Day-to-day values of coefficients of variation, expressed as a fraction, are generally in the range 0.5

to 2.0 when high-quality polychromator readout systems are employed.

Commercial availability at acceptable cost. The literature in the general field of chemical analysis has contained descriptions of a bewildering variety of new methods and techniques. If a new analytical technique is indeed useful for the chemical analysis of things as they are, then acceptance by the practicing analyst and commitment by the commercial instrument maker are quick to follow. The now widely used AAS, XRF, and gas and liquid chromatography techniques are examples of such a history. Currently, ICP-AES appears to be passing through the acceptance and commitment phase. The number of laboratories engaged in analytical investigations and routine applications has increased from about 10 to about 200 during the past 6 years, and the number of commercial suppliers of instruments has increased from none in 1973 to at least nine in 1978.

Conclusion

The high degree of compliance of ICP-AES with the requirements of an ideal analytical system for the determination of the elements suggests that the way elemental determinations will be made in the future will undergo a change and that the technique "is ready to take its place as a mainstay in the elemental analysis field" (53).

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Table 3. Comparison of detection limits for three techniques: inductively coupled plasma-atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS), and laser-excited atomic fluorescence (LEAF).

Element	ICP-AES	AAS	LEAF
Al	0.4-2*	20-30	0.6-2
As	3-6	100	
B	1-4	700	
Ba	0.09-0.5	8-50	8
Be	0.01*-0.02	0.7-2	
Bi	3-9	25-50	3
Ce	6*		
Cd	0.1-1*	1	8
Co	0.3-2*	2-7	1000
Cr	0.2-1*	2-3	1
Cu	0.2*-0.4	1-2	1
Fe	0.4-4*	4-6	30
Ga	3-7*	50-70	0.9
Ge	2-20*	20-1000	
Hf	2*	2000-8000	
Hg	6-30	360-500	
Mg	0.03-0.7	0.1	0.2
Mn	0.03-0.1*	0.8-2	0.4
Mo	3-9	20-30	12
Nb	1.5*	1-1000	
Ni	1-2*	2-5	2
P	4*-33	53,000	
Pb	1	10-11	30
Pd	1*-19	14-30	
Sb	4-30*	40-100	
Sc	0.2*	20-1000	
Se	2-18	75-100	
Si	2-22	100	
Sn	9*-25	100-150	
Sr	0.02*-2	5	0.3
Te	18*	26-100	
Th	3*		
Ti	0.04-5*	40-90	5
Tl	2*-23	20	4
U	11*	30,000	
V	0.2*-0.7	20	50
W	11*	1000-3000	
Y	0.1*-2	50-100	
Zn	0.2*-2	1-5	
Zr	0.3*	350-5000	

*Two percent NaCl.

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NEWS AND COMMENT

Uranium Mill Tailings: Congress Addresses a Long-Neglected Problem

Some 30 city blocks from Utah's state capitol building and downtown Salt Lake City is a 128-acre site containing the radioactive residues from a long-since abandoned and dismantled uranium mill. From 1951 to 1964, the Vitro Chemical Company, now defunct, processed uranium ores to produce ^{238}U , or "yellowcake," for the Atomic Energy Commission (AEC) and U.S. military programs. These operations left about 1.8 million tons of fine, sandy milling wastes or tailings right in the middle of what is now a metropolitan area of more than a half million people.

"Thousands of people work and live in close proximity to the [tailings] pile and are exposed to radioactive dust, radon gas, decay products of radon gas, and gamma radiation," Lyman J. Olsen, director of the Utah State Division of Health, told a congressional committee one day last summer. He was appealing for prompt action on legislation to clean up this site and a score of others scattered over the West, where tailings piles have been left from past uranium milling operations.

It now seems not unlikely that Congress will complete action before adjournment on legislation to deal with the mill tailings problem. Such legislation would have the Nuclear Regulatory Commission (NRC) and the Department of Energy take major new steps to clean

up a mess which the old AEC and its congressional overseers were slow to recognize and do anything about.

The tailings problem is large and ever-growing. Besides the 27 million tons of tailings found at inactive sites such as the one in Salt Lake City, another 113 million tons have accumulated at sites where uranium is currently milled. Given the rapid pace at which the uranium industry is now expanding to meet its contracts with electric utilities, there could be a billion tons by the year 2000.

At an active site, tailings first leave the mill as a slurry that is discharged into a pond contained on one or more sides by dikes which may themselves have been made (often none too securely) at least in part of dry tailings. Once the water in the ponds dries up or seeps away, what remains is a dry tailings pile which, unless stabilized and covered over, may be susceptible to wind and water erosion.

Some piles are immense, with the largest in the United States being the active and still growing pile maintained by the Kerr-McGee Nuclear Corporation at its big mill near Grants, New Mexico, where 7000 tons of ore are processed daily. Containing 23 million tons of tailings, it covers 265 acres and rises to 100 feet at its highest point.

The greatest hazard from mill tailings is associated with radon-222, a short-lived daughter of radium-226 found near

the end of a chain of long-lived radio-nuclides that begins with uranium (half-life, 4.5 billion years) and its daughter thorium-230 (half-life, 80,000 years). Unless covered deeply with clay and other material, a tailings pile may exhale radon gas at up to 500 times the natural background rate. Radon's daughter products can cause lung cancer and are responsible for the notoriously high incidence of this disease found in the past among uranium miners in Europe and the United States. The hazard is especially great in situations where radon gas can accumulate in a confined space.

Although the increases of radioactivity in the general environment attributable to tailings and radon gas are small they are never-ending, and significant health effects can be postulated, especially for people living in the regions where the piles are found. As Victor Gilinsky, a nuclear physicist and member of the NRC, has noted, unless the tailings are isolated from the atmosphere they will continue to release radon for more than 100,000 years, becoming "the dominant contribution to radiation exposure from the nuclear fuel cycle."

In fact, according to the American Physical Society's 1977 report on waste management and the nuclear fuel cycle, the ingestion hazard from tailings becomes greater than that from high-level wastes within the first 1000 years.

Whether any cancer cases have already resulted from radiation exposures associated with tailings remains to be documented. But public health authorities in states such as Utah and Colorado where the tailings piles are found are clearly apprehensive, especially with respect to those all too numerous situations where tailings have been used as a