

The

SPEX

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Speaker

THE INDUCTIVELY COUPLED PLASMA TORCH — A SOURCE FOR ALL REASONS —

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Though optical emission spectroscopy (OES) is one of the oldest of instrumental analytical techniques, it has lost little of its importance as a means for rapidly identifying and quantifying a large number of elements simultaneously in almost any matrix ranging from alloys to ores, from ashes of organic materials to atmospheric dusts. Where it has lost ground, mostly to atomic absorption, is in the analysis of liquids. Techniques involving the traditional arcs and sparks of OES have proved unwieldy for the excitation of liquids. Often the sample consists of an acid solution which can play havoc with metal parts of an arc/spark stand. Further, emission bands and general background from the sample raise the threshold of detection. Finally, a small change in matrix can disrupt analytical calibration curves.

Lately a likely candidate to relieve these problems has appeared in the form of an inductively coupled plasma (ICP) torch. In this device, a stream of inert gas is first ionized and then a concentric coil, which is a source of a high frequency (HF) field, accelerates the electrons until they acquire sufficient energy to excite and ionize atoms. The elements of a sample introduced into this plasma are immediately raised to a higher energy state from which they decay with uv, visible and ir emissions.

The Ideal Source For Emission Spectroscopy

In all probability, the ideal source for all OES problems will never be found, but an analyst, put to the challenge, is likely to engender a list of gratifying properties:

1. applicability to all states of matter
2. capability of exciting lines of a large number of elements
3. a wide dynamic concentration range, free of matrix effects
4. freedom from interference
5. convenience of operation
6. low purchase, operation, and maintenance cost
7. high precision and detectability

Of all sources currently available, the inductively coupled plasma torch most nearly satisfies these criteria. Liquids are easily introduced into an ICP as aerosols generated by a pneumatic nebulizer of the concentric or cross-flow type. Aerosols produced by an ultrasonic transducer can achieve better detectability, but they are not as convenient to operate as the pneumatic devices.

Gases, of course, are the simplest to treat with the plasma. Among the substances that have been introduced in this manner are phosphine, metal hydrides, and ammonia.

Due to differences in densities and particle sizes, all methods for injecting powders into plasmas suffer (to varying degrees), from segregation effects, agglomeration and impacting of powders. First-hand experience suggests, however, that the partial successes reported have been obtained from carefully selected matrices and that a comprehensive practical solution to the problem of injecting powders into plasmas has yet to be found. Separate vaporization of solids, through ohmic heating from graphite supported by tantalum holders, has been reported by Kleinmann (1,2) and others (3,4).

The property that makes a plasma most suitable as an excitation source is that large quantities of electrical energy can be transferred to it once it is sufficiently ionized, raising its temperature as high as 10,000°K. This means that many, if not all, of the lines of most elements introduced into the plasma can be excited by thermal excitation alone (there can be other modes of excitation). Still it must be remembered that a source capable of exciting lines from an element with a high excitation potential is also likely to excite many levels in elements with low excitation potentials and this can result in bothersome spectral interference.

The Fig 1 and 2 calibration curves demonstrate the wide linear dynamic range available to the plasma. It should be noted that the log/log plot, which extends over four orders of magnitude, has a slope of unity; other investigators (5) have reported dynamic ranges of 10⁵-10⁶. Also note that the elements of interest are in a number of different matrices, demonstrating ICP's freedom from matrix effects.

Interference, to which most sources are prone, can be separated into four general classes:

1. Spectral interference, where a line of interest cannot be readily resolved from a line of another element or from a molecular band.
2. Chemical interference, where the presence of another element depresses the intensity of a line because of the reduced population when some free atoms form molecules or radicals.
3. Ionization effects, where the presence of another element (usually of a low

ionization potential) produces a dramatic change in the electron density of the source, thereby shifting the ionization equilibrium.

4. Contamination from the constructive materials of the source.

In emission spectroscopy, spectral interference has always been a fact of life. However, although an ICP will excite many lines of different elements, its detectability is so excellent that truncated emission sampling (i.e. short exposure time) will often bring out strong lines before the weaker ones appear. The background in large parts of the spectrum can also be very low and, as a consequence, there is little difficulty in finding a usable line.

The kinetic temperature, which governs chemical interference, is so elevated in an ICP that this type of interference appears to be absent. The author has yet to encounter a genuine chemical matrix effect in his own

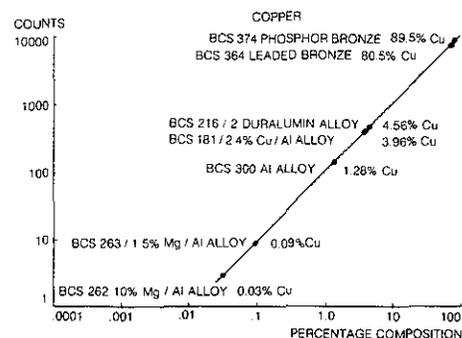


Fig 1 Log/log plot, over four and a half orders of magnitude, of intensity versus copper concentration in different matrices. The ICP is exceptionally free from matrix effects.

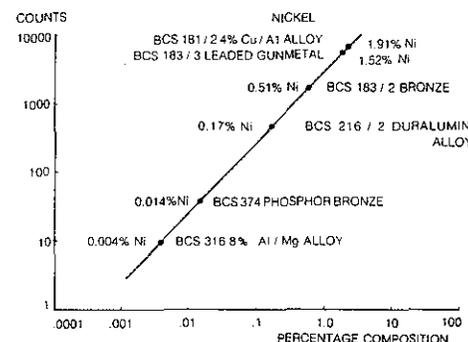


Fig 2 Log/log plot, over four orders of magnitude, of intensity versus nickel concentration in different matrices.

laboratory, although a very wide range of materials is routinely handled. (This is not quite the same as saying the method is immune to matrix errors, of course). Most certainly, with a high-power plasma, such well known effects as the depression of calcium emissions by phosphate are absent up to high concentrations.

ICPs are subject to ionization effects like those that occur when alkali metals are present in the solution. Nonetheless, these influences are weak and tend to be further reduced at high powers. The addition of roughly similar amounts of an alkali into the calibration standard, for instance, will compensate for this effect.

In our apparatus, the plasma is confined by a quartz cell and this does not contribute to the emission from the aerosol. The author knows of no instance where silicon lines, which could be due to an attack on the cell walls, have been detected.

ICPs are readily handled by technicians with no unusual operation or maintenance costs. They do tend to be more expensive to purchase than conventional sources, but this is offset by their adaptability to diverse materials and to being automated with a consequent labor cost reduction. The high precision and sensitivity attainable will be demonstrated more appropriately in a later section.

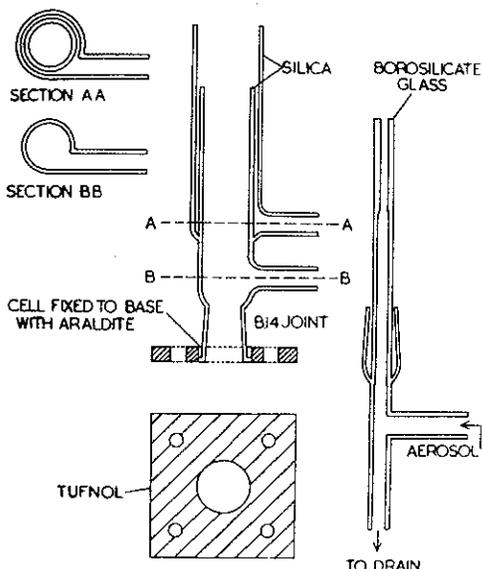


Fig 3 Plasma torch, Greenfield et al.

Design and Historical Considerations

The author's torch (Fig 3) is a veteran of many years of reliable service. Two concentric silica tubes, designed for powers of 6-7 KW in the plasma, contain the plasma, while a third, borosilicate glass, is inserted into the center to inject an aerosol through the plasma after it is formed. The work-coil of an HF generator is positioned around the top of the outer tube. To operate the torch, argon gas is fed tangentially into the inner silica tube, an HF field is applied by the work coil, and a pilot plasma is produced by a tesla coil or a graphite rod insinuated into the field. Once the gas ionizes and begins to conduct, a current is spontaneously induced, and the plasma forms. The action may be compared to a loosely coupled transformer in which the gas constitutes a one-turn secondary

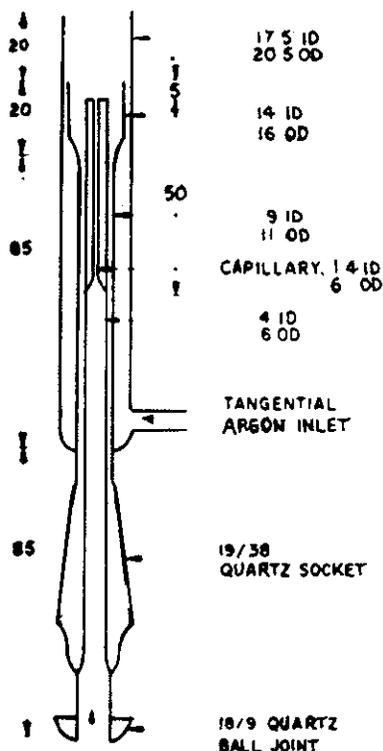


Fig 4 Plasma torch, Scott et al (12).

winding and the work-coil the primary. Additional gas, fed through the outside tube, helps the fireball assume an annular configuration. The reason for this will become apparent as we trace the development of ICPs. Fig 4 shows a torch of smaller dimensions, designed to operate at low powers around 1 KW at 27 MHz.

In 1964 we first reported (6) work with inductively coupled annular plasma and tangential gas flow as an excitation source for trace metals. Shortly afterwards, Wendt and Fassel (7) described their independent results with a plasma with laminar gas flow. Though the pioneering in HF plasma generation by Reed (8) preceded both of these studies, credit for the first investigation into ICPs probably belongs to Babat (9) who, in 1947, published a paper on electrodeless discharge in HF fields.

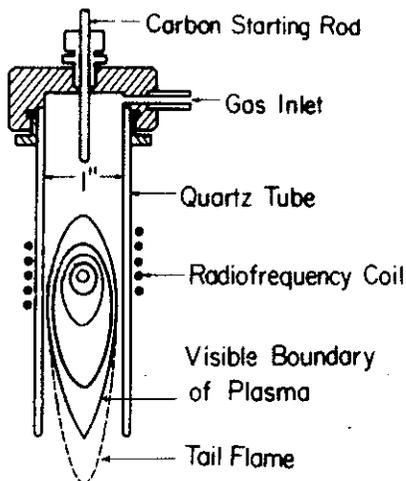


Fig 5 Reed's early ICP, torch for crystal growth where solids were injected into the plasma.

Reed operated his plasma torch (Fig 5) at atmospheric pressure with argon or argon mixtures. The apparatus consisted of a quartz tube on a brass base, provided with tangential gas entry, placed within the work-coils of a 10 KW at 4 MHz HF generator. The pilot plasma was created by a carbon rod inserted into the gas flow to produce thermal electrons by the Joule heating effect of the alternating magnetic field. This initial ionization of the argon enabled coupling to occur and a plasma to form.

In 1961, Reed (10) went on to describe another torch composed of three concentric tubes with a central powder feed originally designed for crystal growth. His paper of 1962 (11) details many of the physical properties of his plasmas and suggests their possible application as spectral sources for solids. Although he directed solid particles into the plasma, it would appear that most of the material went round the outside of the ring, forming a broad tail-flame. This effect, and the consequences of an annular plasma, warrant further discussion.

Personality of the Plasma

When the sample aerosol is allowed to combine with the working gas from which the plasma is formed, emissions from the sample atoms occur throughout the entire volume of the discharge, which takes the shape of a prolate spheroid as shown in Fig 6. This configuration results in poor detectivity since the emission per unit area of the surface is low. In addition, the presence of sample atoms within the discharge alters the electrical properties of the medium and, as a consequence, the amount of power being dissipated is also changed; this renders the plasma unstable.



Fig 6 A prolate spheroid plasma is formed when the sample gas and working gas are combined.

On the other hand, if a second stream of gas (called the coolant) is made to flow tangentially around the plasma gas stream, the shape of the spheroidal discharge is modified by a flattening of its base. This makes it easier for a third stream, containing the sample aerosol, to be injected up the axis of the plasma, further modifying the shape from a prolate spheroid to an annulus. A long, narrow, well-defined tail-flame now emerges from the fireball. This tail-flame becomes the spectroscopic source; it contains all the analyte atoms heated as they pass through the tunnel in the center of the annulus.

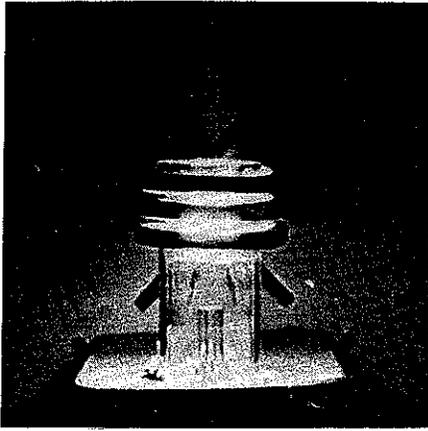


Fig 7 An annular plasma results from separate tangential introduction of a coolant gas and an axial nebulizing of aerosol containing the sample.

In principle, at least, the frequency of the HF should influence the formation of the annular plasma. When a conductor is heated by HF induction, the magnetic field generated falls to $1/e$ of its surface value in a distance known as the skin-depth, and most of the power is dissipated in this region. This skin-depth happens to be inversely proportional to the square root of the frequency, so the higher the frequency, the more power will be dissipated close to the surface and the formation of a cooler central tunnel becomes more likely. In practice, however, the design of the torch and the gas flows are of greater importance and the frequency has little effect on the size of the hole, as can be seen from Fig 8.

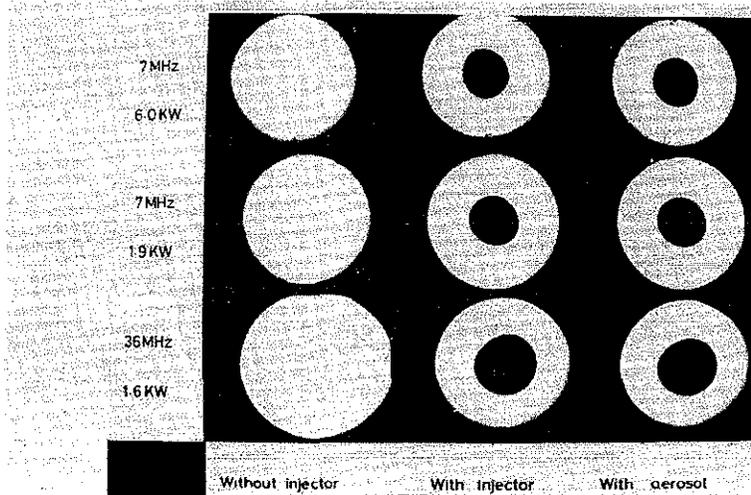


Fig 8 Showing how the frequency of the rf field has little influence on the size of the hole in the annular plasma.

The difficulties involved in injecting an aerosol into a spheroidal plasma are well known and may be explained in terms of the magnetohydrodynamic (MHD) thrust within the system. Measurements of the radial distribution of the magnetic field inside the plasma, by means of magnetic probes, have shown that it reaches a maximum near the tube walls, then decreases steadily to a low value at the center. The magnetic pressure (the tendency of the field to push a charged particle) exhibits a similar behavior. These

factors contribute to an inward radial flow of the plasma by a process called magnetic pumping. As the kinetic pressure begins to build in the center, the incoming plasma is diverted along the axis, toward the upper and lower ends of the tube, until it reaches a point where it can flow back to the boundaries. In this way, vortex rings are superimposed on the main axial flow and thermal expansion of the gas. This is shown in Fig 9.

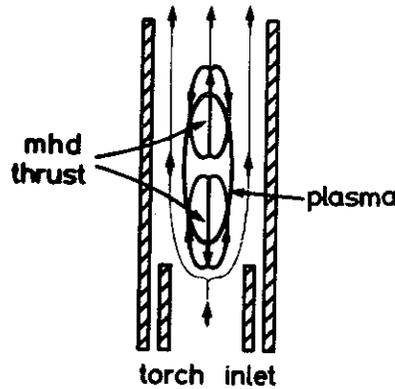


Fig 9 Showing how the MHD thrust must be overcome to form an annular plasma.

Now, in order for the injector flow to penetrate the body of the plasma, the velocity of the aerosol must exceed that of the MHD thrust; that is, the injector pressure must exceed the opposing pressure of the plasma. Once this is accomplished, the tunnel plasma is formed, the injector stream passes through the center, and the desired tail-flame results.

Representative Design of Torches

By its very shape an annular plasma has several inherent advantages. Because of the skin-depth effect, most of the power is dissipated in the outer layers where the electrical conductivity remains unaltered by contamination from sample atoms which are confined to the central tunnel. Since this power dissipation is now substantially independent of the nature and concentration of the sample, stability is greatly improved. In addition to this, while the tail-flame from a spheroidal plasma is

short, wide, and diffuse, a true tunnel plasma has a long, narrow, and sharply defined tail-flame which results in high emission per unit surface area. And this tail-flame, unlike the plasma fireball, emits very little continuum radiation, so the background is unobtrusively weak.

Power Supplies: Free Running or Crystal Controlled?

The high-frequency generator that supplies the energy to the plasma can be controlled by a crystal, so the frequency is held constant, independent of the state of the plasma; or the frequency can be made to depend on the condition of the anode circuit of which the work-coil surrounding the plasma forms a part (free-running). Since the plasma can be thought to be a one-turn secondary winding of a transformer, with the work-coil the primary, in the free-running situation, the impedance of the plasma will be seen to influence that of the anode circuit and, thereby, the frequency at which the generator oscillates.

When the plasma is running under constant conditions of power and gas flow, its impedance is remarkably stable even when different types of samples are introduced, because the samples are effectively confined to the tunnel through the center of the fireball where they are electrically screened from the work-coil. Under these circumstances, it is immaterial which type of control is chosen for the generator. However, should the impedance of the plasma change, for any reason, the coupling between the plasma and the coil also changes, and the frequency to which the anode is tuned alters. For a free-running plasma, to a first approximation, all that happens is that the oscillator adjusts itself automatically to this new frequency. With a crystal-controlled generator, the frequency cannot alter and so a large power loss occurs until the circuit can be retuned. Similarly, retuning has to be carried out after the discharge has begun since there is a vast difference in impedance between a plasma and no plasma.

Although the final judgment has yet to be rendered in favor of either free-running or crystal-controlled ICP, both must, of course, conform to governmental regulations with respect to HF leakage.

How Much Power!

While several groups report that the maximum values of signal to background seem to occur at low powers (typically less than 1 KW), others have claimed that, with the exception of very easily excited elements such as the alkali metals, the best values are found at high powers of around 6 KW. Under similar circumstances, we have found that detectability increases with power. Of course, factors other than power influence qualitative estimates of just what is advantageous. These include the choice of nitrogen or argon as coolant (nitrogen requires high power), the size of the torch, horizontal or vertical slits, and stray light in the system.

Yet, a distinct advantage of high power is the ease of operation it provides. With it, the creation of the discharge is simplified as is the formation of the injection tunnel and the automatic operation of the source in day-to-day analyses. It also enables the

torch to run sample solutions of any kind, including those of high acid concentrations, without desolvation and all its attendant problems. Since high power is expected to give a higher gas temperature, there should be greater freedom from interference due to the formation of refractory species.

If the excitation mechanism happens to be thermal, high power should facilitate meaningful results from elements which are difficult to excite. However, as we shall see, low power sources behave more efficiently than might be expected for such lines, perhaps because of excitations by inelastic collisions with argon metastables, so the advantage of high power in this instance may be small.

Molecules and radicals give rise to band spectra which can be the source of high and troublesome background. An example of this is the Swan bands which occur when carbonaceous material is present. The potential for attenuating these bands in the 500 nm region with high power is illustrated in Fig 10.

Local Thermodynamic Equilibrium in Plasmas

The word "temperature" has popped up a number of times already and it is necessary that we consider what it means when it is applied to characterize a plasma and what effect it has in detectivity. Quite briefly, the energy distribution of particles is dependent on the absolute temperature. Clearly, if there are a number of different kinds of particles in a certain volume, it is possible to have a number of different distributions and, consequently, a similar number of parameters are needed to define each of these distributions. In a monoatomic gas, for instance, there may be four kinds of temperatures—two to describe the kinetic energy distributions of the electrons and gas particles (including the atoms and ions), another to describe the relative populations of the energy levels of a given substance, and the last to characterize ionization equilibria. When all these parameters have the same values, the system is said to be in a state of local thermodynamic equilibrium (LTE).

Considerable interest has been generated by the question of whether ICPs are in LTE or not and just what effect high power has in this situation. Investigations carried out in the 1960s led Raizer (13) to state that "the general result of many investigations is that at a power the order of several or a dozen KW, the temperature of the argon plasma reaches 9000-10,000°K. Measurements of the electron density have shown that the state of the plasma at atmospheric pressure is close to thermodynamic equilibrium."

But the matter was not allowed to rest here for Apsit (14) went on to declare that, while excitation and electron temperatures were the same, the gas temperature was considerably lower. The differences observed between these temperatures ranged from 2500°K at 1 KW to 1500°K at 10 KW. It is probable that these figures for power are only nominal and that half the values would be dissipated in the plasma. In 1970, Kleinman (15) reported that, in contrast to high power plasmas, his plasma, with a 270 W generator, was far from equilibrium. Doppler broadening

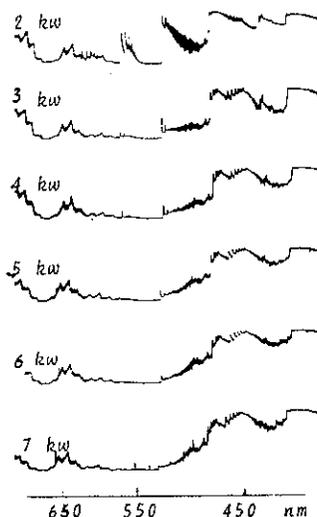


Fig 10 Showing the removal of Swan bands by increasing the power in the plasma.

measurements yielded a gas temperature of about 2000°K, compared with an electron temperature of over 11,000°K obtained from observations in the recombination continuum. However, Britske and Sukach (16) found greater emission from levels with high excitation energy than would normally have been expected from the comparatively low temperature in their plasma. In 1973, Alder and Mermet (17) made a similar observation. Though argon emission and C₂ rotational analysis indicated no deviation from LTE, they were evidently puzzled by the appearance of lines which should have been very difficult to excite. One example of this was an ion line of Br where the ionization energy is 11.8 eV, yet emission was observed from a level 14.2 eV above the ion ground state. It was then suggested that a two-step process may have been responsible for the phenomenon. Though this is allowed in LTE, the probability for the occurrence would be extremely low. So, once again, there appears to be more excitation of high levels than might be anticipated from thermal processes.

Mermet (18), in 1975, reported concordant temperatures of around 6000°K obtained from Ar, Fe, and Cr. Here the electron density from Stark broadening and from the emission of different ionization states of Mg was found to be about 1.8×10^{13} per ml, corresponding to an ionization temperature of about 8600°K. Although the calibrations were plagued by uncertainties in the transition probabilities, it was likely that this difference in temperatures is genuine and that his source was non-thermal.

About the same time, Mermet and Robin (19) undertook an investigation of ionization interference based on Saha's Law which relates electron, ion, and neutral atomic densities to a temperature related constant:

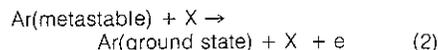
$$C(T) = (n_{A^+})(n_e) / (n_A) \quad (1)$$

where A is the atom, A⁺ the ion, e the electron.

Clearly, if at a given temperature an easily ionized element like sodium is added to a plasma, the electron density would be expected to increase so that the ionization equilibrium for another element present in the medium will move toward the neutral side; that is, the ratio between ionic and atomic species must decrease, leading to a relative suppression of ionic lines and enhancement of the atomic. The effect, however, is not universally valid.

Mermet and Robin calculated that there should be only a small change for phosphorus, but much more for chromium. Nevertheless, when the experiment was performed, the results showed that exactly the opposite was true. To explore the reason for this, they went on to study the effect of sodium on the ratios of a neutral to an ionic line (which indicates the way the electron density is changing) and of two ionic lines (indicating temperature variation). Neither of these ratios altered significantly with the addition of sodium, and this leads to the conclusion that both electron density and temperature remained relatively constant. This failure of Saha's Law is consistent with a system not in LTE.

To explain the apparent breakdown of LTE in his source, Mermet suggested possible collisional ionization of analyte atoms by the excited argon atoms forming the plasma. If this process occurred via the ordinary excited states of argon, there would be no necessity for deviation from LTE. Argon, however, possesses metastable states and this can make a tremendous difference. For the latter situation, the reaction proceeds according to the equation



and is known as Penning ionization. (Here, the densities of electron and ionized analyte atoms are both increased.) Metastable states are those levels which can decay radiatively only by means of "forbidden" transitions where the probability of transition is extremely small when compared with those obeying normal selection rules. These states must then have very long lifetimes—about 10^{-3} seconds in contrast to the 10^{-8} second duration of normal excited states. If the interpretation is correct, the chance for atomic collisions between sample atoms and excited argon atoms may be high, and metastable levels overpopulated relative to normal levels. This overpopulation implies a deviation from LTE.

Mermet observed weak emissions from levels between 20 and 30 eV from ionized S, Cl, Br, Al, and doubly ionized Ti. In practice, the relevant metastable levels of argon are those at 11.55 and 11.62 eV. Thus, atoms with ionization energies exceeding these values would not be expected to be susceptible to Penning ionization from neutral argon. To counter this objection, Mermet points out that ionized argon has a metastable level at 32.16 eV which could account for these emissions.

Whatever the particular mechanism involved, there appears to be considerable evidence that some low power plasmas are not in LTE. For high power plasmas, as we have seen, there is a good indication that at least the central portion is in LTE. Since several investigators have shown that ionization and excitation temperatures agree, there are no grounds for believing that an excess electron density occurs in high power plasmas despite Mermet's experiments. Mermet does not unambiguously define the power in his plasma. Though his generator is rated at 6 KW, he does not state whether it was operating at maximum capacity and, in any case, the amount actually dissipated in the plasma is likely to be only 50% of the nominal figure. Thus, if we think of a high power plasma as one with 5-6 KW in the plasma as opposed to less than half of this value for low power plasmas, we may conclude that the evidence suggests high power plasmas are in LTE.

Instrumentation

Quite understandably, the recently kindled interest in ICP spectroscopy has also spread to manufacturers of torches, power supplies, spectrometers, direct readers, and attendant devices. Yet, since any discussion of equipment now available would probably be obsolete by the time this article is published, we shall describe only our laboratory instrumentation which, although now outdated, remains the core of a productive, reliable analytic facility.

The torch in Fig 3 is coupled to a Radyne Delapena generator, model RD 150/H, which has a power output of 15 KW at a frequency of 7 MHz. A nebulizer taken from a Unicam S.P. 900 Mark I flame photometer is fed samples by a modified Technicon Mk. 1 autosampler. The autosampler also controls a Hilger & Watts F.A. 19 Polychromator which supplies paper-tape output to an off-line computer.

Other workers in the field may have selected different systems, but it must be appreciated that the equipment listed above has been servicing the analyses of real samples over the last ten years—and continues to do so today. Our system operates in an analytical problem-solving laboratory that must satisfy the demands of a number of divisions of the company whose samples cover a wide variety of materials. Oil, blood, urine, dusts, waters, effluents, organic and inorganic chemicals, steels, minerals, ores—all are grist to this particular mill! So it seems natural that, with over 100,000 analyses under his belt, the author is sometimes puzzled at the way some workers continue to mull over the potential of the inductively coupled plasma as an excitation source. As far as he is concerned, it is a firmly established technique!

Little is involved in putting the system to practice, and this can be done by relatively unskilled personnel. After setup, no supervision is required so the analyst is free to concentrate on sample preparation. The cost of the equipment, although magnified by the inclusion of the direct reading spectrometer, is more than offset by the resultant saving in manpower. In the

author's laboratory, for instance, the plasma source has replaced two conventional source units which do not possess its precision and freedom from matrix effects, and the total system has rendered superfluous two atomic absorption spectrometers which do not share its simultaneous multi-element facility.

To give the reader an idea of the true detectivity of this system, Table 1 contains a list of detection limits which should be of particular interest to environmentalists. Because the values were determined simultaneously and, therefore, necessitated some compromises in experimental conditions, detection limits one and two orders of magnitude lower can be expected for single elements under optimum conditions. Other workers have reported still lower values. For those who may consider the precision and accuracy at the one part per million levels to be a better reflection of the system capability, we refer to Table 2.

In these determinations, the normal intake rate of the nebulizer was 2.5 ml per minute and, since the average exposure lasted about 10 seconds, some 0.4 ml of solution were expended. However, the author, in collaboration with his colleagues, has developed a technique that permits analysis at the ppm level with only 1 to 25 microliters of solution. Table 3 illustrates the kind of precision that can be obtained in this way.

Future Developments

It is quite clear that ICP has taken root. Though it may never supplant atomic absorption, it will prove to be a tenacious rival. For automatic, simultaneous analyses especially, plasma spectrometry, while initially more expensive, is a substantial labor-saver. And, as more systems with scanning monochromators come on the market, further inroads will be made into small atomic absorption laboratories now providing analyses with few elements required.

The present controversy concerning which power levels are best for plasma spectroscopy may well have caused cautious analysts to hesitate at purchasing an ICP system; but this disparity will probably be resolved in the near future. It is difficult to imagine that anything revolutionary will occur from research into new torch designs; most problems have been resolved by present practitioners. The optimum choice of gases in which to form plasmas however, is likely to be a fruitful area for experimentalists.

The fly in the ICP ointment turns out to be sample introduction. Both pneumatic and ultrasonic nebulizers are far from ideal. Lacking precision and convenience, they

TABLE 1
Simultaneous Multi-Element Detection Limit Using Compromise Conditions.

ELEMENT	DETECTION LIMIT Pneumatic Nebulizer (without de-solvation) ng/ml (ppb)
Tin	100
Nickel	10
Sodium	30
Aluminium	10
Cadmium	100
Iron	40
Cobalt	20
Boron	100
Zinc	100
Lead	70
Calcium	10
Barium	1
Magnesium	2
Strontium	20
Manganese	3
Copper	10
Vanadium	9
Molybdenum	20
Titanium	30
Silicon	30
Chromium	20

The detection limit is calculated as that concentration of the element that will give a net signal intensity which is twice the standard deviation of the background.

TABLE 2
Automatic, simultaneous multi-element analysis obtained on a 1 ppm solution.

	CONC. (PPM)	C OF V
Vanadium	1.00	2.4%
Aluminium	0.98	2.9%
Cobalt	0.95	5.2%
Calcium	0.96	3.3%
Barium	0.98	3.2%
Magnesium	0.99	2.4%
Manganese	0.99	3.4%
Copper	0.99	2.1%
Sodium	0.93	4.0%
Nickel	1.00	8.0%
Strontium	0.99	6.7%

C. of V. of 12 analyses of one solution containing 11 elements. Time for completion 34 minutes.

are prey to blockage when solutions have a high solute content. Running flow rates that are greater than those for which the nebulizers were designed often overcome this latter failing, though it also necessitates a larger torch and, consequently, more power. Progress will continue to erode the shortcomings of present injection methods, but, as always, the real breakthrough will have to wait for fresh ideas to focus on the subject. Electric fields applied to this could stand further exploration. The introduction of solids is another fertile area for research and a primary plasma or laser to volatilize the sample prior to injecting the vapor into the fireball are possible approaches.

TABLE 3
Precision of the Method When Using μ l Samples.

COMPOUND	SOLUTION conc'n. (μ g/ml)	SAMPLE size (μ l)	WT. OF Ba (ng)	C.O.V.*
Ba(ClO ₄) ₂	1	25	25	2.9
	0.1	10	1	4.6

**10 Determinations were done at each level.*

Still, the most stimulating developments will probably arise out of new designs for spectrometers to couple to an ICP. Two particular systems, the Image Dissecting Echelle Spectrometer (IDES) and the Television Direct Reading Spectrometer (TVDRS), suggest some concept of what lies waiting around the next corner.

The IDES (20) consists of a stigmatic coma-compensated echelle spectrograph that focuses a wide spectral range on the photocathode of an image dissector tube. Read-off of the spectrum, involving wavelength selection and intensity measurements through single photon counting, is carried out by a computer.

The TVDRS (21) has four essential components including an echelle grating spectrograph to disperse light from the source; a proximity focus image intensifier to convert ultraviolet radiation to visible; a random access digital television camera to measure the intensities of many wavelengths simultaneously; and a dedicated minicomputer for control, data processing, and output.

Finally a word or two should be said about resonance spectrometers (22), in which an

atomic vapor is produced in a chamber by cathodic sputtering. Radiation from a plasma might excite some of the atoms in this lamp and the radiation would be emitted in all directions, some falling onto a photomultiplier. Each of these lamps would be a specific detector for its own element.

The author has tried to indicate the practicability of the ICP and suggest the potential for its growth. Truly, the future is never revealed to us until it becomes the present, yet it seems certain that ICP will be a part of it.

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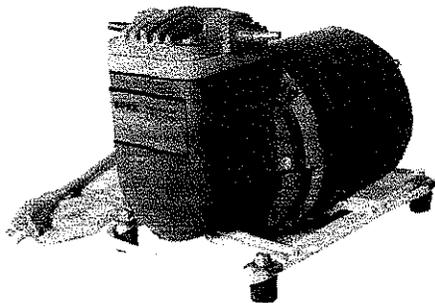
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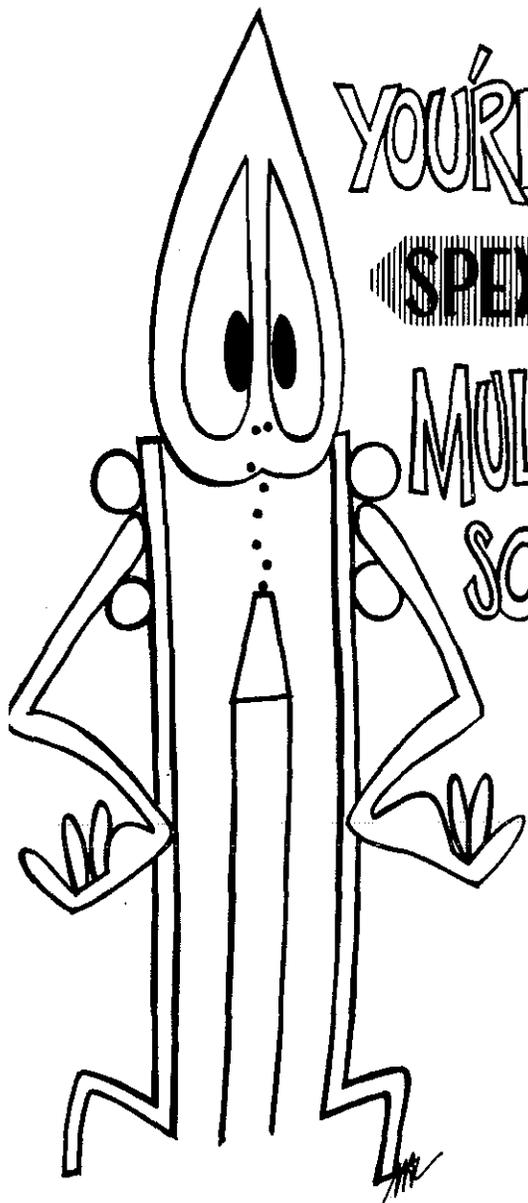
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