PLASMA SPECTROSCOPY COMES OF AGE

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Abstract - The attributes of I.C.P.-O.E.S. are discussed. It is concluded
that the sensitivity and precision of the technique is high and the effect
of a number of interferences small. A definitive answer to the question of
power requirements is precluded by a lack of reliable experimental data.

Eighteen years ago, experiments were started which were to lead to the production of an
exciting new source, an inductively coupled annular plasma, which in turn led to the
renaissance of emission spectroscopy; plasma spectroscopy as it became known.

Today there are some six to seven hundred of these systems in use throughout the world
and their number is growing fast.   Truly the technique of Plasma Spectroscopy can be
said to have achieved respectability.   It has come of age.

It is interesting to look at the circles to which this once precocious infant is now
admitted. In the U.K. plasma systems are in daily use in such prestigious establishments
as The Laboratory of the Government Chemist, The Institute of Geological Sciences,
Metropolitan Police Laboratories, Water Research Centre, Macauley Institute and the
U.K.A.E.A.   Users in the U.S.A. include, The National Bureau of Standards, The
Aerospace Corporation and The Montana Bureau of Mines: in Sweden, The Geological Survey
and The Swedish Institute for Metal Research: in Israel, the Nuclear Research Centre,
and in Germany, The Spectrochemical Institute at Dortmund: South Africa makes extensive
use of I.C.P's in The National Institute for Metallurgy and at C.S.R.I.

An equally prestigious list can be cited for industry.   In the U.K. there are The
British Steel Corporation, British Rail at Derby, British Drug Houses at Poole and, of
course, Albright & Wilson at Oldbury.   In Germany we have the Hoesch Hüttenwerke A.G.
I could continue in this vein, but there is no need; the list of companies is long.

Equally long is the list of applications.   I.C.P.-O.E.S. has been used to analyse
geological samples, ferrous and non-ferrous alloys, precious metals and rare earths,
marine sediments, organisms and coastal sea water, oils for fuels, foodstuffs, urine,
beer and spirits, animal feeds, animal wastes, clinical samples, forensic samples such as
tissue, glass and steel – again I could go on and on, but I think I have made my point;
any material which can be taken into solution can be analysed for a large number of
elements by I.C.P.-O.E.S.   In fact detection limits have been determined by I.C.P. for
nearly 80 elements and whilst on the subject of detection limits, it might be interesting
to compare those obtained by I.C.P.-O.E.S. with those obtained by A.A.

In the early days of atomic absorption it was pointed out that there are always more
atoms in the ground state ready to absorb than there are in an excited energy level
ready to emit.   Absorption techniques therefore might be expected to be more sensitive,
and at ordinary temperatures so much so that, regardless of the noise characteristics,
the detection limits in absorption would always be much better than in emission.
However, a large absorption signal depends not only on the number of atoms ready to
absorb but also on the intensity of the incident beam which is to be absorbed.   You
cannot absorb more than is there.   The dependence on the incident beam destroys the
simplicity and generality of the argument on sensitivity and hence on detection limit,
and indeed it was found in practice that for many elements, the detection limits found
in flame atomic absorption were very similar to those found in flame emission.   This is
illustrated in Fig. 1.

Footnote: A.A. = Atomic Adsorption, I.C.P. = Inductively Coupled Plasma, O.E.S. = Optical
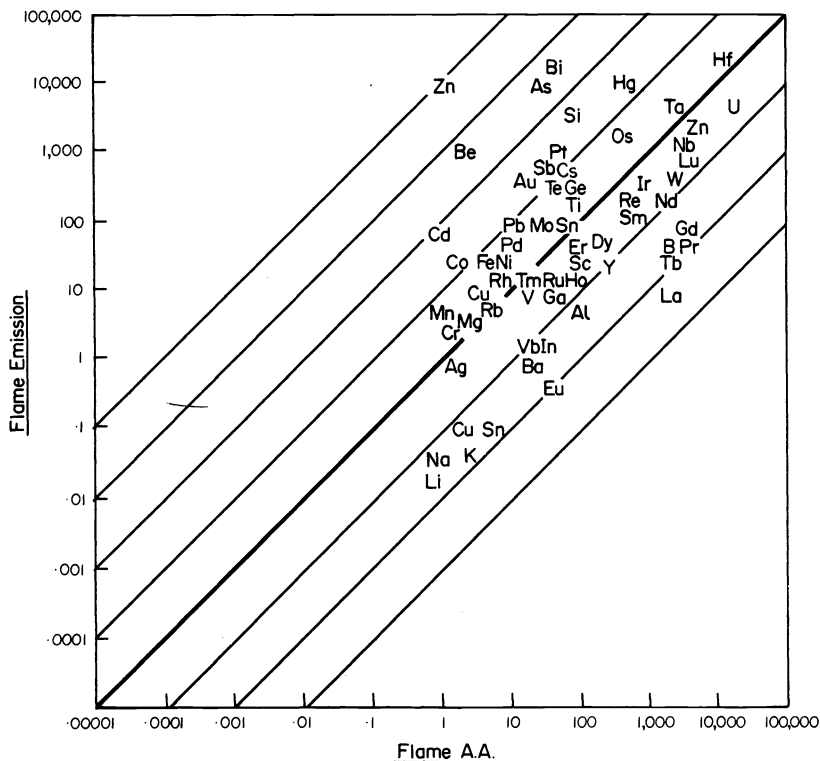Emissions Spectrometry.

Fig.1. Comparison of detection limits (ppb) for flame AA and flame emission.

Here I have plotted on log/log paper the detection limits published by Christian and Feldman (1) in 1971, for the two techniques. The principal diagonal shows where the two detection limits are equal. Those elements above this line have a greater, that is worse, detection limit in flame emission than in flame absorption, while those below the line have a smaller, that is better, detection limit in emission than in absorption. For the 66 elements compared, 29 have lower limits in A.A.,34 have lower limits in emission and 3 are identical. The faint lines are contours representing factors of ten, so that zinc, for instance, near the top of the slide and lying on the fourth contour above the locus of equality, has therefore a detection limit in emission 10^4 times that in absorption. Similarly for Se, again at the top of the slide and lying on the third contour, the ratio is 10^3. We can sum up the data on this slide by saying that the detection limits are better for more elements in emission, but of the elements which are better in absorption, some are very much better.

Many A.A. practitioners seem to think that those obtained in plasma emission are also similar. This is not so. Recent promotional literature from a prominent instrument manufacturer includes a convenient table of A.A. detection limits which are similar, with perhaps a modest overall improvement to those published by Christian and Feldman (1) in 1971 and by Berman (2) in 1975. I have compared these with ICP detection limits taken from Boumans and Barnes' 1975 collection (3). Fig. 2 shows the comparison.
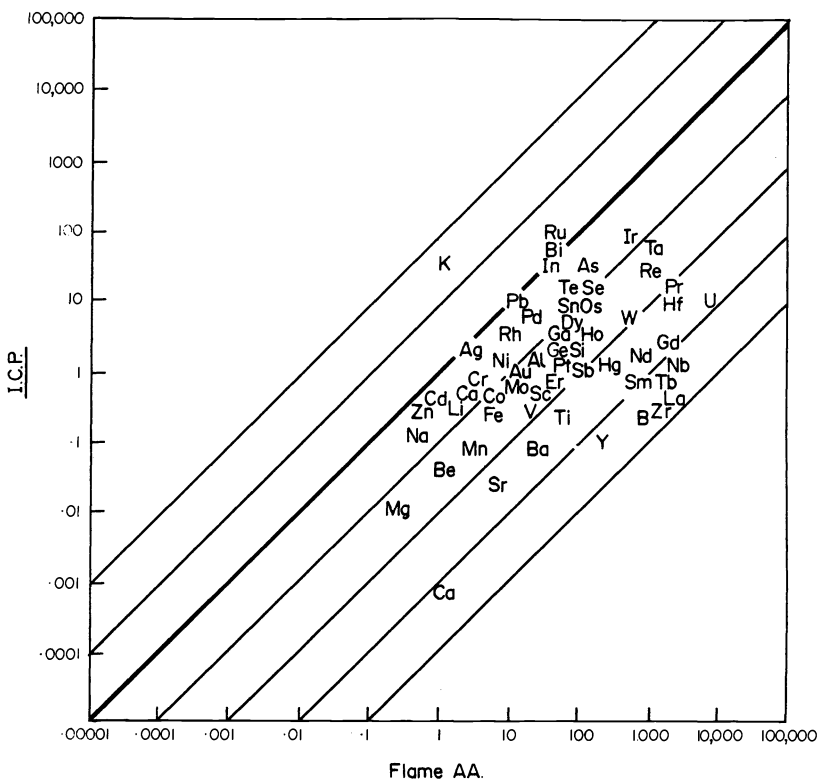
Fig.2.   Comparison of detection limits (ppb) for flame AA
and ICP emission.

Of the 59 elements compared, potassium is notably better in absorption with a factor of
30, ruthenium and bismuth just better, with factors of 1.5 and 1.25, and indium, lead
and silver are equal.   The other 53 elements are all better in emission with factors
going up to 2,000 for calcium and 5,000 for boron.   You may have thought that on my
previous slide the two techniques of flame emission and flame A.A. were more or less
equally balanced.   It is now apparent on this slide that the use of a plasma source in
emission has swung the balance greatly in favour of emission.

At one time, when flame emission was being compared with flame absorption, it was thought
that lines with short wavelengths might give better results in absorption and those with
long wavelengths, in emission.   This was because, for lines whose lower energy level is
the ground state, the energy of the upper level is proportional to $1/\lambda$.   Thus short
wavelength lines are more difficult to excite and their sensitivities in emission might be
low.   This does not seem to be a valid argument in plasma emission since the worst line
for the ICP is potassium 7665A.   The reason is almost certainly that for very easily
excited lines the plasma is too hot.   There can be no doubt that for the great majority
of cases plasma spectrometry gives lower detection limits than flame AA, and by factors
that are often large.

However, when AA is used with non-flame atomisation, exceedingly low detection limits can
be obtained.   In methods of this kind discrete samples are used and the signal measured
is a transient as distinct from the more common type of method we have been considering
where a solution is continuously fed to the source and a steady state signal is measured.
For this the appropriate unit for detection limit is concentration, while for discrete
sampling the mass of analyte is more commonly used.   In comparisons between the two
types, some assumption must be made about the amount of sample used.   Frequently a sample
volume of 1 ml. is postulated for solution analysis, so that an absolute detection limit
of 10^{-9} g would correspond to detection limit of 10^{-9} g/ml, that is a concentration of
1 nanogram/millilitre.

Considerations of this kind make exact comparisons difficult; however, data due to L'vov
(4) indicate that detection limits for A.A. with graphite tube atomisation are much
superior to those obtained with conventional flame atomisation.   The factors by which
they are improved range from 80 (for potassium) to 2 million (for silicon), with most in
the range 10^3–10^5.   A comparison with ICP spectrometry with conventional nebulisation is
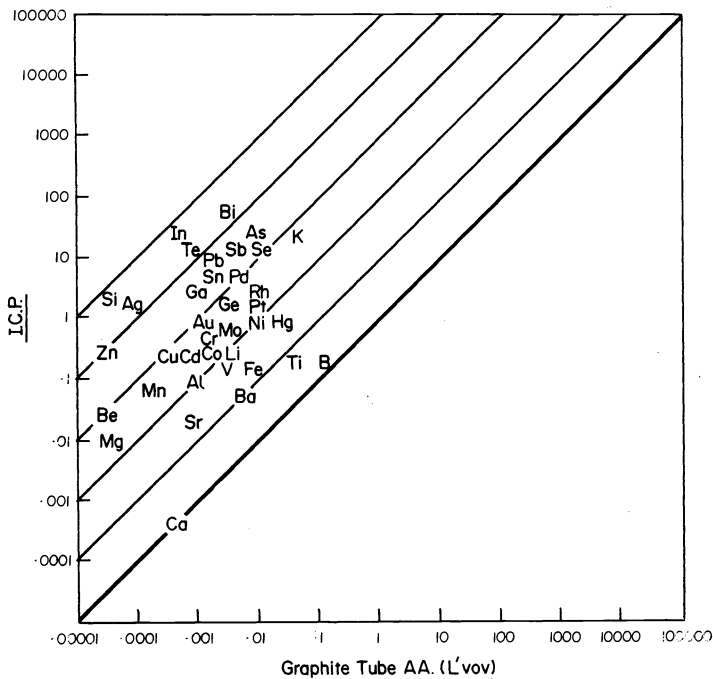shown in Fig. 3.

Fig.3.   Comparison of detection limits (ppb) for graphite tube AA
         and conventional ICP emission.

The swing to A.A. is impressive.   However it is likely that L'vov's very low limits would
be difficult to obtain in a routine analytical laboratory and the careful work of
Chakrabarti (5) confirms this.   Using a commercially available carbon rod atomiser, he
found detection limits typically an order of magnitude higher than L'vov's.

Electrothermal atomisation can also be applied to plasma spectrometry, and was first so
applied by Kleinmann and Svoboda (6), who used a graphite disc.   Nixon, Fassel and
Knisely (7) used a tantalum filament to vaporise their samples and for 100 μl samples
reported detection limits which are smaller than the present-day values for continuous
pneumatic nebulisation;   when their values are transformed to correspond to 1 ml samples,
the factors by which they are superior range from 2 to 2000, most being of the order of
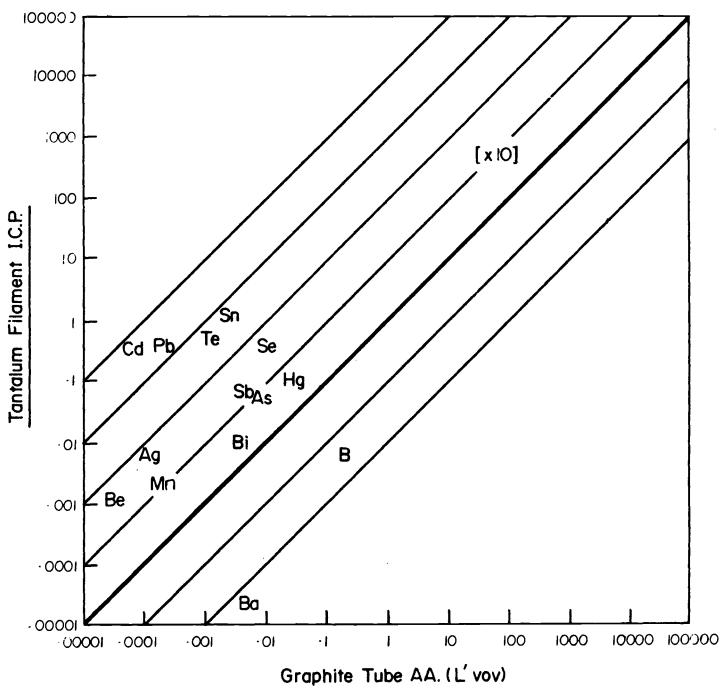tens.   In Fig.4 I compare these values with L'vov's for graphite tube atomisation.

Fig.4.   Comparison of detection limits (ppb) for graphite tube AA
and tantalum filament ICP emission.

They are mostly rather worse, although if we apply Chakrabarti's factor of 10 to L'vov's values (which would effectively make the contour marked X 10 the locus of equality) there is little to choose.   Kirkbright's school (8) used a graphite rod for vaporisation and Fig.5 compares their results with L'vov's values.
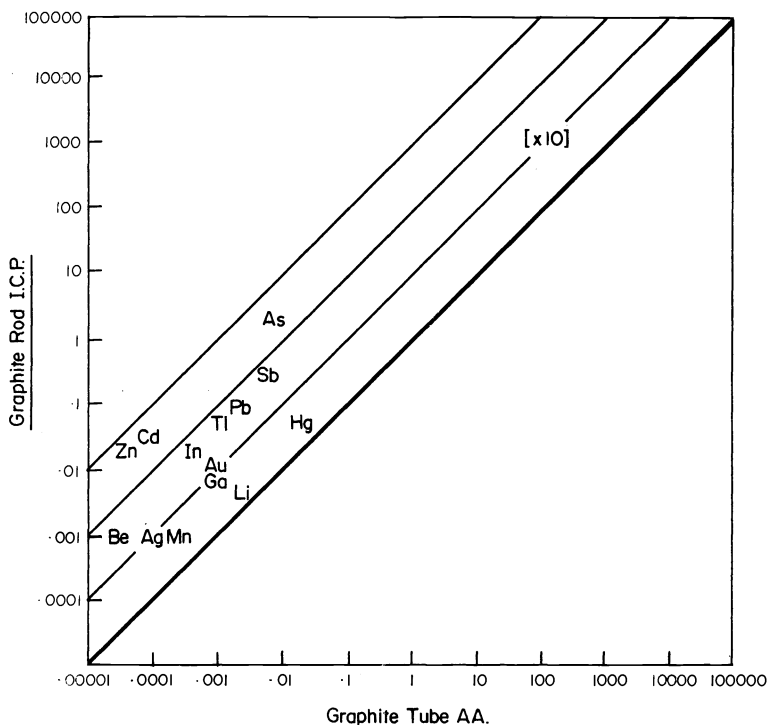

Fig.5.   Comparison of detection limits (ppb) for graphite tube AA and graphite rod ICP emission.

Again, if Chakrabarti's factor of 10 is applied there is not a great deal to choose. Actually this comparison is rather unfair to Kirkbright's results: as I mentioned earlier, if one is comparing results from transient signals with those from steady-state signals, one has to make an assumption about the volume of sample used when a solution is fed continuously to the excitation source.   Commonly the value taken is 1 ml and this has been done here.   This disguises the fact that Kirkbright was using 10 $\mu\ell$ samples and Fassel 100 $\mu\ell$ samples, so that in absolute terms, that is with the detection limit in grams, Kirkbright's results are in most cases superior to Fassel's.

Kirkbright also reported (9) that for elements which form refractory carbides or oxides, and which are therefore difficult to remove completely from the atomiser, the detection limit is much improved, typically by a factor of one or two orders of magnitude, if a small quantity of a halocarbon is mixed with the argon which carries the sample from the atomiser.   The mechanism postulated for this is the preferential formation of halides which precludes the possibility of the formation of carbides at high temperatures. However, since similar techniques are applicable to A.A. as well, this should not be thought of as necessarily favouring the I.C.P.

Recently there have been two reports, by Salin and Horlick (10) and by Ohls and Sommer (11), of a technique where the sample is placed in a graphite cup which is then inserted into the plasma.   An improvement in the detection limit of two orders of magnitude is reported by Ohls.   This, with Fassel's and Kirkbright's results, gives us reason for expecting the improvements in detection limits when electrothermal vaporisation is used with an ICP to result in values which may well be comparable with those obtained in practical applications of graphite furnace A.A.

Another technique used in A.A. to improve the detection limits of the set of difficult elements arsenic, antimony, bismuth, selenium, tellurium, germanium and tin, is to convert the analyte element to its gaseous hydride.   When the sample is introduced as a gas rather than as a solution requiring to be nebulised, the large losses associated with aerosol formation are eliminated and so a much larger fraction of the analyte is useful. This technique has been used in plasma emission spectrometry also, and detection limits of 1 ppb or better have been reported (12).   In Fig.6 you will see that the values for the two techniques are similar, the score being 3-2 in favour of the I.C.P. with two draws.
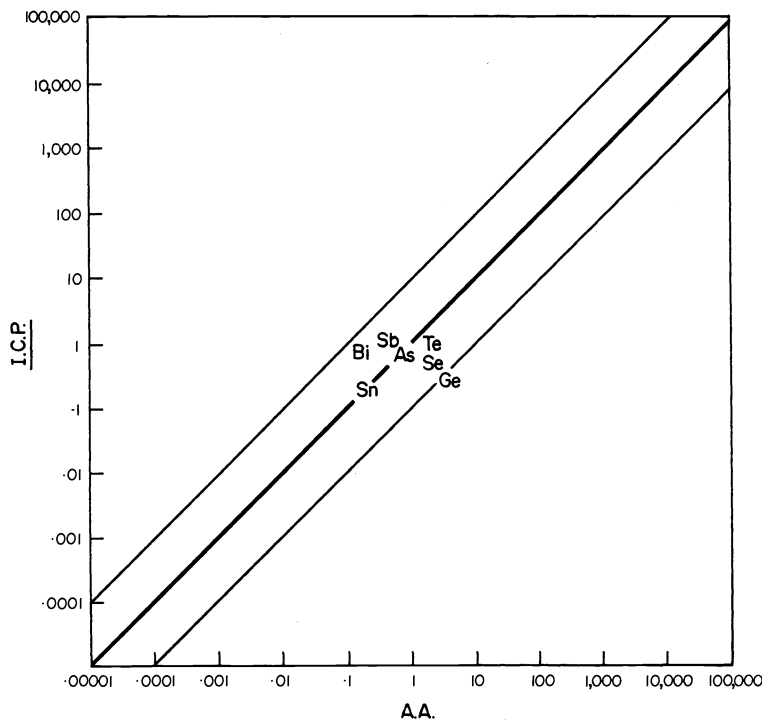
Fig.6.   Comparison of detection limits (ppb) for A.A. and I.C.P.
emission, each with sample as hydride.

Hydrogen, water vapour and carbon dioxide are produced as by-products of the hydride
formation and some plasmas have inadequate power to cope with these.   Systems have been
designed to eliminate these by-products, and at the same time to collect the hydride and
feed it to the plasma as a concentrated plug.   With such a system an improvement in the
detection limit for arsenic by two orders of magnitude has been reported (13).   Without
playing the numbers game too hard, I think it is probably fair to say that detection
limits for ICP and AA are similar when hydride generation is used.

When I read of detection limits of fractions of a ppb, I sometimes wonder how meaningful
these small numbers are in practice.   There are two ways of looking at this.   The
estimated population of the world in 1975 was 4×10^9, so that each of us represents $1/4$
ppb of the world population, in terms of heads.   (No doubt if we were interested in
concentrations in terms of weight, my contribution would be a little higher).   In any
case you might think that a visitor from outer space, searching for traces of Greenfield,
might think himself very lucky if he found me at all.   The other view depends on the very
large numbers of atoms involved.   In a gas at room temperature there are about 10^{19}
particles per ml, so that 1 ppb will correspond to 10^{10} particles in a 1 ml sample.   Thus
if the world's population is atomised (as it may well be) then given time for the system
to come to equilibrium, by mixing, it is exceedingly likely that a few atoms of me may be
found after all.   Although considerations of this kind support the respectability of very
low detection limits, sometimes one may enquire how generally useful these are in
practical analysis.

In April 1978 there was an ICP conference at Noordvijk in the Netherlands, and I was
asked to introduce a session on "Analytical Performance - Limits of Detection, Precision
and Stability".   I opened my comments by saying, perhaps rather abrasively, that "the
present league table of detection limits must be extremely valuable to those people who
spend their lives analysing distilled water".   I then went on to suggest a different
approach, namely to carry out detection limit determinations in a variety of matrices,
which were to be chosen so as to be likely to introduce difficulties of different kinds.
I suggested a 10% solution of NaCl to start with.   With such a solution, many nebulisers,
run under conventional conditions, will block up.   If so the solution must be diluted
by a factor x say, and when the detection limit of a trace element is determined in the
diluted solution, it must be multiplied by this factor x to give a true value of the
detection limit in the 10% solution.   Thus if a solution has to be diluted for any
reason, the detection limit will suffer compared with the idealised case of a dilute
aqueous solution requiring no dilution.

I also suggested using a 10% solution of CaCO$_3$ as a matrix, the idea being to test how detection limits depend on a high level of stray light.   I also suggested solutions of iron or chromium or nickel so that problems of spectral interference could be looked at. Finally I suggested a matrix of olive oil, knowing that organic compounds sometimes cause undesirable effects.

These suggestions were made because it seemed to me that the marvellous values of detection limit which were appearing in the literature were becoming ends in themselves and that the true objective of spectro-chemical analysis was becoming almost forgotten.   This objective is, of course, the analysis of samples of interest to the client.

With this in mind, let me turn to a topic that undoubtedly is of major importance in any kind of chemical analysis, namely precision.   While there are laboratories in which the estimation of ultratrace quantities with moderate or poor precision is of importance, it seems to me that the determination with high precision of quite high concentrations is a problem of much wider application.   Think, for instance, of assay determinations of costly metals in ores.

Many workers have found by experiment on ICP systems that the uncertainty in a measurement, expressed as its standard deviation, is proportional to the magnitude of the signal, so that a constant relative standard deviation (or RSD) is obtained over a wide range.   This is found not only if the signal is varied by varying the concentration of analyte, but also if the integration time is varied, with the surprising conclusion that, provided the signal is not ridiculously small, a short integration gives as precise a value as a long one.   I do not wish to elaborate this point here except to say that it is probably due to the signal drifting rather than being scattered randomly about a mean.   However the result that the RSD of the gross signal is constant can be used quite simply to relate the RSD of the net signal to the signal to background ratio.   In Fig.7 I show the RSD of the net signal, which is often also the RSD of the analysis, as a function of the signal to background ratio x/b, with the assumption that the gross signal has a constant RSD of 2%.
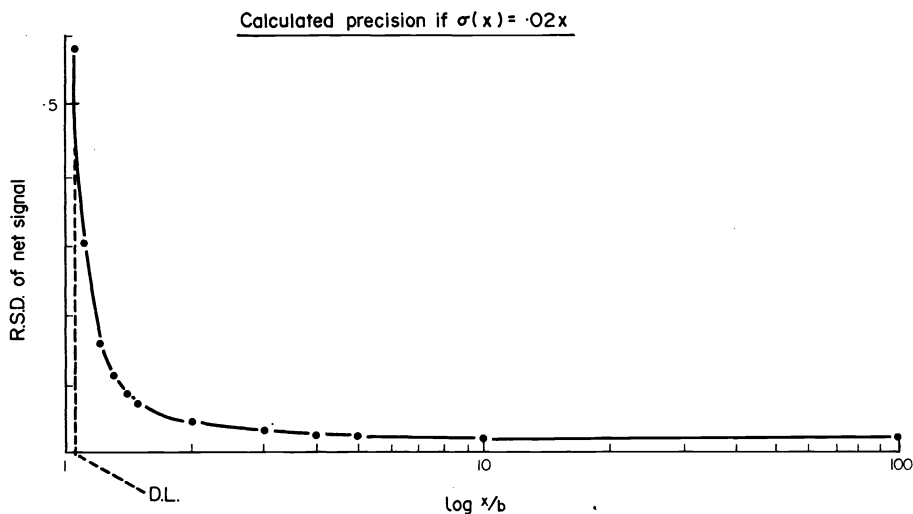

Fig.7.   Relative standard deviation of net signal (x-b) function of x/b.   It is assumed that RSD of x is 2%.

When the signal to background ratio is much greater than 1 the RSD of the analysis approaches 2%; as the ratio approaches 1, the RSD increases rapidly until when the ratio is 1, the RSD goes to infinity since here the net signal is zero, the gross signal consisting entirely of background.   It is not difficult to show that if the detection limit is defined as the concentration corresponding to a net signal which is $2\sqrt{2}$ times the standard deviation of the background, it corresponds to an RSD of 50% as shown on the slide.

Now for some purposes an RSD of 50% is fine, although some people would need convincing of this. For instance if a specification demands less than 10 ppb of an element and it is determined as 5 ppb, the chances of it genuinely passing are 19 out of 20, which may be adequate. In other circumstances such poor precision might be intolerable.

I used the value of 2% RSD in the calculations illustrated in the last slide because for some years this was a typical value obtainable at concentrations well above the detection limit. For the majority of purposes this precision is quite adequate, but not for assay work. I have mentioned that increased precision is not obtainable by increasing the integration time, and unless the time scale of the drift is taken into account, replicate measurements do not help either. Thus the way to achieve higher precision is to take steps to reduce the 2% RSD of the gross signal.

A recent report by Meddings, Kaiser and Anderson (14) is concerned with this problem. They were interested in assays of feed materials for nickel and cobalt refineries, with an annual value of 1 billion dollars. Wet chemical analysis can give results with an RSD of about 0.1% when conducted with the utmost care, while more common routine results have an RSD of about 1%. They therefore tried to match these figures for wet analysis with an ICP spectrometer. Using the commercial system as delivered they found it impossible to control drifts in the calibration of perhaps 10% in an hour or to maintain precision under 1% RSD.

They investigated the problem and the first part of the apparatus to come under scrutiny was the nebuliser. The nebuliser supplied required frequent adjustment. They therefore tried a non-adjustable type which gave improved stability against drift, but poorer short term precision. After observing that the thin glass walls vibrated, they designed and patented a non-adjustable model with thick walls, and incorporated a baffle in the expansion chamber. With this they were able to reduce the RSD to 0.52%, or if an internal standard were used to 0.33%. These values are means for 25 elements. In addition the calibration drift over several hours was reduced to about 1% under normal circumstances.

During further investigation it was noticed that the signal was strongly temperature dependent. This was traced to the gas flows, so mass flow-controllers were installed. Finally the effect of fluctuations in the power was investigated. The effect was different for different elements : in some cases the signal rose with power, in some it fell and for some the effect was minimal. For zinc, the worst case, an apparent change in concentration of 0.01 ppm was caused by a change of only 0.29 watts which is about 0.03% of their applied power. Thus if a precision of 0.1% at concentration levels of 10 ppm is required, a very stable generator is necessary.

When these precautions were taken, precisions of 0.1 to 0.4% RSD were obtainable with ideal aqueous solutions with concentration 10 ppm. When real samples were used the values for nickel were 0.4% as compared with 0.25% for pure solutions.

Thus, provided sufficient care is taken with the nebuliser design and with effective controls for the gas flows and the power supply, it appears that RSD values of less than 0.5%, even at levels of 10 ppm can be achieved, with a "reasonable prospect", as the authors say, of reducing this to 0.1%.

Upto this point I have been describing the attributes of plasma emission spectroscopy from the evidence of factual data and well documented experiments; I am now going on to discuss the interferences to which the technique is subject. Whilst a number of these interferences are also well documented, others are not, and for these the evidence is less conclusive, often partially contradictory and sometimes open to a contrary interpretation.

There is no doubt that the technique, like any other form of emission spectroscopy is subject to spectral interferences. These are of the usual kind, such as instrument broadening of the spectral lines leading to spectral overlap of close packed spectral lines and also of molecular band spectra. In addition to these the high temperature of the plasma causes the introduction of a few extra spectral interferences. Thus, the broadening of the lines as a consequence of the high temperature causes strong lines to have "wings" that may overlap lines of interest even when these are an angstrom, or so, away. Some of these strong lines result in a magnification of the problem of stray light and necessitate great care to be taken in the designing and making of the spectrometer. Radiative recombination, which occurs when a free electron combines with an ion to yield a neutral atom, causes emission of a continuum, which can also cause spectral interference.

Although it is important that the spectroscopist is aware of these effects, they in no way invalidate the technique, and proper selection of lines and operating conditions, and the use, where necessary, of background corrections will nullify these interferences.

Another interference effect, for which there is substantial evidence, is that due to the effect of viscosity and other solution properties of the analyte on the uptake rate of the nebuliser. The effect of this interference can be, and often is, mistakenly attributed to other causes. It can be minimised in a number of ways - by feeding the nebuliser with a pump, by matching the solution properties of the standards to those of the sample, by mathematical correction for the solution properties and by the use of internal standards.

There is little, if any, evidence for another type of interference, chemical interference, associated with the formation of stable refractory compounds. Compound formation is precluded by the high kinetic temperature of the plasma. Such evidence as there is for compound formation arises in the main from experiments conducted with torches and injectors producing solid or non-annular plasmas or from torches operating under eccentric conditions. It must be presumed that under these circumstances the analyte does not reach a temperature high enough to dissociate refractory compounds. Enhancements of the signal, which have been reported, are of course, due to other causes and are not due to compound formation which is always a depressive effect. In passing, it is worth mentioning that there is little, if any, evidence for anion interference.

It might be expected that the influence of the addition of an easily ionised substance, such as sodium, to the analytical matrix, would be to produce ionisation interference. In this case one might expect the emission from atomic lines to be enhanced and that from ionic lines to be depressed as the increase in electron density perturbs the equilibrium. In fact, although some of the evidence would seem to support this expectation, some does not. For instance, Abdallah, Mermet and Trassy (15) traced the enhancement of the 2535Å atomic line of phosphorus to a desolvation effect. The effect varied with the molecular state of the phosphorus and with the temperature of the desolvation oven and it was absent when the desolvator was omitted. These same authors, and also Fassel and his colleagues, found an enhancement of the atom line of calcium and a reduction of the ion line with increasing amounts of sodium. It is interesting to note that they also found the effect to disappear at higher powers, that is, we presume at higher temperatures. Since the two sets of experimenters were using two very different types of nebuliser the indication was that the interference lay within the plasma and could be consistent with a variation in electron density. However, as Mermet and Robin (16) pointed out in an earlier paper, experimentally, sodium did not appear to have an appreciable effect on the electron density or the excitation temperature. Abdallah et al (15) confirmed these findings by measuring the ratio of an atom and an ion line of magnesium and the ratio of two ion lines of titanium, with increasing sodium concentration. The first ratio gives a measure of the electron density and the second the excitation temperature. They found that the electron density and the excitation temperature remained practically constant. From these results they concluded that Saha's equation could not be applied and suggested that the interference was an atomisation interference. The authors conclude their paper with the comment "what these interferences stem from and the means of freeing oneself from them remains to be deeply studied".

We at Oldbury have calculated the electron density in an argon plasma as a function of sodium concentration at various temperatures and these are shown in Fig. 8.
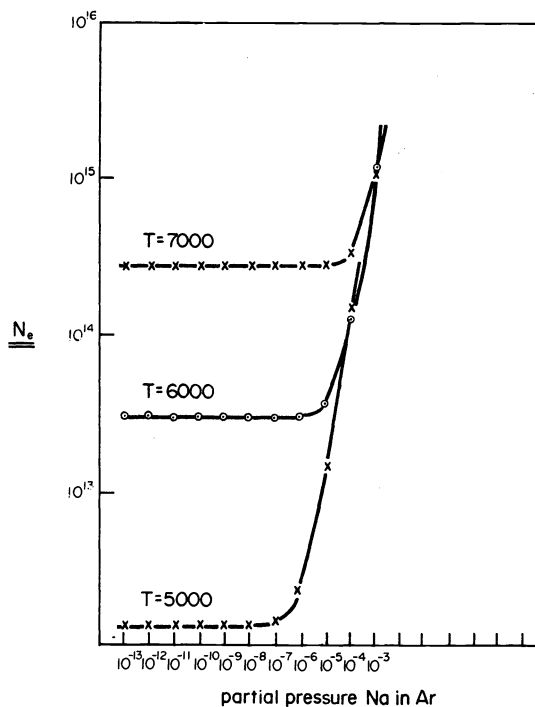
Fig.8.   Electron density in Na/Ar plasma as function of
sodium concentration.

This shows that when a sufficiently low concentration of sodium is introduced, even
if it is highly ionised, its contribution to the electron density is negligible compared
with that due to argon. The figure also shows, that the higher the temperature the
greater the concentration of sodium before the electron density shows a detectable
increase.   From this it might be concluded that sodium should not affect the electron
density unless considerable amounts are present or the temperature of the system is low.

Several workers have suggested that a matrix such as sodium can coat the analyte particles,
causing a change in the rate of volatilisation and thus accounting for the different
optimum observation zones which are found in the presence of sodium.   From this it
follows that if the system has been optimised for, shall we say, detection limits in the
absence of a matrix then it will not be optimised for detection limits in the presence
of a matrix.   Put another way, the system will not be optimised for minimum
interference.

Brockaert and his fellow workers (17) following an examination of the radial distribution
of excitation temperatures found that sodium metaborate reduced the excitation temperature
of the central zone of the plasma.   Kornblum (18) found that the uptake rate of the
nebuliser also altered the temperature of the central zone and hence the emission.
Brockaert found that the metaborate reduced the intensity of yttrium lines, whereas sodium
chloride did not.   Since the sum of the ionisation energy of the yttrium and the
excitation energy of the lines is close to the energies of the argon metastables they
concluded that the decrease in excitation of the yttrium was due to the quenching of the
metastables by the borate.   This, of course, assumes that excitation is via argon
metastables.

Perhaps, for clarification purposes, I can summarise what I see as the present position
with regard to interferences in I.C.P.-O.E.S.

1)   There are spectral interferences.

2)   Annular plasmas do not exhibit chemical matrix effects.

3)   Solution effects can alter uptake rate of nebulisers.

4)   There is evidence that desolvation effects do occur.

5)   Some effects, which occur in the presence of sodium, may be
        ionisation suppression, others may be caused by changes in
        excitation temperature, others may be volatilisation effects.

6)   If a system has been optimised for detection limits it will
        not necessarily be optimised for minimum interference.

Thus it can be seen that our knowledge of the interferences that occur in plasma
spectroscopy is not complete and there remain anomalies that are not easily explained.
It is indeed fortunate that the effect of these interferences is small.   For instance
Larson, Fassel, Scott and Kniseley (19) commented that an easily excited element, sodium,
in concentrations of up to 6900 ppm, exerted an unusually low influence on the observed
emission intensities of three selected elements, calcium, chromium and cadmium.
Boumans (20) observed that concomitants at concentrations of 1000 ppm had small effects.
Kornblum and De Galan (18) found that interferences under normal conditions were so small
that they were lost in the imprecision encountered in Abel inversions and so they had to
adopt unusual conditions to make them bad enough to be measured reliably.

A similar controversial area is that concerning the power rating of the high frequency
generator used to produce the plasma.   The number of watts put into the plasma will
affect not only its temperature but its size, particularly its length, and both these
properties will affect the temperature of the analyte stream flowing through it.   From
this it is easy to see that power supplied to the plasma will affect the detection limit.
This is so because any variation in temperature will affect the spectral radiance of the
analyte signal and also that of the background or continuum, and at different rates.
Since detection limit is related to both signal and to background it too will be
affected.

The temperature will also affect the electron density of the plasma and of the analyte
stream.   Now it can be imagined that if the electron density is very high to start with,
as it will be if the temperature is high, then the addition of an easily ionised material
may be expected to have less effect than it would in a low powered, shall we say < 1.5 kW
plasma system, which will have a lower temperature.   We saw in Fig.8 that calculations
show that the higher the temperature, the greater is the concentration of sodium which can
be tolerated before the electron density is significantly increased.

Again, it can be demonstrated that higher power in the plasma will dissociate molecules
which are not dissociated in lower power plasmas.   A classic case is that of the so-called
Swan bands or carbon-carbon banding which undoubtedly are present when organic solvents
are introduced into low-powered plasmas but are not present in high powered plasmas, as
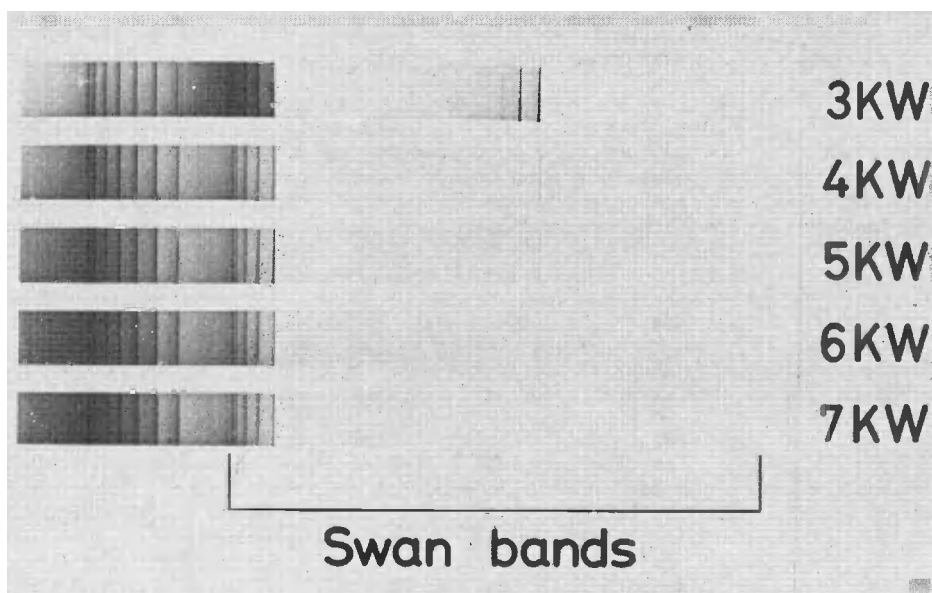Figs. 9 and 10 show.

Fig.9.   Effect of power in the plasma on Swan bands.

POWER

2kW

3kW

4kW

5kW

6kW

7kW

CO H(α)CN C₂   C₂   C₂ H(β) C₂ CN   CN

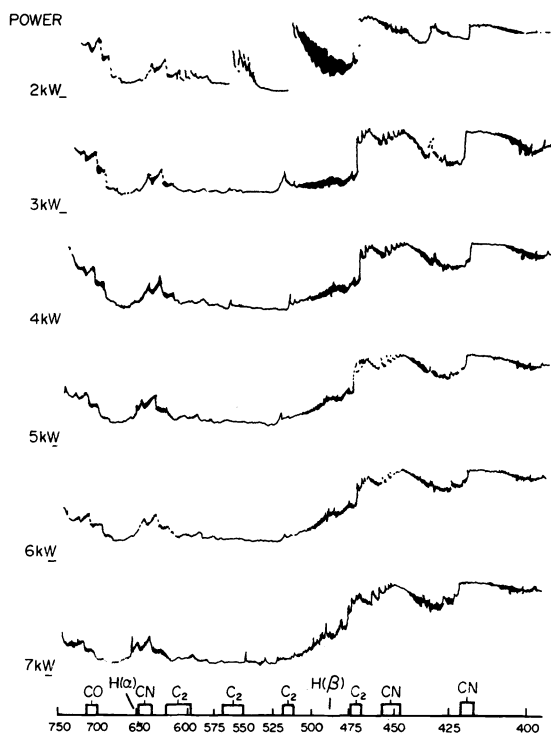750 700   650   600 575 550 525 500 475 450   425   400

Fig.10.   Effect of power in the plasma on Swan bands.

There is reason to believe that the plasma resembles a tube furnace and normally it can be expected that the analyte will pass through the central tunnel without having much effect on the plasma surrounding it.   However, if, as can happen, analyte material does enter the plasma it can well be imagined that the extra demand on power that this makes may be an appreciable fraction of the total power supplied to a low power plasma but is likely to be negligible in the case of a high power plasma.

Why then in view of these apparent advantages of high powered systems are most systems offered for sale, low power?   I believe the reason has less to do with science than it has to do with economics and attractive packaging, that is, smallness and other salesworthy points.

It is said, by at least one manufacturer, that everything which can be done on a high power system can be done equally well on a low power system.   I do not know whether this is true or not and I doubt whether the manufacturer does.   With two exceptions, I know of no systematic work, with optimised systems, which has been carried out to compare high and low powered plasmas for any of the properties which are likely to be affected by power such as those I described a moment ago.

The exceptions were studies of my own (21) and some by Ebdon and his colleagues (22). The main part of the former work lay in comparing the net signal to background ratios of three optimised plasma systems on one spectrometer.   The three systems were the Scott torch with argon coolant and the Greenfield torch with argon and nitrogen coolants.   High and low power generators were used as necessary, in the hope that they would give the power range required.

In Ebdon's work a comparison was made between a Greenfield torch and a demountable torch of their own construction operating with argon and with nitrogen coolants.   The basis of the comparison was the signal to background ratio obtained when these torches were run under optimised conditions with the same generator and spectrometer.

The Scott torch was found to require powers ranging from 0.53 to 1.21 kW, in the plasma, when a series of lines varying in difficulty of excitation were optimised for signal to background ratio.   The Greenfield torch with an argon coolant could not be optimised in most cases as the minimum power obtainable from the generator was greater than the indicated optimum value for the gas flows required.   In two cases, however, true optimisation was obtained.   In one, a power of 3.92 kW was required, for the other 1.86 kW, and it may be said that the bottom end was < 1.39 kW.   At the two powers where optimisation was achieved the net ratios were similar to those obtained with the Scott torch.

When the Greenfield torch was run with a nitrogen coolant, the same set of lines gave, in five cases out of eight and with powers varying from less than 0.79 upto 2.6 kW, better signal to background ratios than the Scott torch. Of the other three cases, two of the lines were subject to molecular interference and the other was not truly optimised, since the optimisation required a lower power than could be obtained from either generator. Ebdon and his colleagues also found that the nitrogen-cooled plasma required more power to reach an optimum for the manganese 2576Å line than did the argon cooled plasma and indeed his generator was unable to supply enough power to give a true optimisation at the gas flows indicated.

The point about these two series of experiments is that in both cases the authors had no doubt what the basis of their comparison was and took steps to ensure that all their systems were operating under optimal conditions before any comparisons were made. In both series of experiments each of the two groups optimised the observation height, the power in the plasma and the injector, plasma and coolant gas flows - in the one case using an alternating variable search method of optimisation, in the other by the use of a variable step-size simplex procedure.

To emphasise this lack of reliable information and to highlight the way in which confusion is engendered in the minds of the scientific layman, let us consider the following example. If we wish to compare, say, a Radyne generator with a Greenfield torch against a Plasmatherm generator with a Scott torch, it is perfectly valid to do so, providing it is understood that it is the total systems which are being compared and that the operating conditions are optimised for the same figure of merit whatever that may be. If the instrument on which the comparison is being made is a simultaneous instrument then compromise conditions can be used. Properly a set of compromise conditions should be derived from a knowledge of the individual optimised conditions. The adjective compromise should not be used as a euphemism for arbitrary. The comparison of one generator and one torch with a different generator and different torch is not a comparison of individual generators or torches and if such a comparison is required then each generator should be run with the same torch and each torch mounted on the same generator. Above all unless conditions are optimised for each combination any comparison will be invalid.

These remarks may appear obvious to you but the literature would suggest that they may not be quite so obvious to your neighbour.

Let me return to the claim that anything that can be done on a high powered plasma can be done on a low powered plasma. I have said there is a lack of systematic evidence but I do know of cases, from personal experience and from reports in the literature, of low powered plasmas which extinguish if the sample cup is removed from the nebuliser inlet and, as a consequence, air is drawn through the plasma. As I have demonstrated, low powered plasmas through which organic solvents are nebulised, exhibit Swan bands and the characteristic green hue is readily seen. It is also said that carbon formation occurs on the injector tip under these circumstances. When hydride-forming elements are introduced into the plasma as hydrides, following a borohydride reduction, the hydrogen formed is not readily tolerated by low power systems - or so it has been reported. Similarly, it has been reported that low-powered systems tend to extinguish when solutions of high acid concentration are nebulised and the resulting aerosol injected through them, and it is noticeable that many workers with low powered plasmas do seem to restrict the salt content of the solutions they nebulise to around 1%. It is my experience, when experimenting with unusual operating conditions which produce instability in the plasma, that stability can often be restored by increasing the power. It is also my experience that high powered plasmas are not subject to the limitations I have just outlined.

Now all this adds up to an overall impression that low powered systems are not as versatile and adaptable as the high powered ones. However, I would again emphasise, it is only an impression and I do not know of any work that I would regard as reliable which substantiates or denies this impression, other than that which I have reported. Until our knowledge of plasma spectroscopy has reached the point where we know exactly what power we require for all circumstances, it seems to me preferable to have a reserve of power and to work with a generator which will produce five or so kilowatts of power in the plasma whilst still being capable of maintaining a plasma of less than half a kilowatt. A high powered generator can always be turned down but there are limits to which a low-powered generator can be turned up.

I have tried to give an honest report on topics in plasma spectrometry which are sometimes contentious, sometimes not, and which I hope will be fully resolved by future research. Perhaps I may conclude by asking the question, what else does the future hold?

2522 S. GREENFIELD

A field where I think substantial advances might be made is that of spectrometers as distinct from sources. The recent developments in gratings are important, and the speeds, both optical and mechanical which scanning monochromators are reported to possess make the use of these very attractive, especially if more than one is used to view a single source under computer control. The developments with echelle gratings have led to development of two new types of spectrometer. The first is the analogue of a scanning monochromator, but with no moving parts, the scanning being done electronically. The second is the corresponding analogue of the conventional direct reader, where the whole spectrum is stored on a vidicon screen and as many wavelengths as are wanted can be chosen to have their intensities measured sequentially. Both these ideas seem to me to be exciting and excellent in principle and it is to be hoped that the practical difficulties will be overcome soon.

Another interesting idea was reported by Gray some years ago (23). Instead of dispersing the radiation emitted by the source and identifying wavelengths associated with an element, we ignore the radiation entirely and use the plasma as a source for a mass spectrometer identifying the elements by mass. There are papers being given on this topic at this conference.

Finally, I believe the future holds a lot for the I.C.P. I am convinced that, now having come of age, it will survive to a ripe old age.

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