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Continuing Developments in Atomizer, Source, Inductively Coupled Plasmas in Atomic Fluorescence Spectrometry (ASIA)

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In 1982 a unique assembly was constructed at Loughborough University; this consisted of a high power plasma acting as a source of radiation to excite fluorescence in a low power plasma acting as an atomizer. The assembly was given the acronym ASIA. At the last three Winter Conferences an updated account was given of the work which has been carried out on this instrument, and this paper will be the fourth such update. First, it is appropriate to summarize what has been discovered so far.

The work started because of an interest in atomic fluorescence spectrometry, with its freedom from spectral interference, aroused by the first commercial instrument employing an inductively coupled plasma as an atomizer and hollow cathode lamps as sources, referring, of course, to the Baird Corporation instrument [1], the work of Demers and Allemand. It was recognized from the outset that the freedom from spectral interference, typical of atomic fluorescence, was only of significance if other properties more commonly associated with ICP-AES also prevailed. These are low detection limits, long linear dynamic range, and relative freedom from chemical and ionization interferences.

Many of the results of investigations carried out using ASIA were predictable from the findings of other workers using different equipment. Nevertheless, it was thought necessary to ascertain that ASIA did not depart from the expected too greatly, and if it did, by how much and where.

It was quickly established that the fluorescence curve of growth obtained when using the high power plasma had the shape and slopes indicative of a line source [2, 3] and, using a large Greenfield torch, that it would run quite happily at high powers with concentrated solutions being nebulized into it.

The expected freedom from spectral interferences was demonstrated quite convincingly. Thus, background shifts due to radiative recombination, reported when using ICP-AES [4], were shown to be absent in ASIA [5] due to the employment of a.c. coupled electronics in the latter technique which discriminate against changes in d.c. signals such as those mentioned. Spectral interferences due to collisional broadening, also reported in ICP-AES [4], were shown to be absent in ASIA [5]. Numerous examples of direct spectral overlaps, which cause spectral interference in ICP-AES and in atomic absorption, were shown to be without effect in ASIA [5].

This relative freedom from spectral interference arises from the fact that atomic fluorescence spectra is relatively simple being confined principally to transitions originating in the ground state and low lying energy levels, excited by resonance lines of the element used in the excitation source. It is also due to the fact that in order to observe spectral interference in atomic fluorescence certain stringent conditions must pertain. The emission profile of the source has to overlap with the absorption profile of the interfering element in the atomizer. The population of the interfering element in the correct energy level (usually the ground or low lying level) must be significantly high, and the energy emitted to that absorbed must also be significant.

It had been shown by Demers *et al.* that the long linear dynamic range of ICP-AES was also possessed by the Baird instrument; ASIA was no exception and dynamic ranges of five to six orders of magnitude were obtained [6].

It is claimed that ICP-AES has relative freedom from chemical matrix effects and ionization interferences. This does not mean that it is totally free from such interference only that quite large ratios of refractory elements and easily ionized elements can be tolerated. This is especially true if the operating conditions of the ICP are optimized for minimum interference. However, it should be noted that under these conditions the detection limits are generally downgraded. ASIA behaved in a similar manner [6]. Thus, with the system optimized for minimum detection limits elements, such as phosphorus, showed no interference on the emission of calcium up to very high ratios. Aluminum showed a depression and sodium a maximum. However, on re-optimization, this time for minimum interference, all these elements could be tolerated up to high ratios. The optimization technique employed was that of alternating variable search (AVS) as during the course of the work this method had been shown to be, in emission spectrometry, as fast, easier to operate, more informative, and as accu-

rate as modified Simplex methods: in fluorescence it was faster and more successful in finding the optimum [7]. From this work on matrix effects it was concluded that ASIA had a similar tolerance to them as ICP-AES. Demers had also reported similar behavior for the commercial instrument.

Demers had also shown that the detection limits attainable by atomic fluorescence using the commercial instrument were broadly similar to those reported for ICP-AES so far as the non-refractory elements were concerned [1] - some better, some worse. The refractory elements gave worse detection limits than those obtained by the emission technique, some, tungsten for instance, gave much worse. These poor results for the refractory elements were attributed to oxide formation in the atomizer tailflame, deduced largely from the fact that hydrocarbons had to be used in the atomizer carrier gas in order to get any respectable detection limits for some of the more refractory elements [2,8]. The story was repeated when detection limits were determined on the ASIA system as Table 1 shows. It can be seen that the detection limits determined by ASIA tended to be in the same ballpark as those obtained for HCL-ICP-AFS and ICP-AES, as far as the non-refractory elements were concerned, and to be rather better than HCL-ICP-AFS but worse than ICP-AES when considering the non-refractory elements.

Table 1. Early detection limits obtained by ASIA and by HCL-ICP-AFS compared with detection limits obtained by ICP-AES

Detection Limits ppb (3s) Non-refractory elements			
Element	ASIA	HCL-ICP-AFS*	ICP-AES**
Ca	0.5	0.6	0.2
Cr	8.0	12.0	6.2
Cu	3.0	1.5	5.4
Fe	19.0	15.0	4.7
Ni	21.0	7.5	10.1
Pb	80.0	105.0	42.0
Zn	6.0	0.6	1.8
Alkali metals			
Na	0.2	0.45	28.5
Refractory elements			
Al	45.0	30.0	22.5
B	56.0	750.0	4.8
Ba	8.0	75.0	1.3
Si	120.0	300.0	12.0
W	923.0	1050.0	30.0

*D.R. Demers, D.A. Busch and C.D. Allemand, *Int. Lab.*, 1982, 14.

**P.W.J.M. Boumans, *Line Coincidence Tables*. both re-calculated to 3s values.

The optical efficiency of the ASIA set-up was known to be poor because available but unsuitable equipment had been used in its construction and, having established that the existing equipment produced meretricious results, it was decided to improve the energy collection from the atomizer to the monochromator and from the source to the

atomizer.

Before going too far down this road, it was thought prudent to compare the source plasma with more conventional sources [9] such as boosted discharge hollow cathode lamps (BDHCL). The BDHCL used were photron "Super Lamps" supplied by Starna Ltd. The detection limits which were obtained for the elements Cu, Ni, and Pb are shown in Table 2. It can be seen that the detection limits are better with the ICP source than with the BDHCL sources when the BDHCL source is located in a position in which maximum radiant power in the image in the atomizer plasma is produced. The results for Cu suggest that this is due to the increased fluorescence signal sensitivity with the ICP source, which more than offsets the BDHCL advantage of lower noise. As the monochromator can measure fluorescence from a cell in the atomizer tailflame irradiated by a 3 mm x 10 mm image of the source plasma (as opposed to a 3 mm circle when a BDHCL is used), it may be that the better performance of the plasma light source is due to its ability to irradiate a greater area rather than to a greater intrinsic radiance. The possibility is suggested by the fact that very similar sensitivities and detection limits are obtained for the BDHCL, and the plasma source when the radiation of the latter is stopped down to a circle of approximately 3 mm diameter by means of an aperture. When the BDHCL is overrun the sensitivity and detection limits are better than those obtained for the stopped down plasma source.

Table 2. Detection Limits obtained with BDHCL and with ICP when used as sources in AFS

Element	Wavelength nm	Source	Detection Limits ppb (3s)
Pb	405.76	BDHCL	380
Pb	$\Sigma 280.2-287.3$	ICP	80
Ni	352.45	BDHCL	110
Ni	$\Sigma 231.1-232.5$	ICP	21
Cu	324.8	BDHCL	14
Cu	324.8	BDHCL	5.2 (lamp overrun)
Cu	$\Sigma 324.8-327.4$	ICP	2.3
Cu	$\Sigma 324.8-327.4$	ICP	8.8 (3 mm aperture)

n = 10 in all examples.

Having established the superiority of the plasma as a source in AFS, improvements in energy collection were undertaken. The Optica monochromator originally used, which had an *f* number around 15, was replaced by a Bentham instrument with an *f* number of 4.5. The two lenses on the monochromator side were replaced by a single lens placed at a position which gave a 1.67 times magnification onto the 2 cm high entrance slit of the monochromator. This magnification had been calculated to give the best collection efficiency and the calculation was confirmed experimentally. The new layout is shown in Figure 1, and the detection limits which were obtained with this new layout are given in Table 3.

Figure 1. Modified Layout for ASIA Instrument

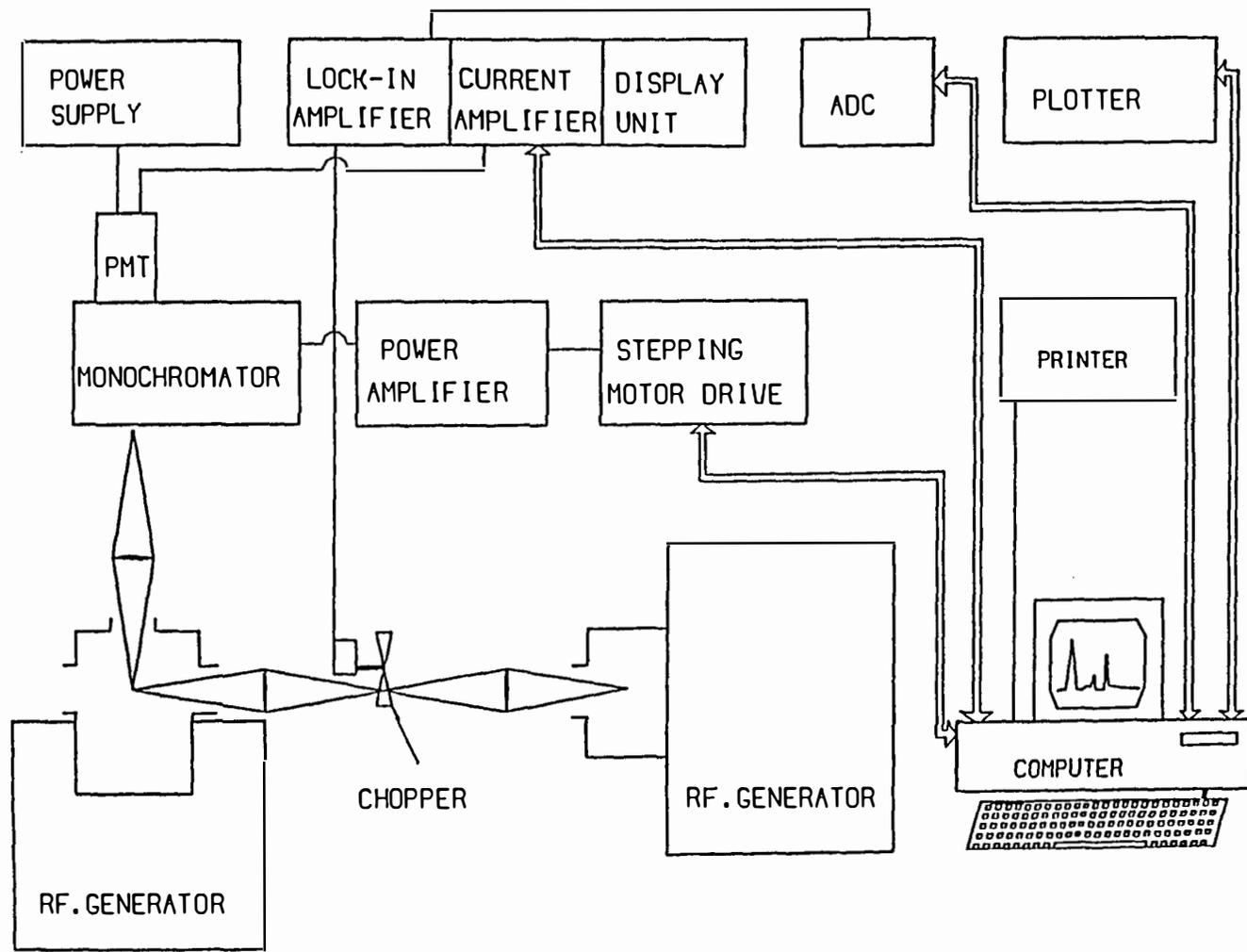


Figure 2. Heated Spray Chamber and Desolvator

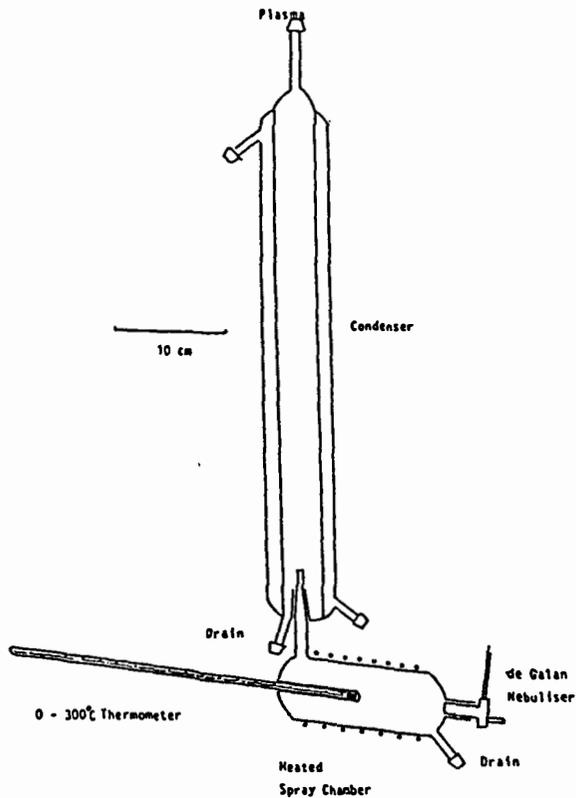


Figure 3. Cu Emission from Source Plasma

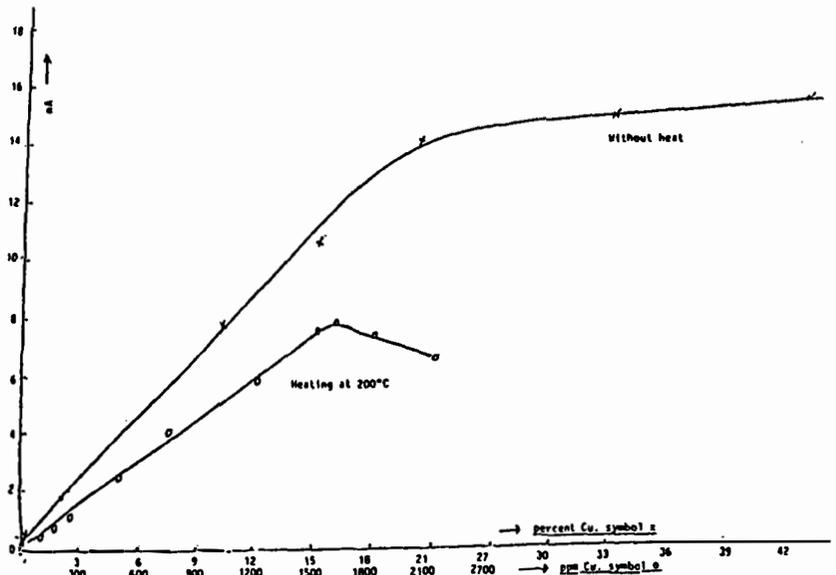


Table 3. Detection limits obtained after modification of the ASIA system compared with those obtained by ICP-AES

Element	ASIA	ICP-AES*	ICP-AES/ASIA
Na	0.1	28.5	285
Cu	0.4	5.4	13.5
Cr	3	6.2	2.07
Ni	6	10.1	1.68
Pb	27	42	1.56
Li	3.2	4.2	1.31
Al	20.5	22.5	1.1
Ca	0.2	0.2	1.0
Fe	5	4.7	0.94
Zn	2	1.8	0.90
Co	9.5	6	0.63
Ba	3.5	1.3	0.37
Si	54.5	12	0.22
B	28	4.8	0.17
Mo	63	8	0.13
W	428	30	0.07

*P.W.J.M. Boumans, *Line Coincidence Tables* re-calculated to 3s values.

Of the 16 elements listed, all the non-refractory elements have similar or better detection limits by ASIA than by ICP-AES. In the case of the refractory elements, all have detection limits less than an order of magnitude worse than those obtainable by ICP-AES, with the exception of the element tungsten which has detection limits 14 times worse. It is thought that an improvement in the transfer of energy from the source plasma to the atomizer plasma and a reduction in the background level, due it is believed to scatter off surfaces, will go a long way towards reducing this detection limit difference.

Great advantages would be gained by improved nebulizer transport efficiency, not only the obvious advantage of an increased fluorescence signal, but the less obvious advantage of a reduction in concentration of the element which is fed to the source plasma. With these objectives in view a heated spray chamber together with a de-solvator was constructed, on similar lines to an earlier model [10], as is shown in Figure 2. In use it was found that a plot of emission from the source *versus* temperature gave a heating curve which, after an initial rise, was substantially flat between 180° - 240°C, and a temperature of 200°C was chosen as an operating temperature.

The emission curve of growth which is obtained when a 20% copper solution is fed to the source plasma using an unheated spray-chamber is shown in Figure 3. On the same graph is shown the curve of growth for copper using a heated spray-chamber and a desolvator. Fifty-five percent of the signal which was obtained using a 20% solution of copper and an unheated spray-chamber, was obtained using a 0.15% solution of copper and a heated spray-chamber followed by desolvation. Unfortunately, at this concentration of copper, black copper oxide started to deposit on the spray-chamber walls and the signal dimin-

ished. Nevertheless, this is an important development, and work will continue with new designs of spray-chamber, employing a sheath gas, in an attempt to prevent this deposition.

Another failing of the heated spray-chamber was that it caused pulsing of the aerosol which meant that when it was used with the atomizer plasma there was a 100-fold increase in the background noise. Thus, despite a 10-fold increase in the fluorescence signal, the detection limits were worse than with conventional nebulization. It is believed that this pulsing results from large aerosol droplets hitting the heated walls and so producing "bursts" of steam. (This has been largely proven by filtering out the large droplets, with a consequent reduction in pulsation.) Again, it is hoped that the use of a different design of spray-chamber may overcome this problem. Another approach to this problem would be to heat the droplets internally by means of microwaves thus achieving a gradual evolution of steam. This possibility is being examined.

Finally, mention should be made of some application work which has been undertaken using the ASIA instrument. In the determination of the elements Zn, Cr, Ni, Pb, Ca, Co, Al, Mn and Mg in very pure solvent extracted phosphoric acid, using a large polychromator (Baird P52-Spectro-Vac) in ICP-AES, it was found that there was ppm interference on all these channels by 1000 ppm concentrations of each of the other concomitants. There was similar interference from the solvent, MIBK, and from the phosphoric acid itself. These interferences were of sufficient magnitude to cause difficulties in carrying out the analyses. When the work was repeated using ASIA these interferences were reduced to a few ppb. This work is continuing and will be reported elsewhere in greater detail. This outline is given simply to illustrate that ASIA has reached a stage where it is being used seriously on application work where its freedom from spectral interference, it is hoped, will assume increasing importance.

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