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great thing

in **AAS**

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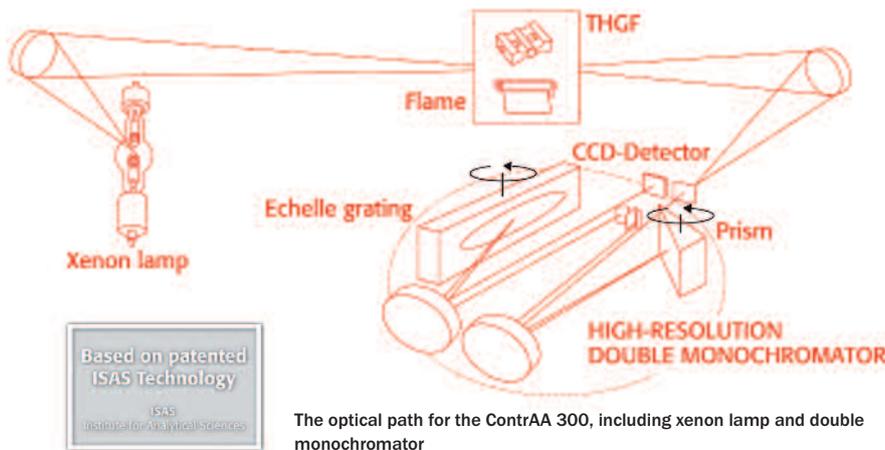
Flame atomic absorption spectroscopy (AAS) has been a mainstay of every one of my laboratories for the past 20 years. Across five different labs, I have run nine of these instruments. Over the years, these have grown in their complexity and capabilities: rotating turrets to hold multiple lamps, automatic burner rotation, deuterium background correction lamps, double-beam optics, automatic samplers, auto sampling and auto dilution. Generally, these capabilities delivered improved performance, either in convenience and/or in reduced operator effects.

However, the underlying technology across all of the instruments has remained essentially unchanged throughout the time I have been using AAS, or indeed for another 20 and more years before that.

I work in hydrometallurgy. My aqueous systems contain high concentrations of metals (up to 100 g/L) in extremely concentrated salt solutions (typically >6 M, or over 400 g/L total dissolved salts). These samples are not easy to analyse by any technique, and over the years I have tried a variety of alternatives to AAS without much success: ion chromatography, energy-dispersive XRF and others.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) and/or mass spectroscopy (ICP-MS) are of course able to analyse my samples, but ICP comes with its own disadvantages, the primary among which are twofold: first, the equipment is far too pricey to operate for my comparatively small number of R&D samples, to yield quick turnarounds on

short sample runs; and second, everybody knows that ICP is closely related to witchcraft – to get really good analyses from ICP, one has to sacrifice a black rooster over the instrument on the full moon. Or putting that in more scientific terms, it is critical to set up the ICP methods



The optical path for the ContrAA 300, including xenon lamp and double monochromator

precisely and with careful attention to matrix matching for really good quality results.

So AAS has always been my 'go to' analytical method for these solutions. The results are somewhat quick and dirty, so to speak, but cheap enough and sufficiently accurate to provide guidance on my R&D.

Given the high metal concentrations in my solutions, AAS's limited sensitivity is seldom an issue for my purposes. Indeed, the multiple dilutions required to get the metals into a useful analytical range tend to introduce additional and cumulative sources of random error that further decrease sensitivity. But AAS can generally handle TDS concentrations up to about 5%, and if I initially dilute 1 millilitre of a 40% sample into 19 millilitres of 3% HCl (to maintain the stability of the metals in solution), the resulting sample contains just under 5%.

Provided that I planned ahead on my assay sequence, restricted the number of elements to a handful of key metals (typically copper, iron, silver, lead and zinc, in order of increasing difficulty), and made sure that my lamps were warmed in readiness for when I needed them, then AAS was generally good enough for my purposes.

But that's a pretty hefty list of caveats. I couldn't do simultaneous analysis, so longer runs of multiple elements become pretty tedious. With

signal instability at least partially due to the salts, I had to use long read times (typically three repeats at 10 seconds), which can consume sample quickly across those runs. And there is a wide range of elements that are well outside my purview. Ultimately, I still had to rely on external labs using ICP for a percentage of my analytical needs.

So I was pretty excited when I first read about continuum source AAS in an ad within the pages of this magazine. I immediately conjured visions of simultaneous analysis, which alone could reduce my operator time considerably.

However, I was also somewhat suspicious. We don't live in the world of Star Trek (yet). I can't wave a 'tricorder' over my sample for instantaneous and complete analysis. And if half a lifetime of science has taught me anything, it would be that there are no 'free rides'. In instrumental analyses, I only look for net gains – a positive balance of advantages over disadvantages. 'Where', I asked myself, 'is the rub?'

The short answer is that I haven't found one so far. By every appearance, continuum source AAS might be the first major advance in this field in the last 50 years. Stemming from the work of Becker-Ross and co-workers in the mid-1990s, German company Analytik Jena has commercialised continuum spectrum instruments for both flame and graphite furnace AAS, and the

resulting instruments appear to fully live up to the hype.

The breakthroughs from Becker-Ross and colleagues are two-fold. First, the xenon short-arc lamp gives a high-intensity emission down

to well below 250 nanometres, which was not possible with previous, weaker-emission xenon lamps. Operating at 10 000 K, the manufacturer claims that it can start quickly, without the long warm-up times associated with traditional hollow cathode lamps (HCLs). This has advantages for quick equipment availability, but the high intensity also significantly aids sensitivity. A paper by Welz from 2005 (*Anal. Bioanal. Chem.* vol. 381, pp. 69–71) suggests that detection limits could be improved by as much as a factor of five, and the manufacturer claims a full order of magnitude.

The other major development was a monochromator of sufficient resolution (>100 000) to provide a spectral bandwidth corresponding to the half-width of atomic absorption lines. The solution is an innovative double monochromator.

Much of the literature extolled the virtues of the high-resolution CCD line detector in the spectrophotometer. With 598 pixels, 200 pixels are dedicated to analysis, with the remainder available for background correction, source drift correction (aiding fast start-up) and other mathematical improvements to aid sensitivity and signal-to-noise ratio. For flame AAS, this is repeatedly referred to as giving fast sequential analysis – not true simultaneous analysis, but a good practical outcome to come closer to the ideal.



The high-intensity continuous spectrum light of the ContrAA's xenon short-arc lamp is visible in the window and along the length of the burner.

However, this may be my main criticism of the instrument so far. Given the massive leaps forward in CCD technology in the last 10 years emanating from the photography and mobile phone markets, surely the capabilities of the instrument could now also be massively upgraded, riding off the back of those advances.

As criticisms go, that's pretty minor. It boils down to 'It's good now, and it looks like it could get even better'.

With all of this in mind, I had the pleasure of visiting the University of Technology Sydney's lab at Ultimo, to view their ContrAA 300 flame CS-AAS. I brought along a few samples of my own, and Mr Harj Sandhu of MEP Instruments took a few hours to show me just what the instrument can do.

Starting with the basics, the lamp intensity is particularly noticeable. Capable of setting fire to a business card held at the focal point above the burner, it is really quite striking. The instrument has automatic burner adjustment, as well as an auto sampler and auto diluter. In general AAS, I more typically view these as being unnecessary – or even just another thing to potentially go wrong. But

operating the ContrAA 300 for multi-elemental analyses, it quickly became apparent how useful these could be for efficient operation.

One of the minor advantages of this operation is that it supports flow injection analysis, and even in standard 'mean mode', the continuous flow of either sample or 'wash' means that the burner maintains an even temperature.

After a relatively quick run of basic method development in single elements, the instrument was set to its first multi-element run. Quite simply, the efficiency gains using this mode were immediately and fully obvious for up to about 8–10 elements. After that, ICP would still have the advantage.

Although the basic mode certainly provides fast sequential elemental analysis, it is noteworthy that there are several transition metal combinations for which the close but separate spectral lines would support true simultaneous analysis. Critically, the resolution of the peaks within the spectra was spectacular.

Our method set-up work was somewhat hampered when the results clearly showed both lead and zinc contamination in the analytical water

supply. But the results we were able to show on the day left me with little doubt that the instrument could give me good results for all of my key elements in a single analytical sequence. MEP Instruments has kept my samples, and there may be a follow-up article to provide a case study on the outcomes.

I was also thrilled with the little 'aside' to our discussion, where Harj showed me how the instrument could be operated to run a semi-quantitative scan for other metals. This isn't a function I would run every day, but it could be incredibly useful at times, and my recommendation to Analytik Jenna is that the capability could be very easily enhanced via some simple software updates.

At a price comparable to conventional models on the market (rotating turret, double beam, and with accessories for a fair comparison), the ContrAA 300 is competitive at current exchange rates. And the cost of operation will be considerably less once labour is taken into account.

As is, the ContrAA 300 could be a considerable enhancement to the capabilities of any mining, wine, water or research lab, and quite a lot more besides. With enhancements to the CCD, to aspects such as sealing and positive-pressure air for industrial environments, and with upgraded software to take full advantage of the capabilities of the instrument, it could be truly phenomenal.

Overall, I'm sold. I believe that this truly is the first major breakthrough in flame AAS in the last 50 years. My birthday is coming soon ... anyone?

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