

## Design Considerations for a new Platform Cuvette in Graphite Furnace Atomic Absorption Spectrometry

### INTRODUCTION

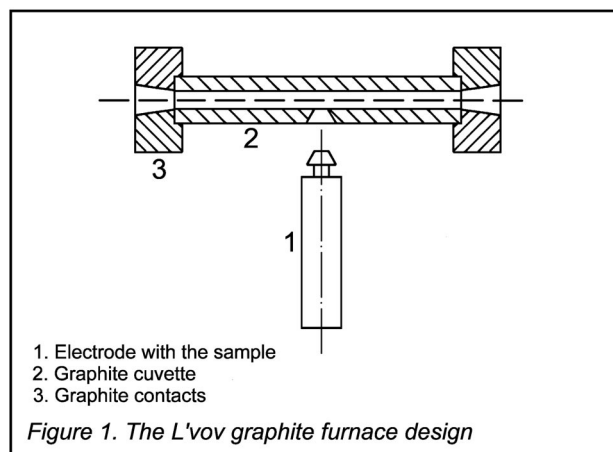
The technique of graphite furnace atomic absorption spectrometry (GFAAS) is now a firmly established analytical technique in many laboratories with an interest in ultra-trace (ng/ml) metal analyses. The inherent advantage of this technique is the selectivity of the atomic absorption measurement and the high sensitivity obtained using electrothermal atomisation. Over the early years, however, the main disadvantage of the technique, when using off-the-wall atomization, was recognised to be the high incidence of chemical interferences. Many of these interferences occurred in the vapour phase during the atomisation stage of the analytical cycle and are, therefore, normally referred to as chemical, vapour phase interferences. The interferences observed were due to the re-combination of species in the vapour phase within the cuvette to form analyte molecules, thus reducing the atom population and giving rise to smaller atomic absorption signals. The interference manifests itself, therefore, as a signal depression and, if standards were not exactly matrix matched to the samples, the analytical results obtained could be in error

As a result of much research, it then became obvious that the magnitude of many of the interferences observed was a function of the graphite furnace design itself. To understand this more fully, it is necessary to review the history of electrothermal atomisation in AAS.

#### A brief history of Electrothermal Atomisation in Atomic Absorption Spectrometry

The first papers describing graphite furnace AAS were published, in Russian, by L'vov in 1959<sup>[1,2]</sup>. L'vov continued to work on graphite furnace AAS and

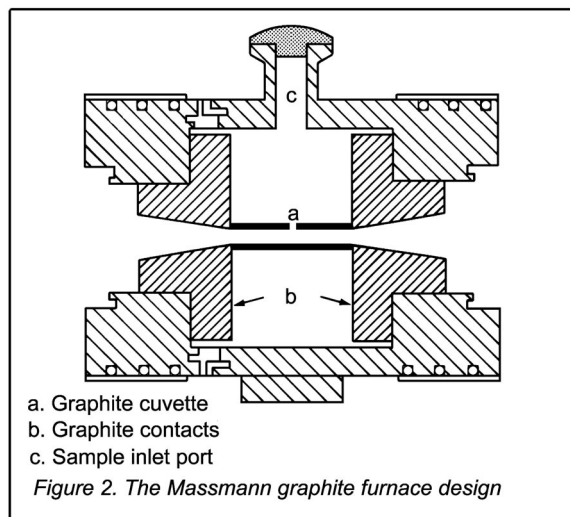
during the 1960s published many papers emphasising the advantages of this technique over flame AAS. These advantages were stated as higher sensitivity, use of small volumes, possibility of direct solid analyses and greater freedom from interferences. The electrothermal atomiser used by L'vov is shown in Figure 1. The sample was placed onto an auxiliary electrode that was heated independently from the graphite cuvette. The cuvette was maintained at a preset atomisation temperature and the sample was vaporised and atomised inside the graphite cuvette. The whole assembly was purged with an inert gas, argon or nitrogen, to prevent oxidative damage to the graphite.



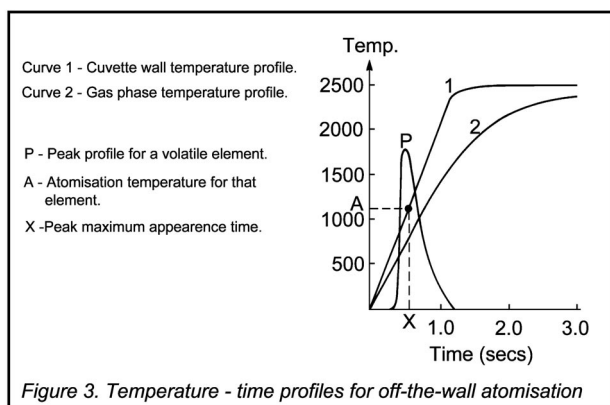
Further development of such a constant temperature furnace was carried out over a number of years by Woodriff and co-workers<sup>[4,5]</sup> but such designs were not found suitable for routine use.

Most important for the commercial exploitation of this technique was the contribution made by Massmann<sup>[6]</sup>, whose design of graphite furnace is shown in Figure 2. The furnace assembly was considerably simplified so that the sample could be injected directly onto the surface of the graphite cuvette. The cuvette was then cycled through a temperature program, the measurement was taken before the cuvette was cooled

for the next sample. The end contacts were also made from graphite and the whole device was housed inside a stainless steel water-cooled jacket. This particular design was further developed and, in 1969, became the basis for the first commercially available graphite furnace system.



Over the next 9 years it became apparent that this type of atomiser did not live up to expectations with respect to its freedom from interferences. Its main advantage was the simplicity of use and the potential for automation. In 1978, L'vov [7] summarised the situation 'Summarising the development of electrothermal atomisers to date, there is no denying that in spite of the great interest in electrothermal atomisation, the most popular among the users (Massmann type atomisers) are the atomisers which least of all meet the requirements of ideal methods of atomisation'. The 'ideal methods of atomisation' referred to by L'vov is the concept of constant temperature atomisation as originally described by him in 1959. At this point in time it was recognised that the increased interferences observed in Massmann-type atomisers were due to the ramp heating or non-isothermal nature of the atomisation phase. In off-the-wall atomisation, samples are vaporised from a hot cuvette wall into a cooler, and rapidly changing vapour phase, which favours the formation of analyte molecules. This is shown in Figure 3.



An additional problem with these early furnace designs was caused their non-linear temperature gradient along the length of the cuvette. The heavily cooled ends were a source of carry-over (due to inefficient heating of the sample and condensation effects), where high blank readings were recorded after high concentration sample readings.

L'vov proposed a number of ways to try to overcome non-isothermal atomisation in commercial graphite furnace atomisers [7]. One of these was to shift the atomisation pulse until the furnace temperature had reached equilibrium. At the present time, the most widely used method to approximate isothermal atomisation conditions, utilising the delayed AA signal approach, is use of platform atomisation [7]. A platform is a small piece of graphite that is located inside the graphite cuvette which has a trough into which is placed the sample, as shown in Figure 4.

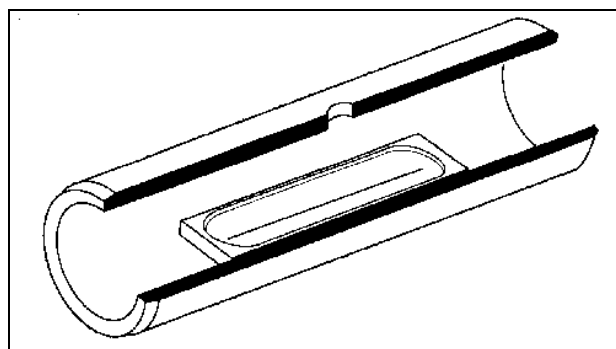
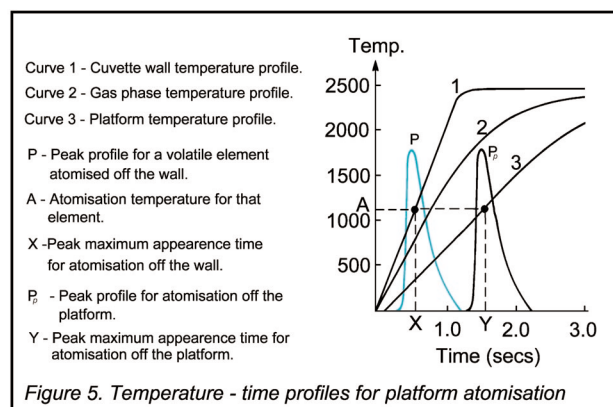


Figure 4. Typical platform design

The platform inside the cuvette is heated mainly by radiation from the cuvette wall and, therefore, the temperature of the platform lags behind that of the cuvette wall. When the sample is eventually vaporised and atomised, it does so into a hotter vapour phase temperature which reduces analyte molecular formation and, therefore, reduces interferences, see Figure 5.



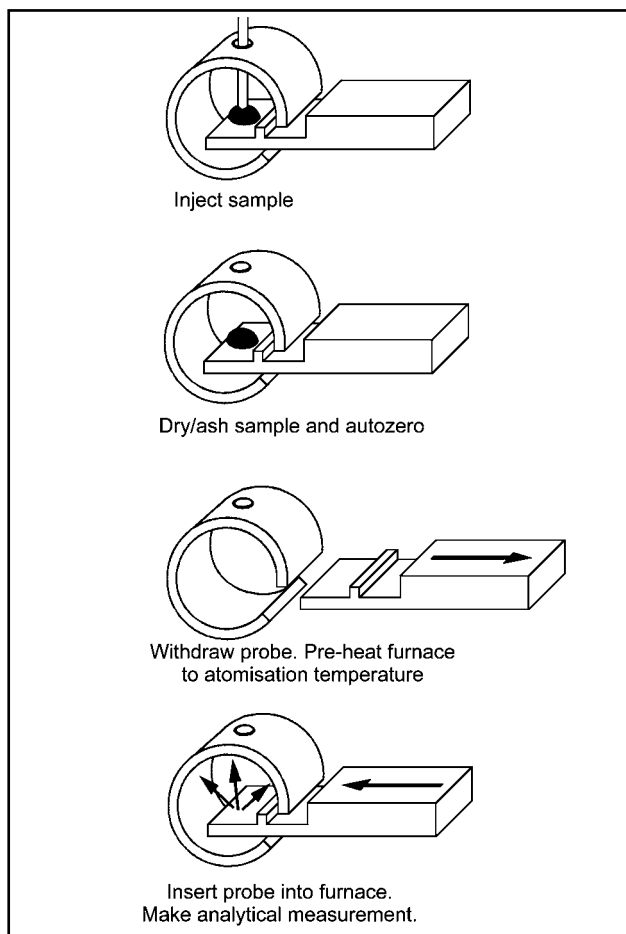
With this method, it is usually necessary to incorporate matrix modifiers (such as  $Mg[NO_3]_2$  or  $NH_4H_2PO_4$ ) which help to delay the AA signal even further, so as to more fully approach isothermal atomisation. This technique has been termed the STPF (Stabilised Temperature Platform Furnace) technique and the key components are (1) the platform, (2) use of matrix modifiers and (3) the use of peak area measurements (because of the peak broadening caused by the platform/modifier procedures). As discussed by L'vov [7] the specific necessity of adding a component to a particular element should be considered a drawback of this technique, particularly since there is a risk of contamination from added reagents.

### Platform Atomisation and alternative techniques

Platform atomisation has now been used in laboratories throughout the world for a number of years and consequently the technique has been well characterised. There is no doubt that platform

atomisation using the early designs of platform solved some analytical problems[101; however, there was doubt that platform atomisation at that time could be classified as true isothermal atomisation. A paper by Ottaway et al.[12] stated "Although the platform provides a useful delay in the atomisation or volatilisation process, the temperature of the atomisation surface is still changing when this takes place and it is not always certain that the tube vapour temperature is constant during the whole lifetime of the atomic absorption pulse".'

Due to these findings, attention focussed on alternatives to platform atomisation in graphite furnace AAS. These alternatives centred on the original L'vov principle, ie. introduction of the analyte only when constant temperature conditions have been established inside the graphite furnace. One such method, which again was suggested by L'vov[13'14], was based on the introduction of the sample on a graphite probe. This probe was introduced into the furnace cuvette only when isothermal conditions had been established. Such a device (based on work by Ottaway's group) was introduced by Thermo Elemental in 1987 as the AP90 Autoprobe accessory.



Essentially, four main steps are required for graphite probe atomisation. Initially, the sample is automatically injected onto the probe while it is inside the graphite cuvette. The sample is then dried and ashed (pyrolysed) before the spectrometer signal is zeroed automatically. After the auto-zero, the probe is withdrawn from the graphite cuvette and the furnace heats up to the pre-set atomisation temperature. When the cuvette temperature has stabilised, the probe is automatically inserted into the constant temperature environment for isothermal atomisation and analytical

measurement. Finally, a cuvette and probe clean stage is initiated. The process is shown diagrammatically in Figure 6.

This approach showed much better control of vapour phase interferences but there were a number of limitations, mainly its complex handling and small volume capability.

Changes to furnace design occurred in 1990 with the introduction of a new generation of platforms that clipped into the cuvettes (to prevent the platform moving around during the analysis). Another change was the move to transverse heating of the cuvette of a Zeeman background correction system. This was claimed to eliminate the temperature gradient along the tube length encountered with longitudinal heating, thus preventing carry-over and reducing vapour phase recombination effects. Figure 7 shows the characteristics of the two types.

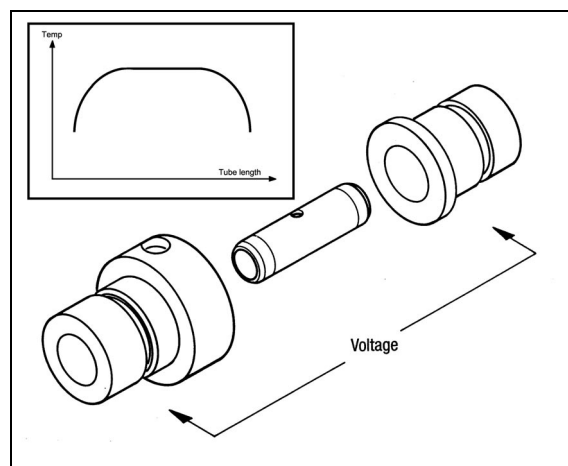


Figure 7a. Longitudinal heating of the furnace cuvette.

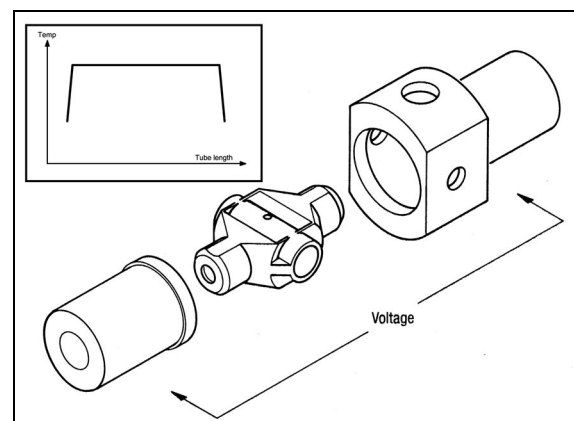


Figure 7b. Transverse heating of the furnace cuvette.

This change resulted in a number of compromises due to system constraints so that there are a number of limitations with this approach. Firstly, the Zeeman requirement results in a small volume cuvette and this, in turn, gives poorer sensitivity (as predicted by L'vov in his original papers) and secondly the cuvette is much more complex in shape and has greater mass, thus reducing heating rates (and sensitivity again, because L'vov showed that sensitivity is related to heating rates). A comparison of the published performance of a modern longitudinally heated furnace (the SOLAAR GF95Z) with the transverse design in Figure 8 demonstrates this very clearly.

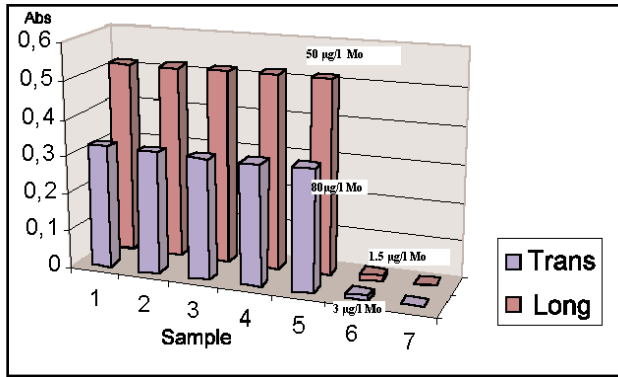


Figure 8. Sensitivity comparison between longitudinal and transversely heated furnaces.

In terms of correction, the longitudinally-heated furnace with Zeeman correction and conventional platform also outperforms the transverse equivalent, as shown in Figure 9. The example is the interference of 1,000 mg/L  $\text{SO}_4^{2-}$  on 40 µg/L Sn and it is important to note the cleaner and more uniform peak shape with the longitudinal furnace.

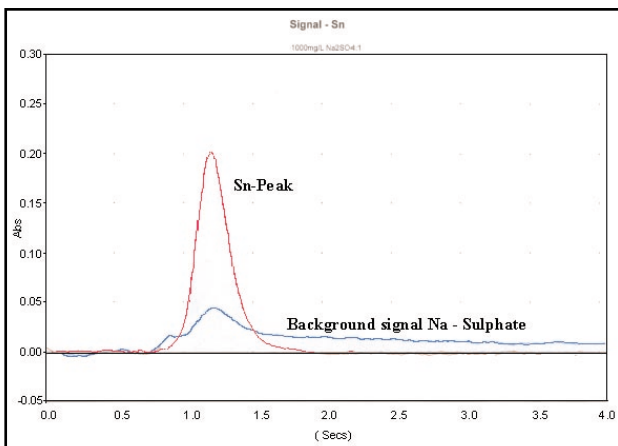
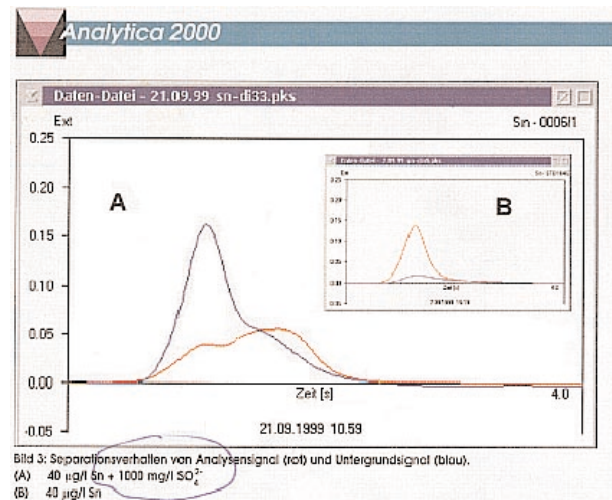


Figure 9. Comparison of peak shapes and correction capability, transverse (top) vs longitudinal heated (bottom) furnaces. Example is sulphate interference on Sn.

The standard platform cuvette, with its thin pyrolytic coating, offers excellent performance in terms of interference control for volatiles, such as Pb and Cd, but does not handle the more refractory elements as well. It also has a practical volume limit of 20 - 25 µL when used for samples of low viscosity and surface tension.

### The new Omega Cuvette

For this reason, a new cuvette with integrated platform has been designed which takes advantage of the superior performance given by our ELC (Extended Lifetime Cuvette) technology. It is known as the Omega cuvette and is shown schematically in Figure 10.

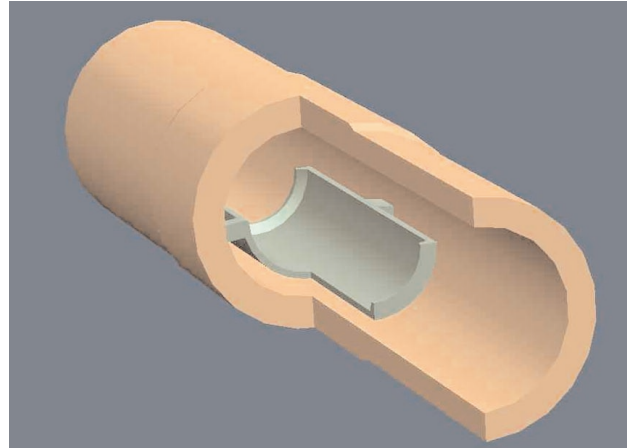


Figure 10. The new Omega cuvette with its integrated platform.

The Omega cuvette has dimensions very close to the standard ELC cuvette, apart from small changes to the centre thickness to improve the temperature profile. This means that the temperature settings required are close to those of the standard cuvette. The new integrated platform is 11mm long, with an internal diameter of 3.6mm and a wall thickness of 0.2mm. It only touches the cuvette wall via two very small contacts and is very lightweight, so that temperature delays and risetimes are high enough for it to be used for refractory elements such as Cr and Ni. The ELC pyrolytic layer is applied after the platform is fitted, so that it is fixed in position and cannot move. In earlier platform systems the groove to hold the platform was machined out after the coating had been applied, thus causing a weakness in the coating. With the Omega cuvette the coating is continuous and, therefore, more robust. **The new platform has a superior volume capability of up to 60 µL**

To demonstrate the usefulness of the new Omega cuvette, a number of examples of its performance will be given. Figure 11 shows the performance for Nickel of a standard ELC cuvette, normal uncoated graphite, a platform of the older type and the new Omega cuvette.

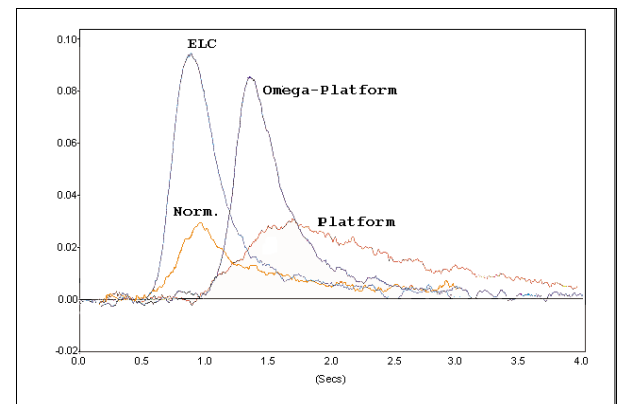


Figure 11. Comparative performance of a number of cuvette options for Nickel.

This demonstrates the superior sensitivity of the Omega cuvette over the previous platform system for refractory elements. It also shows how the appearance time of the peak is virtually doubled and this gives better interference control, as will be demonstrated later

The volume capability is shown in Figure 12. The Peak Area plot is for volumes varying between 5 and 50  $\mu\text{L}$  of a 10ppb Pb solution (each point represents the shown volume plus 5  $\mu\text{L}$  of an ammonium phosphate matrix modifier). The excellent linearity is obvious.

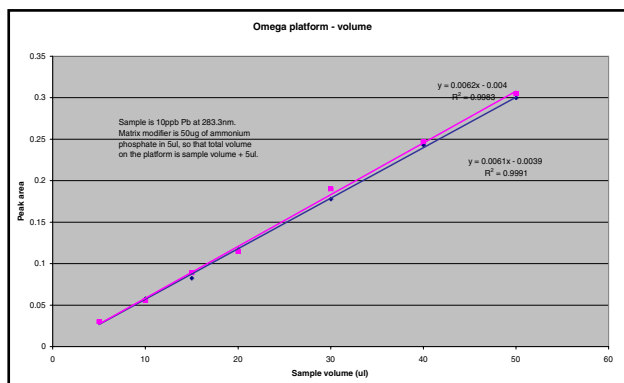


Figure 12. The effect on linearity of varying volumes of solution added to the Omega cuvette platform

### Examples of the Omega Cuvette in use

To demonstrate the efficiency of interference control, a classic example of a strong interference problem with Cd analysis in urine was chosen. This is a useful test for a volatile element because of the high and variable amount of salts present in such samples.

#### (1) Cadmium analysis

Sample preparation: A simple 1:3 dilution with 1% v/v  $\text{HNO}_3$  was utilized with no addition of any matrix modifier.

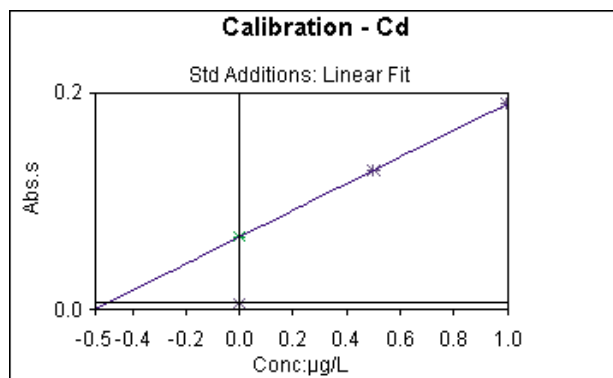
#### Temperature program:

Temperature ( $^{\circ}\text{C}$ )	Time (secs)	Ramp rate ( $^{\circ}\text{C}/\text{sec}$ )	Gas flow (L/min)	Control
120	40	10	0.2	
400	20	50	0.2	
1300	3.5	0	0	TC RD
2000	3.0	0	0.2	TC

Injection volume: 15 $\mu\text{L}$

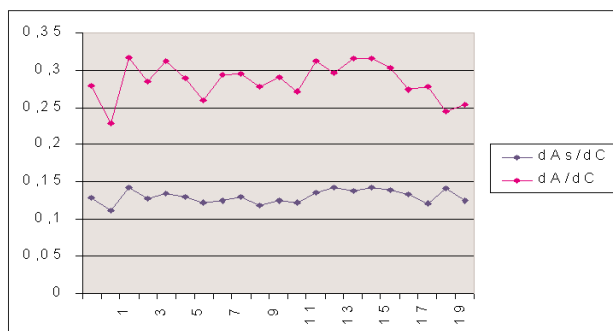
Figure 13 shows the Standard Additions plot (based on Peak Area measurements) for this analysis of a reference sample.

The Standard Additions analysis was repeated 19 times and the results were calculated for both Peak Height and Area mode. From these analyses the variation in the measured slope over the 19 repeats was then plotted, as shown below in Figure 14. An average slope value was calculated and compared against the slope for normal calibration in both modes. This comparison demonstrated that in Peak Area mode normal calibration against aqueous standards is possible.



Calibration coefficients:  $Y = 0.122 X + 0.067$   
 Corr<sup>n</sup> coeff = 1.000

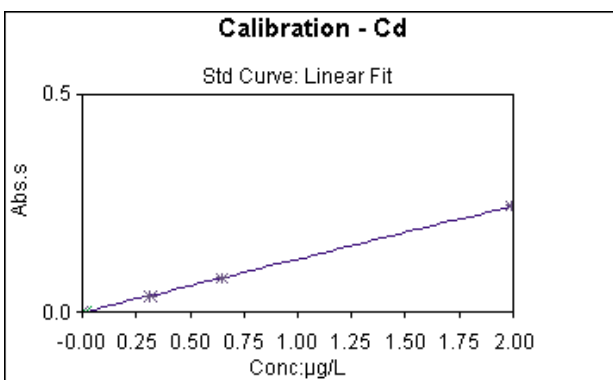
Figure 13. Standard additions plot for Cd in urine.



Mode	Urine matrix	RSD	Normal calibration
Area, std additions average slope	0.126	6%	0.122
Height, std additions average slope	0.285	8%	0.213

Figure 14. Repeatability of the Standard Additions slope and comparison against normal calibration values.

Figure 15 is the normal calibration plot with a typical concentration range, from such information the detection limit for Cd in a urine matrix has been calculated as 0.05  $\mu\text{g}/\text{L}$ .



Concentration	Peak area	$y = 0.122 x - 0.0012$
0.00	0.0006	Corr <sup>n</sup> coeff = 0.9998
0.32	0.0358	
0.65	0.0772	
2.00	0.2437	

Figure 15. Calibration graph for Cd in urine using normal standards.

Figure 16 compares the Cd peak signals for the Omega cuvette and off-the-wall atomization to demonstrate the interference and its correction. In the off-the-wall example, the Cd signal is characterized by double peaks and high background signals (that are nearly coincident with the Cd signal appearance time). With the Omega cuvette, the Cd signal is a single, clean peak and with good separation from the background signal maximum.

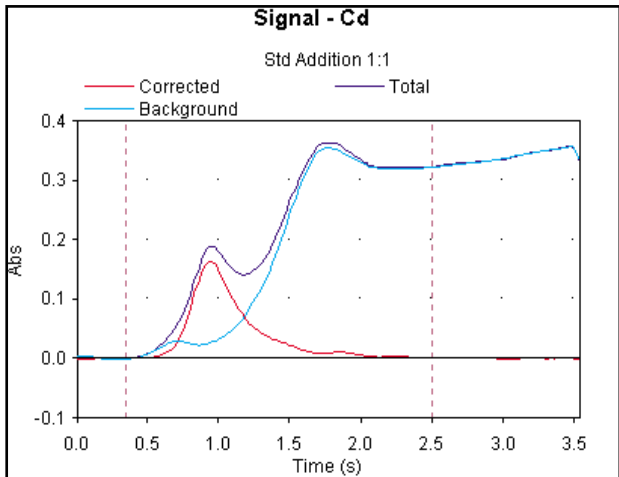


Figure 16a. Atomisation from Omega cuvette

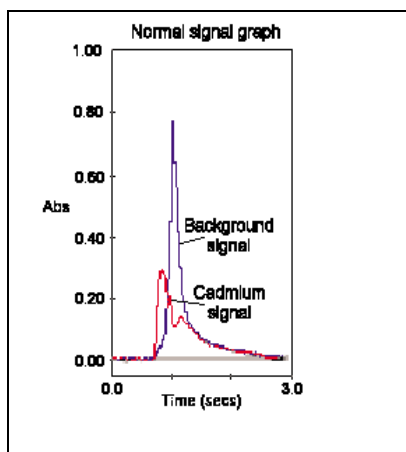


Figure 16b. Off-the-wall atomization

## (2) Chromium analysis

Finally an example of the use of the Omega cuvette for a more refractory situation is where both analyte and matrix require high temperatures, one for atomization and the other to remove the matrix. The analysis is to determine Cr in a 2.5% m/v calcium nitrate solution and dilution cannot be used due to the low concentration of Cr present. The refractory nature of the calcium matrix means that, even when high ashing temperatures are used, it is not possible to remove the matrix completely. Under these circumstances some degree of interference will be certain and the use of a platform would be desirable, although off-the-wall atomization and standard additions calibration work reasonably well.

Figure 17 shows off-the-wall signals for an ELC and platform atomization signals from the Omega cuvette, demonstrating the signal delay and enhanced peak area of the signal.

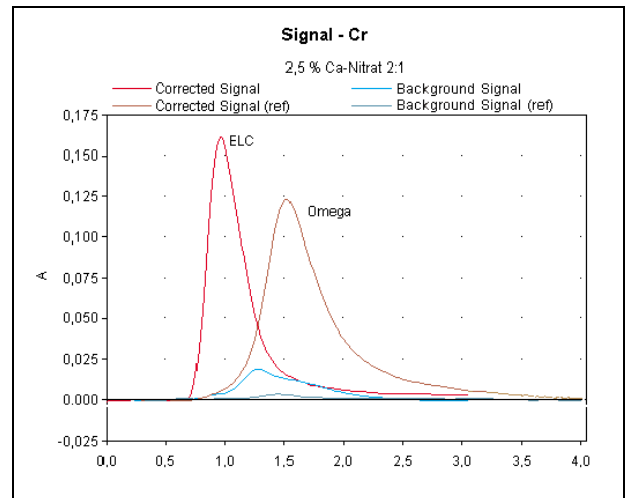


Figure 17. Comparison of a Cr signal from an ELC and the Omega cuvette

Results for both conventional off-the-wall/standard additions and the Omega cuvette can be seen in Figure 18. Analysis 105 is for the Omega cuvette and yields an answer of 25.4  $\mu\text{g/L}$  while Analysis 100 is for the conventional off-the-wall procedure, also producing an answer of 25.8  $\mu\text{g/L}$ . The good agreement indicates that the simpler Omega cuvette analysis can replace the longer standard additions procedure used previously.

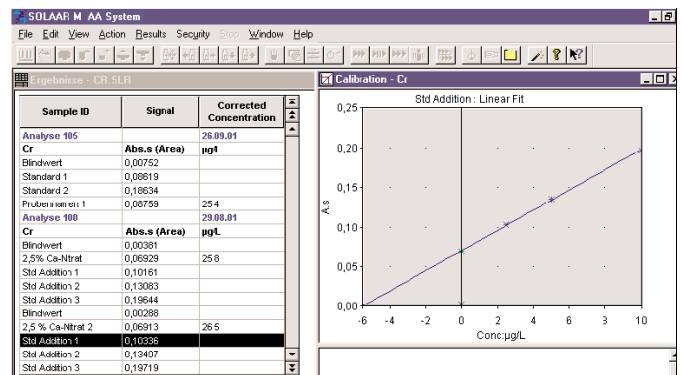


Figure 18. Results for Cr analysis using both Omega cuvette and off-the-wall/standard additions.

## Conclusions

In summary, the new Omega cuvette with integrated platform represents another step forward in the drive to produce interference-free analysis for the widest range of elements and matrix types. It has a number of clear advantages over the previous generation of platforms:

- (1) It is useable with less-volatile elements requiring quite high atomization temperatures.
- (2) It produces a more than adequate shift in appearance time which results in good interference correction for traditionally difficult matrices.
- (3) The increase in sample volume that can be accommodated enables better detection limits to be achieved.
- (4) The use of ELC technology ensures a cuvette/platform combination with considerably longer lifetimes than previously possible with typical thin pyrolytic coating products.

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