7 Injection methods for solid samples

7.1 Introduction to solid sample injection methods

The normal method of quantifying an ICP response is to integrate for a fixed period the constant signal produced when the analyte is fed continuously, at a constant rate, into the instrument. For aqueous solutions this continuous flow is easily achieved by nebulizers and hydride generators. For solid samples the continuous introduction of powdered material into the plasma has been attempted by methods such as insufflation (Dagnall et al., 1971) and spark elutriation (Scott, 1978), but these methods have not yet proved practicable for routine analysis. Spark ablation has proved to be much more satisfactory, but only for conducting samples. The results obtained are at best comparable with arc-spark spectrography for metallurgical work. However, nebulization of slurries by means of Babington nebulizers (section 3.4.6) seems likely to prove the best approach to the continuous introduction of solids, especially non-conductors.

In contrast to these continuous methods, there are also the discrete injection methods, that do not attempt continuous introduction of solid. They depend rather on the injection of a pulse of material derived from the sample. This in turn produces a transient signal from the ICP which rises from the baseline to

![Figure 7.1](image-url)  
Figure 7.1 The time-resolved response of a single channel of an ICP instrument after a discrete sample injection. The integration period shown (shaded area) includes most of the peak and as little as possible of the background.
a maximum, and then declines again to the baseline (Figure 7.1). Such a signal can be quantified by the maximum height of the peak above the baseline, as in graphite furnace atomization in atomic absorption spectrophotometry. However, it is generally recognized that the peak area is a more reproducible measure of the total analyte signal than peak height, and this is easily contrived on ICP instruments by integrating the signal from start to finish, incorporating as little as possible of the baseline signal in the integration.

Methods that have been attempted include: (i) electrothermal volatilization from various substrates, mostly graphite rods; (ii) direct introduction of the sample from a graphite rod into the plasma; (iii) volatilization of solid samples by means of a laser; (iv) the explosive release of material from fluid inclusions when they are ruptured by the internal pressure generated by heating; and (v) volatilization by thermolytic release of labile constituents when a sample is heated to moderate temperatures in a linear temperature gradient.

Many of these methods of introducing solids have been applied to geological and metallurgical samples, and some show considerable promise for future development. However, it is important to emphasize that solids injection methods are mostly experimental tools, still actively under investigation for specialist applications. They do not generally have the same status as the methods described in Chapters 4–6, which are well-established methods widely used for routine analysis. Nevertheless solid injection methods deserve attention because they demonstrate with clarity the ease with which ICP–AES can be applied to novel measurement tasks and, in effect, be used as a multielement detector for all kinds of analytical processes. Any material which can be converted either into a gas, or into a dispersed phase with particle size of less than about 5 μm, can be carried with the ICP in a stream of argon and hence analysed. Useful reviews of solids injection methods can be found in recent books (Routh and Tikkanen, 1987).

It should be noted that discrete sample injection methods require the use of a polychromator system for useful results. Off-peak methods for the correction of background interference cannot be applied to transient signals, so the only possibility for correction is the simultaneous on-peak method unique to polychromators.

### 7.2 Sample injection following electrothermal vaporization

The application of electrothermal vaporization to the discrete injection of sample material into the plasma is a direct use of a technique which has already been characterized in detail for AAS work. In the principal form of the method (for AAS analysis), sample solution is injected into a graphite tube located in the light path of the AAS instrument. After the water has been driven off and any organic matter destroyed by heating to about 500°C, the tube is suddenly raised to a high temperature (up to 2600 K) by resistive heating. Analyte atoms are liberated in the tube and cause absorption which