6 Gas phase sample injection

6.1 The development of gas phase injection methods

In principle the introduction of sample material in the gas phase is an ideal technique for the ICP. It would be widely practised if methods were available by which large suites of elements could be volatilized in a manner which was both convenient and compatible with ICP instrumentation. The principal benefits of vapour phase injection are (a) the avoidance of the use of a nebulizer, which is a major cause of problems in ICP–AES, and which sets a limit to the salt content of the test solution; (b) the potential for 100% efficiency of injection compared with a maximum of about 2–5% obtainable with a pneumatic nebulizer; and (c) the injection of a homogeneous medium into the plasma, which demands a lower power input to achieve complete atomization of the sample. Unfortunately few such gas phase injection systems have been proposed and, indeed, few are even conceivable which would operate at normal laboratory temperatures for a reasonably large suite of elements.

The elements germanium, tin, lead, arsenic, antimony, bismuth, selenium and tellurium form hydrides which are gaseous at ambient temperatures, and which can be generated easily from aqueous solutions. This capability has been exploited in AAS analysis since Fernandez (1973) showed that a convenient technique with good sensitivity could be obtained by the use of aqueous sodium tetrahydroborate (NaBH₄) as a reducing agent, atomization being effected by a cool flame. Since the work of Thompson and Thomerson (1974), who used a hot (800°C) silica tube atom cell, the AAS-hydride method has come into widespread use for the determination of these important elements which are otherwise rather difficult to determine. Smith (1975) showed, however, that there were numerous interference effects in the method, both chemical effects at the reduction stage, and compound formation problems in the atom cell. Clearly, if these gaseous hydrides could be injected into an ICP for an atomic emission source, at least two benefits would result, namely: (a) compound formation in the atom cell would be eliminated, and (b) a simultaneous determination for some of the elements could be attempted.

Early attempts by several investigators to inject hydrides into the plasma, however, met with little success. The main problem stemmed from the use of hydride generators similar to those popular at the time (and still currently used) for AAS work. These generators rely on the discrete addition of an
aliquot of sodium tetrahydroborate to the acidified test solution in a reaction vessel. The hydrides, plus much excess hydrogen, are then carried as a pulse into the atom chamber (Figure 6.1). The reaction vessel is then cleaned out and the process is repeated. The pulse of hydrogen has no deleterious effect in the AAS system as molecular hydrogen has little absorption at the relevant wavelengths. However, in the ICP, the introduction of hydrogen has two main effects: it reduces the background radiation, and it causes an impedance mismatch between the plasma and the generator, which results in high reflected power and often the extinguishing of the plasma. Thus results obtained when pulses of hydrogen were injected were erratic, and the system was difficult to use. Consequently attention drifted away from hydrides to other potential candidates for gas phase injection. As a result systems have been suggested or described for the generation of bromides and chlorides for injection into the ICP. However, the systems have presumably been impracticable for routine use, despite the reasonable number of elements encompassed, because of the elevated temperatures required to volatilize the halides.

Interest in the hydrides revived, however, when Thompson and co-workers (1978a,b) showed that stable plasma conditions could be achieved with hydride injection if the sodium tetrahydroborate solution and test solution were mixed in a continuous flow system. The rate of production of hydrogen is then constant and the radiofrequency generator can be tuned exactly to the impedance of the plasma. This results in stable plasma conditions and low