

10.3.4.6 Vapour generation methods

10.3.4.6.1 Chemical vapour generation systems

In *chemical vapour generation* the analyte is separated from the sample matrix by the generation of gaseous species as a result of a chemical reaction. This technique has received its widest application in atomic absorption spectrometry (AAS) in the forms of *cold vapour AAS (CVAAS)* for the determination of mercury and *hydride generation AAS (HGAAS)* for elements forming gaseous covalent hydrides (As, Bi, Ge, In, Pb, Sb, Se, Sn and Te). Chemical vapour generation is also used in combination with optical emission and atomic fluorescence spectrometry. *Carbonyl generation, halogen generation* and the generation of other volatile species have so far only been used rather exceptionally in spectrochemical analysis. The gaseous species generated, is introduced, usually with a stream of *purge gas*, into a sampling source for measurement by AAS or other atomic spectrometric methods.

The vapour-generating assembly, including gas flow controls and means for the addition of reactants used for the production of the volatile species, is the *hydride generator, mercury-vapour generator*, or other generator.

If specified volumes of the sample and reactant solutions are mixed at the beginning of the measuring process the generation proceeds in a *batch mode*. In a *continuous mode* the blank, the reference or the sample solutions are added successively to a continuous flow of the reactant.

In the continuous mode the volatile species formed is liberated from the reacting solution spontaneously in a *phase separator*. In the batch mode liberation takes place in the generator vessel and is accelerated by stirring, agitating or by passing a purge gas through the solution.

10.3.4.6.2 Gas flow systems

In a *direct transfer system* the purge gas transports the analyte directly to the sampling or excitation sources. In a *collection system* the analyte is carried to a collecting device called the *collector* which may be an amalgamator for mercury, a *cold trap* for some of the more stable hydrides, an *absorbing solution* in which the analyte is absorbed by some chemical reaction, an electrothermal atomizer, or a reservoir.

Collection systems may be used as concentrators, in order to lower the limits of detection. This is achieved if the analyte is released during a shorter time period, the *release time*, than, the *collection time*. A collector may also be used simply to make the vapour generation and the measurement independent in time and space or to separate interfering species. In this case *vapour generation with analyte collection* is equivalent to a separation technique, the collector then becoming the actual analytical sample (See Section 10.3.4.9.1).

10.3.4.6.3 Flow systems for mercury

For mercury released directly as atomic vapour, different direct transfer systems have been used. In an *open dynamic system* the liberated analyte is transported by a *carrier gas* through the sampling or excitation source and swept away. To eliminate the effects caused by the kinetics of reduction and liberation of mercury, equilibrium between the gas and liquid phases may first be established before mercury is swept through the sampling or excitation source.

In an (open) *static system* the equilibrated gaseous phase is forced into the *absorption cell* by displacement, e.g. by water. During measurement the gaseous phase is thus static.

In a *closed system* the analyte and carrier gas are circulated through the absorption cell and the generator vessel until equilibrium between the liquid and gaseous phases is established.

10.3.4.6.4 Sampling and excitation sources used with hydride generation techniques

For AES and AFS measurements a conventional plasma source such as an ICP or a microwave induced plasma is generally used. The flames used for AFS or AAS measurements are usually specialised types such as the *hydrogen diffusion flame* or the *inert gas-hydrogen diffusion flame* which have lower background absorbance and exhibit less quenching than premixed hydrocarbon flames yet have high atomization efficiency for hydrides.

For AAS measurements the *electrically-* or *flame-heated silica tube furnace* is most often used. In a *flame-in-tube atomizer*, hydrogen, used as carrier gas, is partially combusted in the inlet arm of a T-shaped tube furnace by introducing a limited amount of oxygen or air.