18 Gas source mass spectrometry

18.1 Geological applications

Geological applications of gas source mass spectrometry are centred on three specialized areas of analysis.

18.1.1 The measurement of stable isotope ratios of the elements H, C, N, O, S

Although stable in the sense that these elements are not radioactive, variations can occur in the isotopic abundances of these elements in geological samples. This arises because many physical and chemical processes in nature can induce mass fractionation between lighter and heavier isotopes of the same element. Fractionation can be caused, for example, by kinetic effects in chemical reactions, the rate of diffusion of molecular species through a porous matrix or the variations in the volatility of heavy and light water. The rate at which all these phenomena proceed is dependent to a small extent on the mass of isotopes participating. However, these effects are apparent only if the relative mass difference between isotopes of an element is large. Thus, at one extreme, there is a 100% difference between the mass of hydrogen (H) and deuterium (D), giving rise to a large potential mass fractionation effect. At the other end of the scale, the mass difference between $^{207}$Pb and $^{208}$Pb is only 0.5%. In natural samples, therefore, isotopic fractionation is detected only for elements lighter than about calcium and, of these, the elements which can be readily analysed as gaseous compounds are the ones which have received most attention. These include hydrogen (analysed as H$_2$), carbon (CO$_2$), nitrogen (N$_2$), oxygen (normally analysed as CO$_2$) and sulphur (SO$_2$). Applications include investigations of water–rock interactions, palaeotemperature measurements, ore genesis studies (S), the analysis of basaltic glasses to elucidate mantle processes, and meteorite studies.

18.1.2 Noble gas analysis

Considerable interest has been shown in the analysis of noble gases in silicate material to determine both the elemental abundance and isotopic composition. The elements of interest include helium, neon, argon, krypton and xenon. The latter two present considerable technical difficulties due to their very low abundances in terrestrial samples. These samples are of interest both for the estimation of the primordial noble gas composition of the Earth from the analysis of basaltic glasses, for example, and for the elucidation of nuclear synthetic processes involved in the formation of the solar system. In the latter field there is considerable activity in the analysis of meteoritic fragments.

18.1.3 Potassium–argon and $^{40}$Ar/$^{39}$Ar dating

The isotope $^{40}$K is a naturally-occurring radioactive species which decays, with a half-life of 1.25×10$^9$ years, to $^{40}$Ar and $^{40}$Ca. Following the development of sensitive gas source mass spectrometers in the 1950s there has been considerable interest in dating rocks by measuring the $^{40}$Ar content. In the case of conventional potassium–argon dating this involves determining the potassium content of the sample by an alternative technique, normally XRF or flame photometry. In the $^{40}$Ar/$^{39}$Ar technique, samples are irradiated in a nuclear reactor, inducing the production of $^{39}$Ar by neutron interaction with $^{40}$K. The age of the sample is then determined by measuring the $^{40}$Ar/$^{39}$Ar ratio by gas source mass spectrometry using a suitable reference sample as neutron dose monitor. Independent determination of potassium on a separate sample aliquot is not then necessary. The advantage of this latter technique is that by using a stepwise heating technique to extract $^{40}$Ar and $^{39}$Ar from a sample, it is possible to investigate the alteration history of the rock and decide if an age determination is primary.

18.2 Instrumentation

The general principles of mass spectrometric instrumentation have been discussed in Chapter 16. Gas source mass spectrometers are normally based on a single magnetic sector and differ from other forms of mass spectrometer in two respects. First, the ion gun is almost always an electron impact source in instruments designed for geological applications. (Chemical ionization sources are extensively used in instruments designed for organic molecule analysis.) Secondly, instruments are designed with double or triple collection of the ion beam (depending on the application), permitting simultaneous detection of isotope ratios of interest.

18.2.1 Electron impact ion source

Gas samples introduced into an electron impact source are ionized by collision with a stream of electrons, as shown schematically in Figure 18.1. The electron beam is created by thermionic emission from a filament. Traditionally, the filament is made of tungsten wire about 200 μm in diameter that requires a current of between 3–4 A to sustain an emission temperature of 2200 K. However, carbon, especially from cracked hydrocarbon molecules, can react with such a filament, forming a coating of tungsten carbide. This causes variable emission current densities. To overcome such problems, rhenium can be used a filament material as it does not form carbide or oxide coatings at its normal operating temperature, nor does it become brittle like tungsten. Unfortunately, rhenium has a significantly higher vapour pressure and therefore a shorter operating life.
The electrons emitted from the filament are collimated by slits and accelerated across an ionization chamber. The potential difference between filament and anode can normally be adjusted by the user between 0–100 V, 70 V being a normal setting. In order to minimize the energy spread of ions generated in the electron impact source, it is important to keep the electron beam as narrow as possible so that ions originate on an equipotential plane. This can be achieved by placing a small permanent magnet (50–300 gauss) across the gun so that any divergent electrons are deflected into helical paths away from the ionization region. It is desirable to surround the electron anode by an electron trap held at a potential of about 20 V higher than the ionization chamber to suppress secondary emission of electrons from the anode. The field strengths in the ionization region created by the drawing-out plate are kept small, perhaps 10 V cm⁻¹. All these factors help to minimize the energy spread of ions generated in the ion source.

Electron bombardment is a rather crude method of ionization. Ions so formed are given considerable vibrational and rotational energy during the ionization process. Sufficient energy transfer occurs to break up a fraction of molecular species into ionic fragments. Thus the ion spectrum of CO₂ will also contain CO⁺ fragments, for example. Since the electron beam is not mono-energetic, and energy transfer during electron–molecule impact is not constant, a range of translational energies will be imparted to the resulting ion species. The maximum energy spread is generally considered to be in the range 0.5–3 eV. Once ions have been drawn out of the ionization chamber they are accelerated through a potential of several kilovolts. Since the energy spread of ions is small compared with this accelerating potential, the effect on degrading mass spectrometer resolution is small.

The efficiency of ionization depends in part on the voltage applied between filament and anode of the electron gun. The relative ion yield as a function of this gun accelerating potential is plotted for argon in Figure 18.2. Gases usually show a maximum ion yield in the range 50–100 V, and 70 V is frequently selected for the ionization of heavier gases.