CHAPTER 9

Mass Spectrometry in the Environmental and Surface Sciences

9.1 ENVIRONMENTAL ANALYSIS

The mass spectrometer is the most widely used detector to analyse the effects of natural and man-made substances on the environment. Social pressures as well as the need for ecological sustainability have necessitated that changes to our environment are monitored with some precision. The Earth's growing population has placed increased demands on the planet's resources and there is now a greater appreciation than ever before of the affect of man-made pollutants and wastes on the environment and their impact on climate change. The compounds studied by mass spectrometry include heavy metals, man-made pesticides, components of industrial waste and their by-products, disinfecting agents, explosives, and those excreted or obtained from naturally occurring algae, toxins and microorganisms. These substances are often present at trace levels within complex mixtures and can only be studied using a mass spectrometer.

9.1.1 Heavy Metals and Elemental Analysis

Although trace concentrations of some metals such as iron and zinc obtained from certain foods are essential to our well-being, others such as lead and mercury have long been known to cause serious adverse effects to human health. Exposure to lead in paints, petrol and other industrial waste, for example, has long been associated with mental illness and even paralysis. Lead has four natural isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb of which the latter three are produced by radioactive decay of isotopes of uranium and thallium.

9.1.1.1 Thermal Ionisation Mass Spectrometry. Thermal ionisation mass spectrometry (TIMS) is a common technique applied to the

analysis of elements at low ng g^{-1} levels in environmental samples. In TIMS, a small volume of an aqueous sample solution containing between μg and ng of the element of interest is deposited onto a clean filament surface and evaporated to dryness. The filament, usually composed of a thin film of ruthenium, is heated to thermally evaporate the sample. A second like-filament that emits electrons to ionise the sample. Thermal ionisation is highly selective, with different elements ionised according to the filament temperature at any point in time. Isotopes are separated and detected simultaneously using a magnetic sector mass spectrometer equipped with a multiple ion collector.

9.1.1.2 Inductively Coupled Plasma Mass Spectrometry. Inductively coupled plasma mass spectrometry (ICP-MS) is also widely used for elemental analysis (Figure 9.1). The sample, usually in a liquid form, is introduced at approximately 1 ml min^{-1} via a nebuliser where it is converted into a fine aerosol with a gas (normally argon). The fine droplets of the aerosol are transported into the plasma torch *via* a sample injector where they are converted from a liquid aerosol to a solid and then to a gas. This sample gas is then "atomised" and ionised. Ionisation is achieved by electron impact using electrons from a high-voltage spark. This results in a high temperature (~7,000 K) ion plasma being emitted from the open end of the tube which reflects the elemental composition of the sample. Solid samples can be analysed directly by *laser ablation ICP-MS*. Here a portion of the sample is ablated by a laser in an inert atmosphere (usually of argon) under atmospheric pressure and then atomised and ionised in the plasma.

Most commercial ICP mass spectrometers contain a single ion detector to detect elements to low part-per-trillion (ppt) levels. However, specialised magnetic sector ICP-MS instrumentation fitted with multiple detectors are also used for isotope ratio analysis (see also Section 9.2).

The concentrations of heavy metals such as chromium (Cr) in soil and

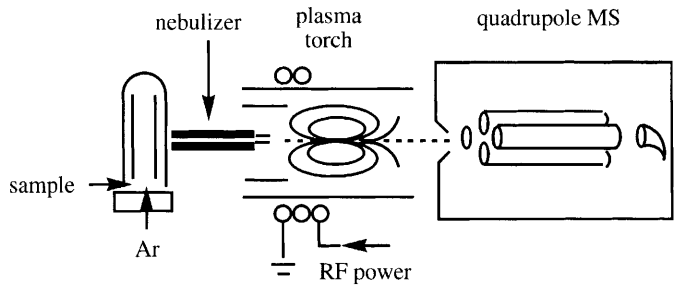

Figure 9.1 *Schematic representation of an inductively coupled plasma mass spectrometer (ICP-MS) featuring a quadrupole mass analyser*

water samples have been analysed by ICP-MS. Cr(VI)-containing compounds are found in the environment as a result of industrial pollution and fertilisers. Ion exchange chromatography has been coupled to ICP-MS to measure chromium levels in waters from industrial waste and sewage treatment plants. Both cationic Cr(III) and anionic Cr(VI) species were detected below 0.5 μg/l by monitoring ^{52}Cr using ICP-MS.

A disadvantage of ICP-MS is that there is a multitude of plasma-derived chemical reactions that can occur, resulting in molecular ions that can mask or diminish ions of the elements of interest. In order to improve detection limits and/or reduce the amount of sample that needs to be analysed, alternate low-pressure helium sources have been constructed with collision cells used to dissociate molecular ions formed within the plasma.

9.1.1.3 Isotope Dilution. Isotope dilution is a method used in conjunction with TIMS and ICP-MS to quantitate the elemental abundances of trace elements that contain two or more naturally occurring isotopes. It does so with unmatched sensitivity and accuracy and thus is in widespread use. The isotope dilution method involves spiking and blending the sample (S) of interest with a reference (R) material containing the same element at known concentration. The quantitation of trace elements in the samples is then determined by equation 9.1 where Q_S is the element concentration of interest, Q_R is the concentration of the element in the reference material, R the ratio of isotopes in the reference, S the isotope ratio of the same isotopes in the sample, B the isotope ratio of the elements in the blend, m_S the atomic mass of the lighter isotope for the element, and $m_R$the atomic mass of the heavy isotope.

$$Q_s = Q_R(R - B)\, m_S/(B - S)m_R \tag{9.1}$$

To minimise errors, the purities of samples S and R must be approximately the same and the mass spectrometric measurements recorded under the same conditions. When this is observed, measurements to within 0.1% of true values are possible.

TIMS in conjunction with the isotope dilution method has been used in environmental research to determine heavy metals in the atmosphere. The presence of thallium in the atmosphere over Antarctica was measured at 0.2 pg m^{-3} using this approach.

9.1.2 Organic Pesticides

GC and LC coupled mass spectrometric-based methods are preferred over other analytical approaches for the characterisation and

quantitation of organic pesticides. New pesticides are developed every year, in part to keep abreast of the resistance of insects and other pests to existing ones. For each new pesticide, a thorough evaluation of its fate in the environment is required including knowledge of its transport properties and degradation products. Pesticides can accumulate in soils, infect ground water and water supplies and be ingested by humans by way of crops and livestock. An accurate measure of the levels of pesticides in the environment is routinely needed in order to minimise their adverse effects on human health.

Some modern pesticides are active as a single enantiomeric form such that regulatory authorities mandate that only this enantiomer may be administered where the inactive enantiomer has a low degradation rate. This necessitates that enantiomeric forms of a pesticide in a racemic mixture are resolved and independently quantified in environmental samples.

As an illustration, soil samples from the south-east of Spain treated with the propionic acid-derived herbicides mecoprop and dichloroprop were characterised by HPLC using a chiral stationary phase and GC-MS. Selected ion chromatograms from the GC-MS analysis of mecoprop (MCPP) (*m/z* 169) and dichlorprop (DCPP) (*m/z* 189) show that the methylated forms of *R,S*-MCPP and *R,S*-DCPP are clearly resolved in two soil samples (denoted a and b in Figure 9.2).

Quantitation of the ion signals demonstrated detection levels of greater than 80% for both MCPP and DCPP from control soil-doped experiments. For each pesticide, the *R*-enantiomer was found to degrade faster than its inactive *S*-form.

9.2 ISOTOPE RATIO MASS SPECTROMETRY

Beyond the characterisation and quantitation of compounds in the environment, isotope ratio mass spectrometry can be used to distinguish the source of such chemicals. The uptake of water, nitrogen and carbon in plants, nutrient transfer in aquatic ecosystems, and the rates of chemical and biochemical degradation processes can all be studied by mass spectrometry.

Isotope Ratio Mass Spectrometry (IRMS) is performed using a specially constructed mass spectrometer designed to maximise ion beam stability and sensitivity at the expense of mass resolution. These instruments (Figure 9.3) usually feature an electron impact source with a gas inlet. As in a single magnetic sector mass spectrometer (described in Section 3.3.2), ions are accelerated down a flight tube between a magnet where their curved trajectories depend on the ion's *m/z* ratio (equation

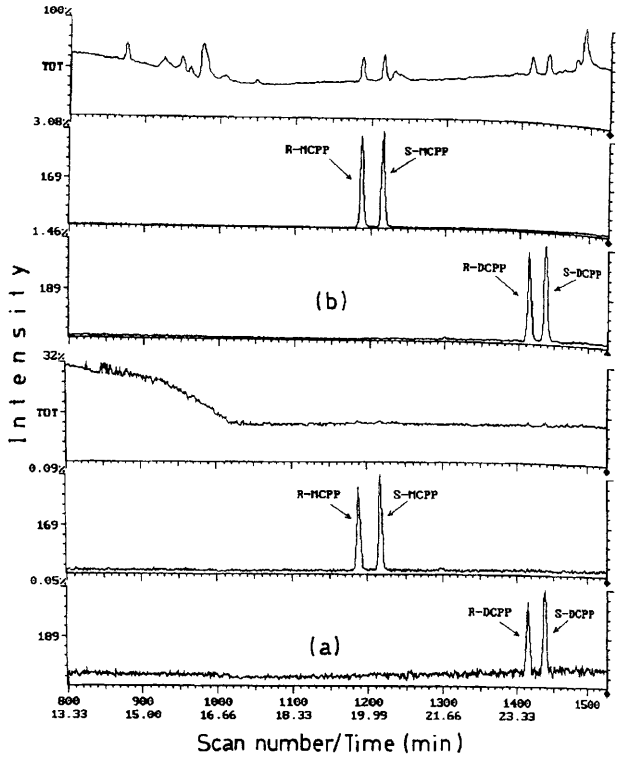

Figure 9.2 *GC – MS chromatograms of methylated* R- *and* S-*MCPP plus* R- *and* S-*DCPP in a silty loam sample (a) without and (b) with added peat. In both cases, the total-ion chromatogram and the single-ion chromatograms corresponding to* m/z *values of 169 (specific for the enantiomers of MCPP) and 189 (for those of DCPP) are shown*
(Source: F. Sánchez-Rasero, M.B. Matallo, G. Dios, E. Romero and A. Peña, Simultaneous determination and enantiomeric resolution of mecoprop and dichlorprop in soil samples by high-performance liquid chromatography and gas chromatography – mass spectrometry, *J. Chromatography A*, 1998, **799(1–2)**, 355–360, Figure 2)

3.22). Instead of scanning the magnetic field or accelerating voltage, these values are fixed for a particular measurement to transmit to the Faraday cup detector (Section 3.4.1) ions with a *m/z* range of just a few mass units. The mass limit of an isotope ratio mass spectrometer is typically 100.

Slits on the instrument are large to maximise ion transmission. As a result, the ion signals typically have a flat top (Figure 9.4). Isotope ratios are measured based upon the area under the isotopic ion signals. The analytes are often simple gases such as H_2, O_2, N_2 and CO_2 or pyrolysis or combustion products formed by heating of the sample at

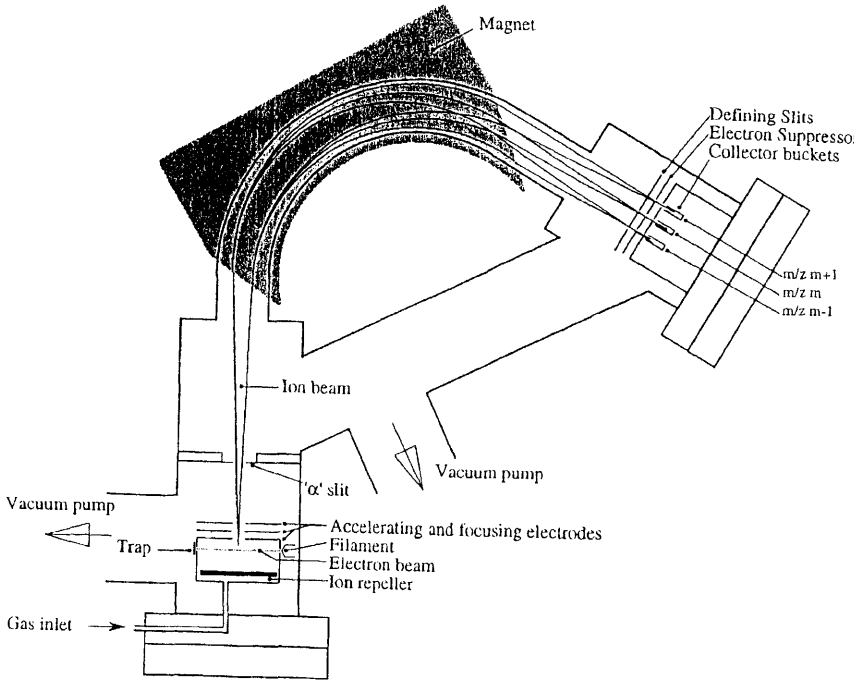

Figure 9.3 *Schematic diagram of an isotope ratio mass spectrometer* (Source: A. Barrie and S.J. Prosser, in *Mass Spectrometry of Soils*, T.W. Boutton and S.-I. Yamasaki (ed), Marcel Dekker, New York, 1996, Ch. 1, p. 9, Figure 1)

high temperatures. A gas chromatograph can be used to separate these combusted species prior to entry into the ion source.

9.3 PORTABLE MASS SPECTROMETERS

There are many instances where it is desirable to analyse environmental compounds or organisms in the field. A variety of miniature, portable mass spectrometers have been used for this purpose. Small quadrupole ion trap and time-of-flight mass analysers are typically employed over heavier magnetic-based instruments. These truck or hand-portable mass spectrometers are used by government laboratories, academic researchers and by the military in applications as diverse as environmental monitoring, forensic science, oceanographic research, and the detection of nerve gas and other agents of warfare.

Field portable GC-MS mass spectrometers feature a sensing device or sniffer with which to sample volatile agents in air. Submergeable mass spectrometers have also been developed for oceanographic research to

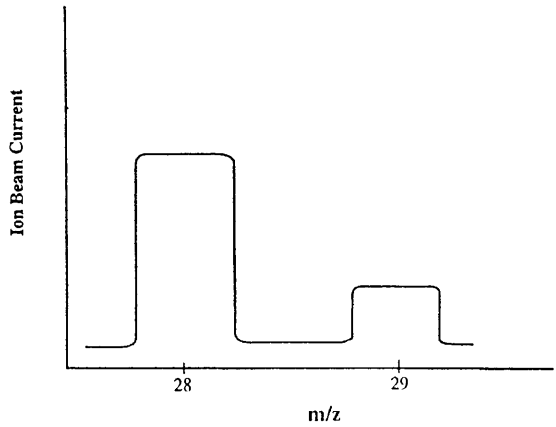

Figure 9.4 *Ion signals measured on a isotope ratio mass spectrometer typically have a flat top*
(Source: adapted from A. Barrie and S.J. Prosser, in *Mass Spectrometry of Soils*, T.W. Boutton and S.-I. Yamasaki (ed), Marcel Dekker, New York, 1996, Ch. 1, p. 10, Fig. 2)

monitor water quality, including the influences of tidal flows or the effects of dredging on water quality. These analytical measurements have particular challenges for a mass spectrometer including maintaining a vacuum in such an instrument underwater, providing a sufficient power source during the course of the experiments, transmitting the data to the shore, and sampling the analytes underwater. This latter challenge can be met by using *membrane introduction mass spectrometry* (MIMS) in which a sample is exposed to a semi-permeable membrane through which compounds are selectively transferred into the mass spectrometer. Components, sampled from such environments, can be analysed in concentrations down to the parts-per-trillion level.

Despite their ban under the Geneva Protocol of 1925, chemical warfare agents have continued to be produced and in some cases inflicted on both military and civilian populations. Military personnel are particularly susceptible to exposure to chemical weapons. These include mustard gas and lewisite that cause blistering of the skin, diphenylcyanoarsine that leads to vomiting, tearing agents and the nerve agents sarin, tabun and so-called VX. Aircraft, ground-based vehicles or personnel can carry portable mass spectrometers to check for such agents prior to the deployment of large numbers of troops. The EI mass spectrum of mustard gas or 1,1-thiobis(2-chloroethane) is shown in Figure 9.5. Mustard gas is a highly fat soluble compound and accumulates in tissues with a high fat content. Absorption of just a few milligrams of mustard gas within human tissue can be fatal.

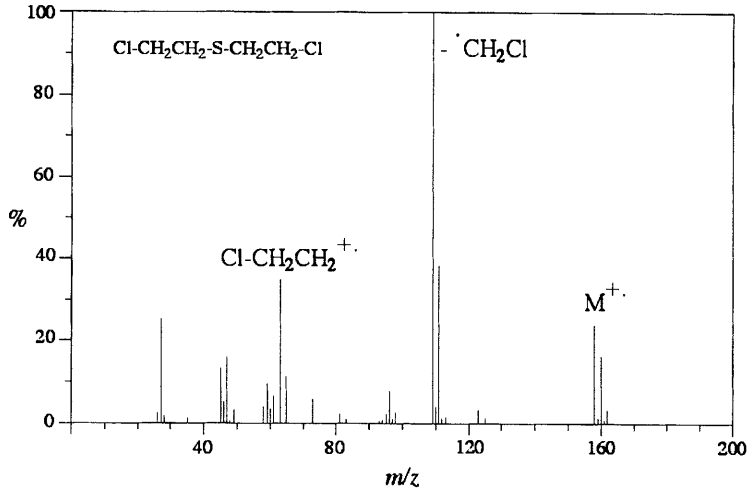

Figure 9.5 *EI mass spectrum of mustard gas or 1,1-thiobis(2-chloroethane)* (Source: RSC database)

9.4 CHEMISTRY OF THE EARTH'S IONOSPHERE

The Earth's atmosphere and ionosphere are rich in ion chemistry made possible due to the production of ions by electrical discharges and radiation. A significant understanding of the chemistries above the surface of the planet has been achieved by experiments that mimic such processes in the laboratory and by *in situ* measurements using rocket-borne mass spectrometers. Of particular interest is the effect of man-made pollutants on the Earth's atmosphere.

The Earth's atmosphere is divided up by altitude according to a range of criteria where the ionosphere is described as the region where free electrons exist at some 60–1000 km above the Earth's surface. At the highest altitudes, levels of solar radiation are the greatest but since there are few atoms or molecules present, few ions form. Below the ionosphere, electrons spontaneously react with gases to form both positive and negative ions. From the standpoint of ion chemistry, most can be classified as occurring at low altitudes below some 80 km, or at high altitudes or low pressures above this height. The lower atmosphere above 10–15 km is defined as the stratosphere and below that the troposphere where the major gases present are oxygen (21%) and nitrogen (78%) together with argon and varying amounts of water, carbon monoxide and dioxide, and nitrogen dioxide.

In the upper atmosphere, solar radiation reaches the earth at a power of 1.37 kJ m^{-2} s^{-1}. The photoionisation of an atom of oxygen by solar

radiation in the ionosphere results in $O^{+\bullet}$ (Chapter 2, equation 2.1) that can subsequently react to form the molecular ions $NO^{+\bullet}$ and O_2^+ (equations 9.2 and 9.3).

$$O^{+\bullet} + N_2 \rightarrow NO^{+\bullet} + N^{\bullet} \tag{9.2}$$

$$O^{+\bullet} + O_2 \rightarrow O_2^+ + O^{\bullet} \tag{9.3}$$

Rates for these reactions have been measured in the laboratory within high pressure and flowing afterglow mass spectrometers to be approximately 1.2×10^{-12} cm^3 s^{-1} and 2×10^{-11} cm^3 s^{-1} respectively at 300 K.

Cluster ions are also evident in the ionosphere formed by the weak association of water, nitrogen (equation 9.4) and carbon dioxide with ions in three-body associations.

$$NO^{+\bullet} + nH_2O + N_2 \rightleftharpoons NO^{+\bullet}(H_2O)_n(N_2) \tag{9.4}$$

Cosmic rays are the primary ionisation source in the stratosphere and upper troposphere. One reaction of interest within the stratosphere is the recombination of molecular oxygen with oxygen atoms to form ozone. This gas reaches a peak density of a few parts per million at an altitude of 25 km above the Earth. The ozone layer protects the Earth from ultraviolet (UV) radiation that can penetrate the atmosphere by absorbing this radiation and dissociating back to its constituents. Negatively charged ions have been postulated to regulate ozone levels in the lower atmosphere as illustrated in equation 9.5 though this has been questioned based on a measured rate for this reaction.

$$NO_3^- + O_3 \rightarrow NO_2^- + 2O_2 \tag{9.5}$$

It has further been shown that most ions do not react with man-made pollutants such as trichlorofluorocarbon ($CFCl_3$) and as such these pollutants cannot be depleted before they reach the stratosphere where they degrade ozone levels.

9.5 MASS SPECTROMETERS IN SPACE

It might be argued that the best environment in which to operate a mass spectrometer is one in natural vacuum. Beyond the environment within and around our own planet, mass spectrometers have been employed in space to study the cosmos. Expeditions to Mars, investigations of interstellar dust and the chemical composition of the tails of comets have all involved mass spectrometers. Earlier mass spectrometry experiments were performed on rocks returned to Earth during the Apollo missions.

9.5.1 Apollo Missions

Samples of the lunar surface returned to Earth as part of the six Apollo missions 11–17 (except the ill-fated Apollo 13 mission!) were subsequently examined by mass spectrometry. NASA scientists used *secondary ion mass spectrometry* (SIMS) (Section 3.2.5) to analyse the elemental composition of the moon rocks. This data has shown the moon to be enriched in the elements aluminium, uranium and thallium, in addition to ferric oxide, over that found on Earth. Samples obtained from the lunar highlands are rich in potassium, phosphorous and rare earth elements. The distribution of these elements on the lunar surface provides information about how the lunar crust was formed and has evolved over time.

Samples of finely pulverised lunar surface material were also analysed for traces of organic compounds by GC-MS. Samples were volatilised directly, after extraction with benzene and methanol, or extraction and pre-treatment with hydrogen fluoride and chloride. A number of organic compounds were detected at concentrations of less than 1 ppm, but all could have been associated with contamination on Earth and therefore no evidence of life (as we know it) on the surface of the moon has been found to date.

9.5.2 Viking and Mars Express Missions

To preclude the possibility of contamination of returned specimens, the objectives of the Viking experiments were to sample the composition of the atmosphere at the surface of Mars and to identify any volatile organic and inorganic compounds on the surface at the landing site. These data were measured directly at the surface of Mars and transmitted electronically back to Earth. The Viking spacecraft of the 1975 mission transported a Mars lander fitted with a gas chromatograph mass spectrometer designed for isotope ratio experiments.

Analysis of the atmosphere found the isotopic levels of oxygen to be within 10% of those values on Earth. A higher level of ^{15}N (74%), however, was detected at the surface of Mars with an isotope ratio of $^{15}N/^{14}N$ of 0.0064 (without background correction). ^{38}Ar was also detected above the Martian surface.

Soil samples collected at the Martian surface were robotically loaded into a pyrolysis source at the lander site and heated to 500 °C in a series of three chambers. The volatiles were passed into the carrier gas stream of a gas chromatograph interfaced to a mass spectrometer operating over

a mass range of 12–200. The data, together with operating parameters, were transmitted back to Earth from the Martian surface. Only water and carbon dioxide were detected in these measurements and there was no evidence or organic compounds above the detectable levels of a few parts-per-billion. The absence of such compounds at the lander site does not preclude that life as we know it could be found elsewhere on the planet surface or interior. It is also possible that traces of micro-organisms in the samples did not release sufficient levels of organic material for detection or that such organic matter had been destroyed on the surface by solar radiation.

An opportunity to re-evaluate the planet's surface was afforded by the European Mars Express mission of late 2003 in a British-led expedition. The Beagle 2 lander carried an onboard minature 90° sector mass spectrometer with a magnet weighing less than 1 kg. It was fitted with a dual inlet source so that light elemental samples and standards can be sequentially studied in high precision isotope ratio measurements. Regrettably, signals from Beagle 2 were lost leaving its fate unknown and mysteries of the Red planet firmly intact.

9.5.3 Composition of a Comet

Unlike Mars, there is little doubt that organic compounds are ubiquitous within the nuclei of comets. There is considerable data to support the existence of molecular species within a comet. Data from ground-based spectroscopic measurements have been supplemented by both spectroscopic and mass spectrometric measurements in the Giotto and Vega missions to Halley's comet. Water makes up about 80% of the volatile content of the comet but hydrogen cyanide, carbon monoxide and dioxide, methanol, ammonia and formaldehyde have all been detected. Many of these molecules are likely to be ionised fragments of even larger parent molecules. The identity of these parent molecules, however, is not known since it is virtually impossible to observe the comet surface directly, even when a spacecraft is nearby.

The dust from Halley's comet was also examined using mass spectrometers on board both the Giotto and Vega probes. Of primary interest was the detection of intermediate-sized organic compounds that gave rise to mass spectra with ion signals separated by repeating 14–16 mass units. These ions indicated that the molecules exhibit a linear polymeric structure interpreted to be a signature of hydrocarbons, with a repeating $-(CH_2)_n-$ structure. The Giotto and Vega spacecraft further revealed a substantial enrichment of ^{12}C over that observed on Earth indicating an interstellar source for some of the organic compounds.

9.6 APPLICATIONS OF SECONDARY ION MASS SPECTROMETRY TO MATERIALS SCIENCE

Beyond moon rocks and interstellar particles, *secondary ion mass spectrometry* (SIMS) (Section 3.2.5) is in widespread use for the analysis of solid surfaces and materials, including thin films and semiconductors. SIMS is used to detect atomic ions as well as molecular ions, the latter often detected as clusters. Detection limits of the order of 10^{12} and 10^{16} atoms per cubic centimetre. Mass interferences (peaks from different molecules or atoms that share a common *m/z* value) are a common feature of SIMS experiments, and it is necessary to anticipate them in advance such possibilities in the design of an experiment.

9.6.1 Depth Profiling

Since the primary ion beam can be focused to a diameter of less than one μm, SIMS provides a means with which to characterise a surface with high resolution. Where continuous sputtering of the surface is performed, an analysis of the material as a function of depth (a depth profile) can be produced. Typical surface depths are of the order of 1 nm. This analysis is useful in industrial applications in order to study the quality of manufactured coatings or the processes used to construct them. A SIMS depth profile of a stainless steel surface coated with layer of titanium is shown in Figure 9.6. The figure shows that the titanium coating has a depth of 1.4 μm.

One application of SIMS is *ion microscopy*. Here the primary beam is focused on the sample over an area of approximately 10 μm. Secondary ions released from the surface are passed into an electrostatic mirror in which they are energy-focused and reflected back to the mass analyser and onto an image converter. The image converter translates the spatial distribution of the atoms on the surface onto a fluorescent screen for visualisation. In combination with a depth profile, ion microscopy enables three-dimensional maps of a material over a diameter of 250 μm to be constructed with resolutions of the order of 1 μm. Larger surface areas can also be studied though usually at reduced resolution.

9.6.2 Analysis of Impurities

The characterisation of surfaces containing aluminium, silicon, tungsten, gallium and titanium has been accomplished using SIMS including the identification of impurities such as oxygen. The strength

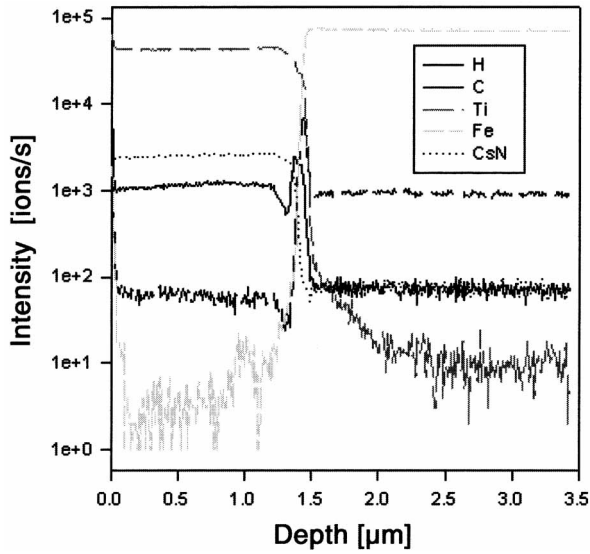

Figure 9.6 *SIMS depth profile of a stainless steel surface coated with layer of titanium. The titanium has a depth of 1.4 μm*

and mechanical properties of metals and polymers can be substantially altered by the presence of inert impurities or gas pockets. SIMS has found particular application in the semiconductor industry since impurities or doped elements incorporated into the material can either reduce or enhance the electrical properties of the material. Semiconductors are usually constructed of single crystals of silicon and gallium within which undesired impurities must be kept well below the 1% level.

SIMS analysis can determine the distribution of trace levels of impurities (down to 10 pg per gram of material) in high purity materials in three-dimensions. In the case of borosilicate glass, it can reveal impurities such as lithium and sodium at particular depths that can be responsible for weaknesses and subsequent fractures. It can also be exploited to examine glass coatings used for optics in scientific and industrial applications.

9.6.3 Reaction Catalysts

SIMS has been further applied to the study of reaction catalysts in terms of their molecular structure and that of their clusters. Transition metal complexes are one type of catalyst that can promote chemical transformations without being consumed during a reaction. The structures

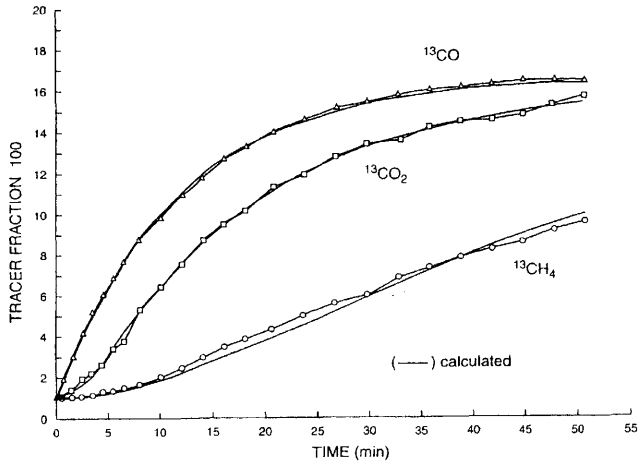

Figure 9.7 *Conversion of carbon monoxide into methane above a nickel catalyst followed by SIMS using a ^{13}C tracer*
(Source: M. Otarod, S. Ozawa, F. Yin, M. Chew, H.Y. Cheh and J. Happel, Multiple isotopic tracing of methanation over nickel catalysts, *J. Catalysis*, 1983, **84**, 156–159)

of metal complexes such as nickel oxide have been studied on polymeric supports and oxide coatings. The poisoning of such catalysts has also been investigated by mass spectrometry.

Nickel oxides act as catalysts to promote the conversion of carbon monoxide and molecular hydrogen into methane above their surface which can be followed by SIMS (Figure 9.7). When hydrogen disulfide is used to "poison" the catalyst, a reduction in the formation of methane can be followed as a function of the proportion of the nickel oxide surface covered with sulphur.

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