JOURNAL OF MATERIALS SCIENCE 3 (1968) 259-261

An Instrument for Mass Analysis using a Laser

N. C. FENNER, N. R. DALY
UKAEA, Atomic Weapons Research Establishment, Aldermaston, Berks, UK

Received 27 November 1967

An apparatus has been constructed that will give a complete elemental analysis of a solid sample in the size range 10^{-8} to 10^{-10} g. The beam from a *Q*-switched ruby laser is focused on to the sample, and the ions produced are used to give time resolved spectra. Analysis of several types of sample is described, illustrating the capabilities and limitations of the instrument.

1. Introduction

The analysis of the materials that go to make up a given sample has been one of the major interests of science since its earliest times. There are few techniques available at the present time, however, for the analysis of solid samples weighing less than 10^{-8} g; these include the electron microprobe, the laser microprobe, and the mass spectrometer. For instance, the spark source mass spectrometer will analyse elements present in only 0.01 ppm from very small samples, but at 10^{-8} g this instrument is running into problems of sample handling and sensitivity. The instrument described in this paper is a mass spectrometer capable of giving a semiquantitative analysis of the elements in a sample in the range 10^{-8} to 10^{-10} g. The method is based on ionisation by irradiation with a laser beam, followed by energy selection and time of flight analysis.

2. Basic Features of the Instrument

The sample, normally in the form of a thin foil, a fine fibre or a small particle, is held at the focus of the beam from a *Q*-switched ruby laser. The laser delivers up to 3 millijoule in 30 nanosec, and when focused gives a power density of about 10^{10} watt/cm^2. This very high energy input to the sample vapourises and ionises it in a small plasma region. The plasma absorbs most of the laser energy, and reaches a very high temperature ($\sim 10^5$ ° K), and a pressure of several atmospheres. The mechanism of ion acceleration is not completely understood, but the plasma rapidly expands, giving some ions a forward velocity of the order of 10^6 cm/sec. The ions from a sample consisting of many elements all have the same velocity distribution [1] and so to separate them for time of flight analysis they are passed through a parallel plate energy selector. The potential difference between the plates is set to cover the required range of ion masses, and is normally set to select ions of 20 eV. Since all the selected ions now have the same energy, the velocity and therefore the time of flight vary with the ion mass. The ions are recorded by a magnetic scintillation detector [2], and the signal is fed to an oscilloscope and photographed.

In earlier work [3] a small number of ions were produced, accelerated to 5 kV and drifted down a 1 m tube before energy selection. In the present apparatus, a larger number of ions are produced and it is not possible to accelerate them, owing to the density of the plasma formed near the laser focus. Fig. 1 shows the apparatus used at present consisting of a short drift space, to allow the plasma to expand, the electrostatic analyser, and the detector.

Fig. 2 shows a typical picture of the oscilloscope trace (the top trace being 10× amplification of the lower trace); the distance along the trace is characteristic of the mass of the element, and the area under the peak is its abundance in the sample. This trace covers the whole mass range (from 1 to 250), and as the time separation of the ions is proportional to the square root of the mass, elements with the same weight *difference* are closer together at the end of the trace. The resolution of the instrument is 30 at

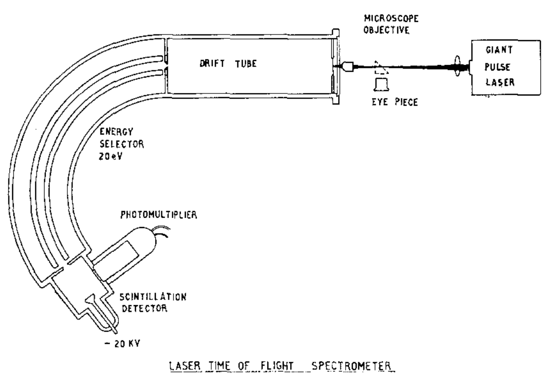

Figure 1 A line drawing of the apparatus showing the most important features.

mass 30, but falls off at higher masses, owing to the square root law and also to space charge effects in the analyser.

The energy selection has the effect of taking the ions of different elements from a different part of the velocity distribution, and so a correction factor must be used, particularly for elements at the ends of the periodic table. Some correction is also required because, although at "normal" laser power the ionisation is high, it is found that elements with low ionisation potential are preferentially ionised. This effect is less marked if higher powers are used, but in this case a substantial fraction of ions are doubly ionised and this complicates the spectrum. Because of these two effects the analysis does not give a direct elemental composition, but requires calibration.

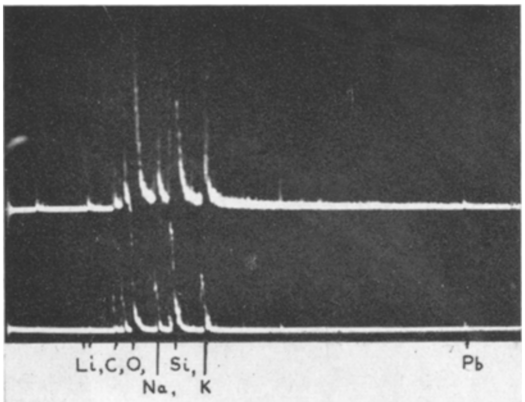

Figure 2 A photograph obtained from the analysis of a chip of lead glass with 8 at. % of lithium added.

3. Types of Sample Analysed

3.1. Glass to Calibrate the Instrument

Glass was chosen as a material suitable for calibration purposes because with careful mixing it should be reasonably homogeneous down to the 3 μm level, and it can be made with a wide selection of elements. Two glasses were used in this calibration; one made by mixing lithium into a lead glass, the other made specially by Pilkington Brothers, Research and Development Laboratories, Lathom, and containing the elements Li, Na, Si, Ba, Pb, and O. The glasses were ground and chips 5 to 10 μm were analysed, and from the results correction factors for a number of elements were deduced. Fig. 2 is a trace from the lead glass showing a wide range of elements. The errors on these factors were rather larger than had been hoped, being over 10 % on the major elements and up to 50 % on those that are about 10 % abundant. These factors and their errors also tend to be larger for elements at each end of the periodic table, where ions are taken from the extremes of the velocity distribution. The factor also depends to some extent on the laser power for a given sample weight, and the selection of laser power is the most important factor in the analysis of samples at the present time. Unfortunately this is a particularly acute problem in the case of glass which is normally transparent to red light, and is initially heated only by second order effects due to the high power density.

Several other samples in the form of small particles of material in the 5 to 10 μm range have been analysed with the instrument, although the results obtained are only semiquantitative, because the correction factors and their errors quoted above must be applied to them. The instrument has been used, however, to identify the origins of some samples from their composition and, on other occasions, to show that the sample was not the material that had been expected from other considerations.

3.2. Ceramic Whiskers

Measurements were made on whiskers of alumina that were being grown by new techniques. Many of the fibres resulting from one process, although strong, were cellular in shape, looking more like rope than smooth fibres. Analysis showed that these were mainly organic in origin, although many had silicon and aluminium in their structure. There was also a 1 % level of argon in the fibres. This was presumably trapped in the organic fibres from the inert atmosphere of the process. From a second technique, fine whiskers were produced which were shown to be alumina with very few impurities. This process also produced some large plate-like fibres which had a large proportion of carbon, at least on the edges. Analysis of the bulk of these large whiskers was not possible because most of the laser power was absorbed in evaporating material and insufficient ions were produced for a meaningful analysis.

3.3. Human Hair

Analysis of a human hair was undertaken in the first place to test the reproducibility of the analysis from shot to shot. A single hair was mounted and several shots were made along its length. As expected, the main elements detected were carbon, nitrogen, and oxygen. The hydrogen did not appear as a large peak for the reasons given above about energy selection over the whole mass range. We clearly observed also many of the elements present in only small amounts, e.g. sulphur, calcium, sodium, and potassium.

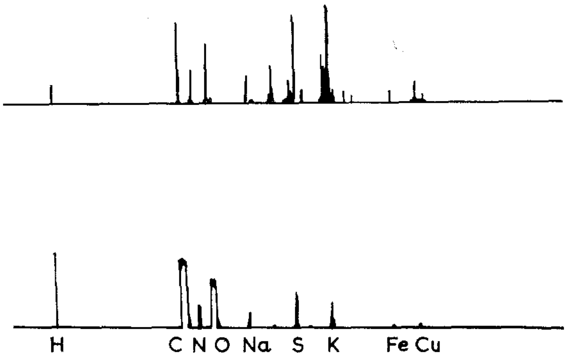

Figure 3 A line drawing of the traces from a treated and an untreated hair, showing the reduction of the elements C, N and O on the treated hair (top trace), and the relative increase of the minor elements.

From this work it was proposed that, if the main constituents could be removed, it would be possible to analyse the proportions of the minor constituents mentioned above, and also the proportions of elements present in only a few ppm in the original hair. Such an analysis would be of interest in forensic research and possibly in other physiological studies.

Several methods of reduction were investigated and rejected because, although the concentrations of the major elements were reduced, the minor elements were also reduced, very often selectively. The most promising method attempted at present is the cold ashing technique as described by Gleit and Holland [4] in which the hair is treated with atomic oxygen produced in an RF discharge. In this method, the major elements are reduced by two orders of magnitude, as seen by the two traces of fig. 3. The conditions in the discharge are somewhat critical if a selective reduction of the minor elements is to be avoided. At present this is being investigated and, if successful, will be a quick, cheap alternative to neutron activation for this type of measurement.

Acknowledgements

Thanks are due to Mr S. Pocock for much of the experimental work, to Dr R. G. Ridley for many very helpful discussions, and to the Director of the Atomic Weapons Research Establishment for permission to publish this paper.

References

1. N. C. FENNER, *Phys. Letters* **22** (1966) 421.
2. N. R. DALY, R. E. POWELL, and R. G. RIDLEY, *Nucl. Instr. & Meth.* **36** (1965) 226.
3. N. C. FENNER and N. R. DALY, *Rev. Sci. Instr.* **37** (1966) 1068.
4. C. E. GLEIT and W. D. HOLLAND, *Analyt. Chem.* **34** 1454.