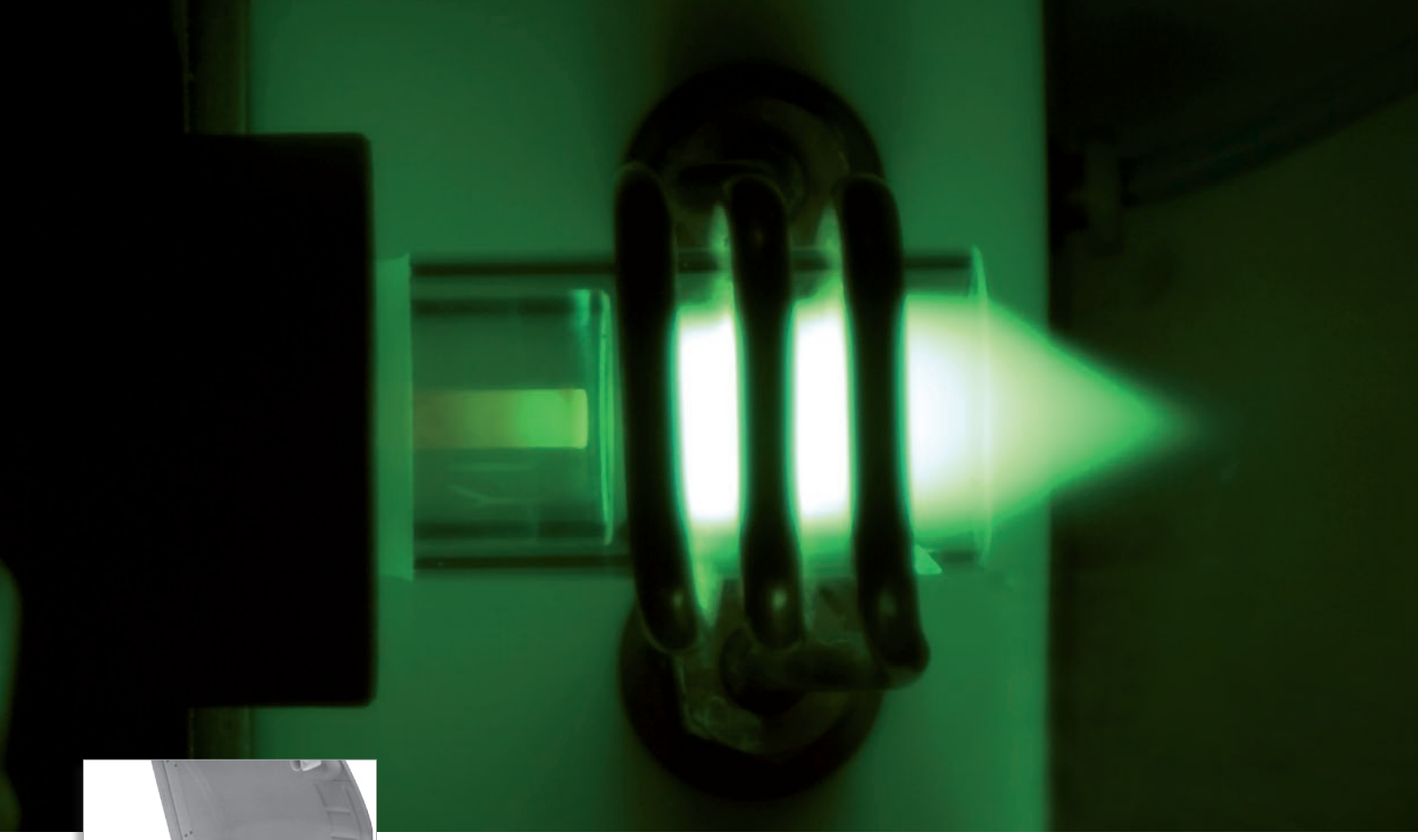

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

- elemental analysis
- main to ultra trace components
- survey analysis
- quantitative analysis

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is a very sensitive analytical technique with a high linear dynamic range (ultra-trace to main components). It is capable of analyzing all elements from Li to U and can be applied to solutions, solids and gasses.

In ICP-MS sampled material is transferred by an argon flow into an inductively coupled plasma in which an effective temperature of 7000 K results in atomisation and ionisation of the material. Subsequently, the ions are extracted into a mass spectrometer, with which the elemental composition of the material is determined.

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Principle of ICP-MS

Using ICP-MS, all kinds of materials can be measured. Solutions are vaporized using a nebulizer, while solids can be sampled using laser ablation. Gasses can be sampled directly. The sampled material is introduced into a high-energy argon plasma that consists of electrons and positively charged argon ions. In the plasma, the material is split into individual atoms. These atoms will lose electrons and become (singly) charged positive ions. Most elements ionize very efficiently (> 90%) in the hot plasma.

The layout of an ICP-MS is shown in fig. 1. To allow their identification, the elemental ions produced in the plasma (ICP) must be transferred from 7000 K to room temperature and from atmospheric pressure to high vacuum. To do so, the ions are extracted through a number of apertures.

Besides ions also photons are produced in the plasma. Photons also pass through the apertures. They are not removed by vacuum and produce high background signal when they reach the detector. To minimize this background, a so-called photon-stop is present (see fig. 2). This is a small metal plate placed in the centre of the ion beam, which reflects the photons away from the detector. The positive ions are not stopped by the photon-stop because a positively charged cylinder lens guides them around it.

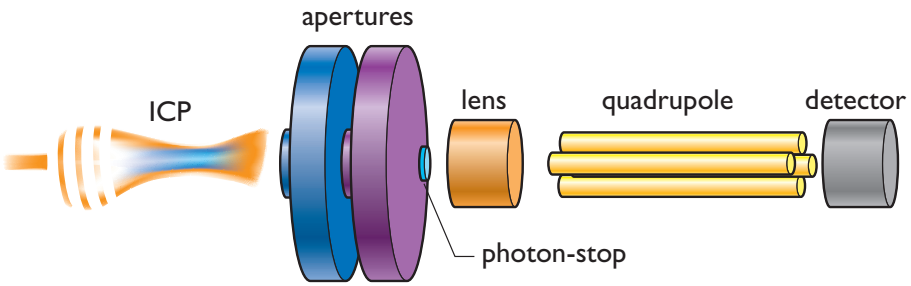

Fig. 1: Layout of an ICP-MS.

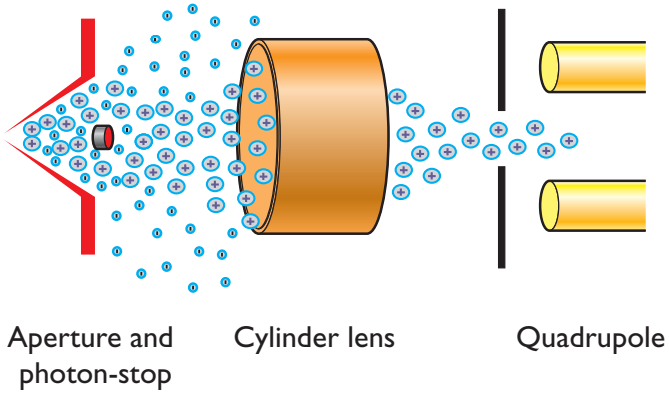

Fig. 2: Detailed layout of cylinder lens.

Subsequently, the ion beam enters the quadrupole mass analyser. In the quadrupole the ions are separated on the basis of their mass-to-charge ratio. Each element has its own characteristic isotopes and masses and will therefore produce its own mass spectrum. After passing the quadrupole the ions hit a special detector(fig. 3).

It contains two stages to allow simultaneous measurements of high and low signals. This allows simultaneous detection of main components and ultra-trace elements in a single run, which makes the ICP-MS a perfect tool for survey analysis of totally unknown samples.

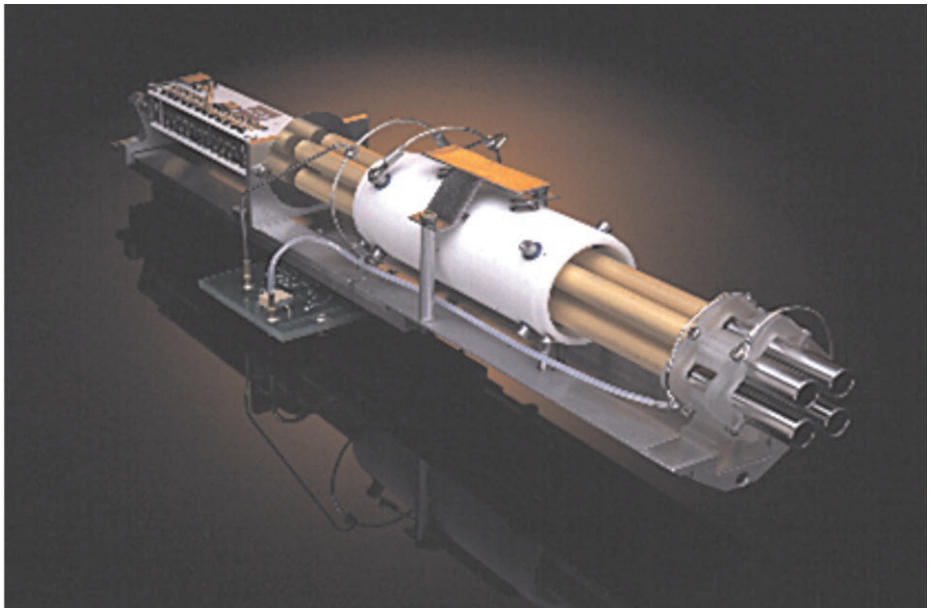

Fig. 3: Quadrupole and detector.

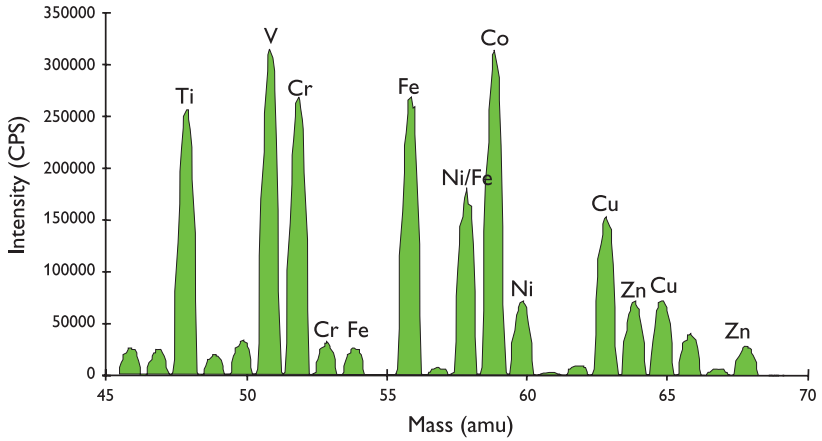

Fig. 4: Typical mass spectrum of a metallic coating.

Interferences

If an ion is singly charged, its position in the mass spectrum corresponds to its mass, but also interfering peaks are produced:

- If an ion is doubly charged, it will appear in the spectrum at half its mass. At this mass it will interfere with isotopes of different elements. Elements are predominantly singly charged in an argon plasma and therefore doubly charged ions are rarely a problem.
- The chemical and physical conditions existing in the plasma and interface region may allow the formation of polyatomic, or molecular ions, i.e. OH, CO and ArH.
- The mass spectrum produced by introducing aqueous solutions into the plasma include masses originating from the solvent and any associated impurities i.e. SO, ArCl and OCl.

The ICP-MS spectrum

An ICP-MS spectrum is a plot of ion intensity (y-axis) versus mass-to-charge ratio (x-axis). In an argon plasma, predominantly singly charged ions are produced. This means in practice that the mass-to-charge ratio can be replaced by mass in the spectrum (fig. 4).

Most elements have more than one isotope and each isotope has a specific mass. Copper (Cu), for example, has two isotopes: ^{63}Cu with 34 neutrons and ^{65}Cu with 36 neutrons in the nucleus. Thus, the mass spectrum of copper consists of two peaks, mass 63 and mass 65. The natural ratio of the different isotopes of an element is constant in nature. Therefore it is not difficult to correct for overlap of isotopes of different elements. In addition, a non-interfered isotope is present for almost all elements. Remaining interfering signals (see separate textbox Interferences) are removed by "in-house" software. This approach makes fast overview analysis of the total elemental composition possible.

Applications

- *quantitative analysis* of main and ultra-trace elements in both organic and inorganic samples
- *survey analysis* of main and ultra-trace elements in both organic and inorganic samples
- *depth profiles* of elements in solids by using laser ablation as a sampling technique
- *isotope ratio analysis*

Typical analysis

Quantitative analysis of ultra-trace elements in glass

For many companies, including Philips, environmental laws require that their products do not contain certain elements. Very sensitive analytical techniques such as ICP-MS are used to check for their presence, as the allowed concentrations of these elements, for example Hg, Sb and Pb, are very low. A quantitative analysis in products focuses only on a few isotopes of interest. With well-defined standards very accurate analysis is possible.

An example is the analysis of alpha-emitters in glass used for image sensors. Because determination of the bulk concentration is required, a large sample is required. Glass is best dissolved in hydrofluoric acid but the elements of interest are rare earth metals. These metals will react with fluoride to compounds that will precipitate.

To dissolve a glass without hydrofluoric acid, high temperatures and pressures are needed. These can be achieved in a so-called "carius-tube". This is a quartz tube in which the sample and hydrochloric acid are sealed.

When the tube is heated to 200°C, the pressure in the tube increases. Under these extreme circumstances the glass sample will dissolve even in hydrochloric acid. After dilution, the elements capable of producing alpha-radiation are determined using ICP-MS. Table 1 shows typical concentrations of alpha-emitters in a glass sample.

Table 1: Quantitative determination of alpha-emitters in glass.

	Glass (µg/g)
U	0.29 ± 0.03
Th	< 0.05
Pb	7.4 ± 0.7
Os	< 0.5
Pt	43 ± 4
Hf	6.7 ± 0.6
Nd	0.19 ± 0.02
Sm	< 0.05
Gd	7.7 ± 0.7

	White sample (µg/g)	Grey sample (µg/g)
Na	100	120
K	90	80
Mg	200	150
Cu	3	3
Mo	< 1	100
Y	30	25
W	5	3

Table 2: A selection of the results of a survey analysis of ceramic materials.

Survey analysis using laser ablation

For many problems, the exact concentration of a certain element in a matrix is not important. It is only of interest to know if there is a difference between two samples. In such cases a quick survey analysis will provide sufficient information. During this analysis, we look at the entire mass spectrum. Although only a single, non-matrix matched standard is used, an acceptable accuracy is obtained as in ICP-MS the sensitivity for the various elements is similar and well known.

Survey analysis has been applied to certain types of ceramics. Small changes in composition resulted in differences in appearance of the white material. Occasionally grey spots were detected for unknown reasons. With laser ablation a small amount of material was sampled. Survey analysis showed that molybdenum contamination causes the grey colour (see table 2), even at concentrations as low as 10-100 µg/g.

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Characteristics

Obtained information

- elemental composition
- isotope ratio of enriched materials
- quantitative analysis and survey analysis possible

Sample type

- solids, liquids, gasses
- bulk materials and thin films
- both organic and inorganic materials

Detection limits

- most elements (Li-U) less than 0.01 µg/l for liquids and less than 10 ng/g for solids, depending on the amount of material available

Accuracy

- 1-3 % relative for quantitative analysis
- within a factor 2 for survey analysis

Analytical range

- ultra-trace (ng/g) to main (%) components