## 3.3 Spectroscopy at Inductively Coupled Plasma

Atomic emission spectroscopy dissolves and excites the sample in flames or electrically heated ovens. The process is almost always performed in the normal atmosphere. For inductively coupled plasma (ICP) and laser ICP spectroscopy, sample chambers are also used, which has the advantage of processing under an inert safety gas, thus avoiding interference and possibly allowing measurements below 190 nm. It also permits sucking out the plasma products. The liquid sample material will be introduced to the sample burner by the carrier gas (mostly argon) or the plasma will "burn" in vacuum. The plasma zone is the area close above the inductor (plasma generator), which runs at high frequency (most systems use 10–40 MHz). There, the sample is transferred into the plasma phase, similar to the plasma in a high-pressure xenon lamp. The collection optics will recover a substantial part of the emission. The best efficiency is reached if the spectrometer is fixed to the window of the chamber or sample environment. If the chamber and spectrometer are purged by a noble gas or are evacuated, the measured spectrum may reach far below 190 nm. For solid samples, the plasma may be replaced by a spark (Section 3.4), or a laser pulse (Section 3.5). A complementary method involves ICP with a mass spectrometer (ICP-MS). The plasma products are sucked into the vacuum chamber of a mass spectrometer for elemental analysis.
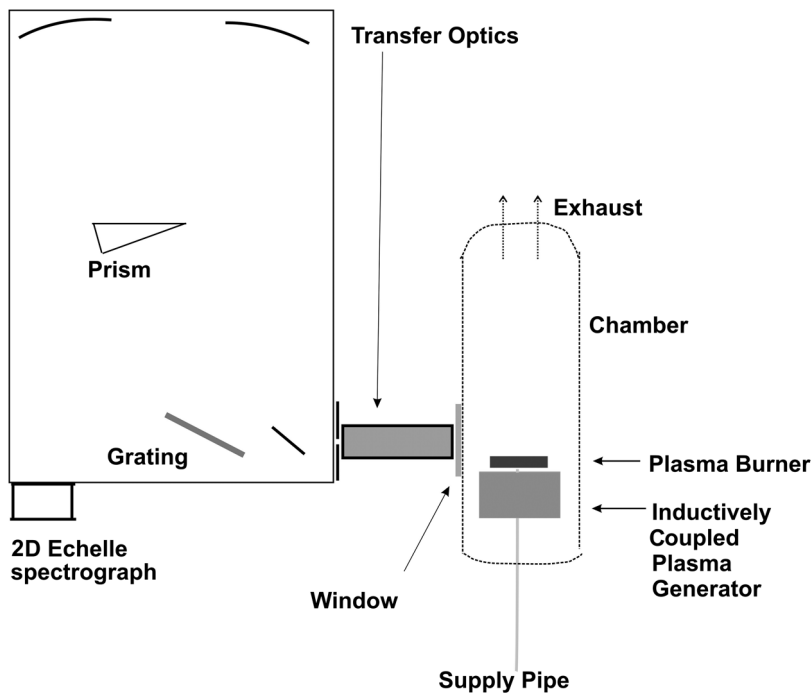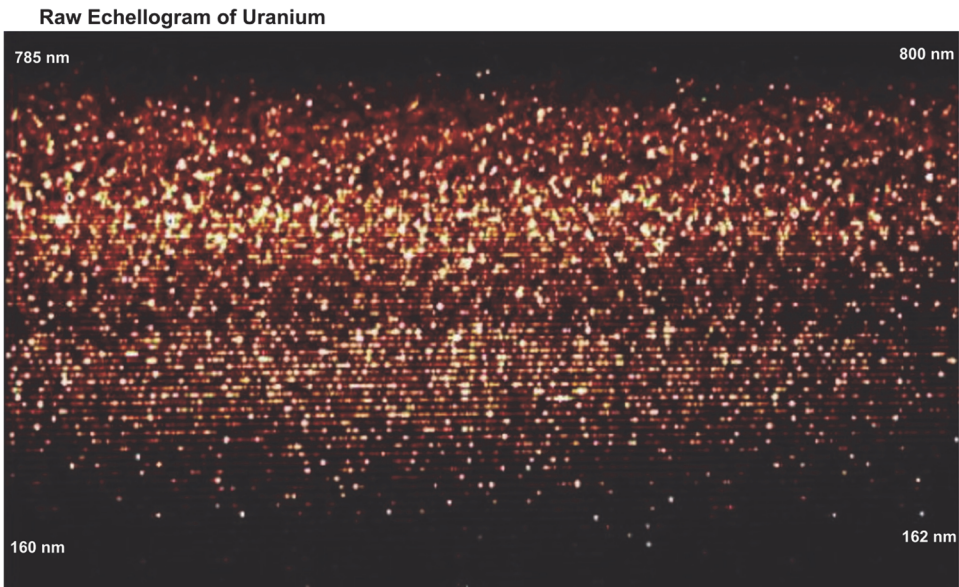

Figure 3.6   One of many ICP spectrometer versions available.

In the diagram shown in Fig. 3.6, the plasma generator is positioned beneath the plasma torch. It provides the high energy necessary to convert the liquid sample into the plasma state via high frequency. The atomized material exits at the torch and immediately emits the atomic lines. The entire process happens in a chamber. The light is collected by efficient wide-range optics and transferred into a high-resolution, nitrogen-purged 2D Echelle spectrograph. If a vacuum chamber is used, the entire optical system can be designed for the VUV. The chamber and spectrograph may be filled with a different gas, or one or both may be evacuated. The working range is typically <170–1000 nm. If the detector is a CCD, it will be coated with a VUV scintillator, which allows detection (practically without disadvantage) down to the wavelength limit of the window (see Section 5.8.11 of *Fundamentals*[1]). Likewise, image-intensified detectors may also be coated with a scintillator (see Section 5.2.5 of *Fundamentals*[1]). In addition to the atomic lines, the ICP spectrum also carries the lines of the solvent and carrier gas. In a so-called "empty" measurement, those data are stored for reduction from the sample spectrum, similar to AAS. ICP is a proven quantitative method, and powerful data-reduction software is required for the final result. If, for example, organic liquids are analyzed for their qualitative content of O, P, S, and other contents, numerous C lines will occur in the range between 160 and 220 nm. The application of ICP requires very high reproducibility of wavelength, along with online wavelength calibration and correlation techniques, e.g., some of the C lines can be used for that.
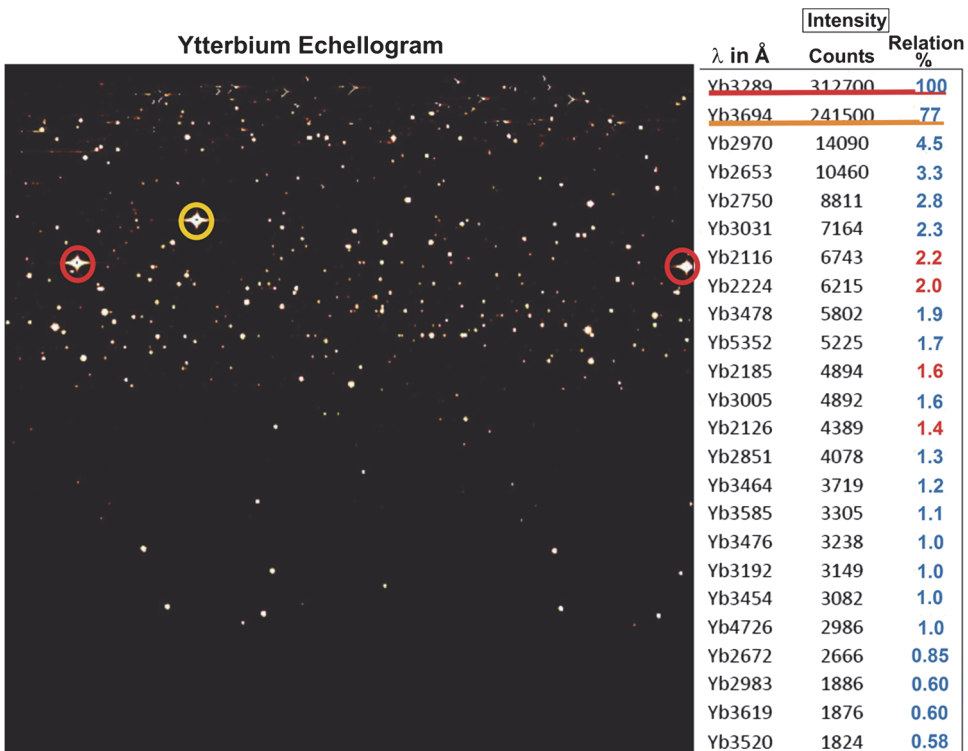
3.3.1 ICP examples

The element uranium (U) provides several hundred spectral emission lines, creating an Echellogram like that shown in Fig. 3.7. The many hundred emission lines are distributed over the range between 166 through 800 nm. In the image, the shorter wavelengths appear at the lower end, and the longer ones are toward the upper end. Within one order, the shorter wavelengths are on the left, and the longer ones are on the right. The brightness of the spots marks the intensity. In addition to the spectral points, it is easy to monitor the slightly tilted orientation of the lines within one order. The horizontal structures are called stripes.

Less complicated is the Echellogram of the rare-earth ytterbium (Yb), shown in Fig. 3.8. The roughly 100 emission lines cover the range of 211.67 nm through 555.65 nm, equaling 245 spectral orders in the Echellogram. Each piece of spectral information is easily viewed and well resolved. The main lines are listed in the table, descending from strong to weak. The strongest line, at 328.95 nm, is marked red; it appears in two neighboring orders. The second-strongest signal, at 369.42 nm, is marked yellow. Here, also, the short-wavelength information is located at the bottom, and the long wavelengths are at the top. Inside one order, the wavelength increases from left to right.

Raw Echellogram of Uranium

Figure 3.7 3D Echellogram of uranium (figure courtesy of Thermo Fisher Scientific GmbH).

λ in Å	Intensity Counts	Relation %
Yb3289	312700	100
Yb3694	241500	77
Yb2970	14090	4.5
Yb2653	10460	3.3
Yb2750	8811	2.8
Yb3031	7164	2.3
Yb2116	6743	2.2
Yb2224	6215	2.0
Yb3478	5802	1.9
Yb5352	5225	1.7
Yb2185	4894	1.6
Yb3005	4892	1.6
Yb2126	4389	1.4
Yb2851	4078	1.3
Yb3464	3719	1.2
Yb3585	3305	1.1
Yb3476	3238	1.0
Yb3192	3149	1.0
Yb3454	3082	1.0
Yb4726	2986	1.0
Yb2672	2666	0.85
Yb2983	1886	0.60
Yb3619	1876	0.60
Yb3520	1824	0.58

Figure 3.8 3D Echellogram of ytterbium (figure courtesy of Thermo Fisher Scientific GmbH).

3.4 Spark Optical Emission Spectroscopy

Spark optical emission spectroscopy (Spark-OES) is a frequently applied method in metallurgy. It is used to define the material mix in metallic alloys. The sample must be electrically conductive. Similar to ICP, this method can be applied in the open atmosphere or in a chamber with inert gas. The sample is fixed to the table, which also makes up the cathode. Above that, the tip of the spark gap, which is the anode, is adjusted close above the point of analysis. The high-voltage power supply generates a short spark that atomizes the sample material out of the surface. The measurement works as described earlier: by a monochromator, a Rowland spectrograph, or a 2D Echelle spectrograph. Handheld portable systems are also often used.

The spark emission spectrometer is very similar to the ICP setup; the optical system may even be the same. A metallic sample table and an adjustable spark tip are placed inside the experimental chamber. Again, the wavelength range of interest is ~170–1000 nm. The data acquisition is synchronized with the high-voltage unit, which does not mean that a gateable detector is required—it only means that the read-out happens after a certain number of sparks. Immediately after one or more sparks, the spark generator is blocked, and the CCD is read. In addition to the atomic lines, a rather-strong "white" background signal is involved, created by the spark itself. The lines and continuum are separated by applying a curve fit and elemental peak search software. Spark-OES is a fully quantitative method; the right part of Fig. 3.9 illustrates a mobile version. The contact with the sample, which is also the cathode, is realized by an extension from the holder and can be ring-shaped. It also defines the length of the spark gap. The spark is supplied by cables from the central unit. The emitted light is collected and refocused to a fiber optic cable that leads to the spectrometer.
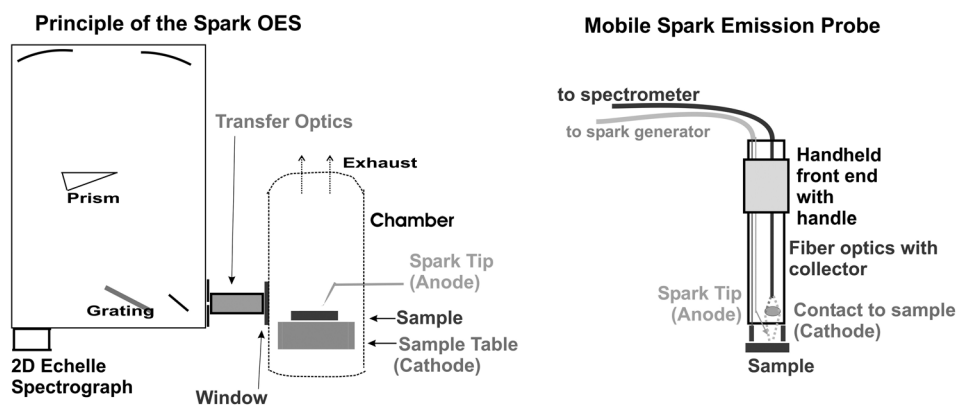

Figure 3.9 The spark emission spectrometer.

3.5 Laser Ablation

The methods of laser ablation (LA), laser-induced breakdown spectroscopy (LIBS), laser-induced plasma spectroscopy (LIPS), and laser deposition (LD) are all used for very different technical purposes, although the opto-spectroscopic part is similar for all four. Laser ablation is used for the analysis and modification of solid state materials; it is the only one of the applications that is useful for analysis, material processing, and deposition. With LIBS and LIPS, the system may be operated in the open atmosphere, except in cases that require signal collection below 190 nm. In the case of deposition, a vacuum chamber is required. A strong laser (such as an Nd-YAG at 1064 nm or an excimer in the UV) supplies a pulse nanoseconds long. The geometrical size of the light beam often is variable. Its power density is so strong that all molecular and atomic links in the upper micrometers of the sample break down (thus the name "breakdown"), and all molecules and elements are transferred into the plasma state. Like in the other methods, the cloud emits light in a spherical shape. Part of the radiation is lead to the spectrometer and the detector. A small crater is left at the sample after ablation. Automatic ablation systems are available that enable the sample to be *xy* positioned. Those systems can ablate layers from the sample and modify the structure. After each shot, the emission can be detected, and the spectrum can be compared to the reference. Therefore, the status of the process can be monitored after each single shot of the laser. If that is sufficient, the sample is moved to the next position, and the process starts again. Thus far, no vacuum or electrical contact is required. If the experiment is done inside a vacuum chamber, and a sample intended for deposition is placed near the ablated sample, the material can be transferred. Both partners must be conductors: one works as an anode, the other as a cathode. This process is called laser-induced deposition.

As shown in Fig. 3.10, laser ablation is similar to the ICP system. After a strong laser pulse, a small plasma volume is created above the ablated sample. The laser is normally fixed in position, and the sample is moved, if required by the application program. Therefore, the optical position of the light out of the cloud is stationary. The electric connection (electrodes) is optional; it assures that the ablation product does not return to the specimen. The material collected at the anode may be used for further evaluation, and the collected light is refocused into the entrance slit of the spectrometer. Depending on the application, with known elements, it is usually not necessary to apply a very-high-resolution spectrometer. The ratio between the predefined lines must be calculated and traced in time. A 1D spectrograph with a line array or standard CCD may often fulfill the requirements. In comparison to a 2D Echelle system, it provides faster repetitions, fewer calculations, and improved luminosity. Thus, pulse rep rates of milliseconds can be reached. In preparative ablation or deposition processes, the target sample may be measured in parallel by a second spectrometer in reflection mode (not shown in the figure), enabling an additive process control.