6 Analytical Techniques

6.1 Inductively Coupled Plasma

Inductively Coupled Plasma (ICP) is an analytical technique used for the detection of trace metals in environmental samples. The primary goal of ICP is to get elements to emit characteristic wavelength specific light which can then measured. The technology for the ICP method was first employed in the early 1960's with the intention of improving upon crystal growing techniques. Since then, ICP has been refined and used in conjunction with other procedures for quantitative analysis.

An ICP is a very high temperature (7000-8000k) excitation source that efficiently desolvates, vaporizes, excites, and ionises atoms. Molecular interferences are greatly reduced with this excitation source but are not eliminated completely.

An ICP typically includes the following components:

- Sample introduction system (nebulizer)
- ICP torch
- High frequency generator
- Transfer optics and spectrometer
- Computer interface

An ICP requires that the elements which are to be analysed be in solution. An aqueous solution is preferred over an organic solution, as organic solutions require special manipulation prior to injection into the ICP.

The sample is nebulized and entrained in the flow of plasma support gas, which is typically Ar. The plasma torch consists of concentric quartz tubes, with the

inner tube containing the sample aerosol and Ar support gas and outer tube containing an Ar gas flow to cool the tubes (Figure 6.1). A radiofrequency (RF) generator (typically 1-5 kW @ 27 MHz or 41MHz) produces an oscillating current in an induction coil that wraps around the tubes. The induction coil creates an oscillating magnetic field. The magnetic field in turn sets up an oscillating current in the ions and electrons of the support gas. These ions and electrons transfer energy to other atoms in the support gas by collisions to create a very high temperature plasma.

The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measurated quantitatively. This is accomplished by resolving the light into its component radiation (nearly always by means of a diffraction grafting) and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element line. The light emitted by the atoms or ions in the ICP is converted to electrical signals by the photomultiplier in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and a concentration is computed. Each element will have many specific wavelengths in the spectrum which could be used for analysis. Thus, the selection of the best line the analytical application in hand requires considerable experience of ICP wavelengths.

6.1.1 Advantages and Disadvantages

Advantages of using an ICP include its ability to identify and quantify all elements with the exception of Argon; since many wavelengths of varied sensitivity are available for determination of any one element, the ICP is suitable for all concentration from ultratrace levels to major components; detection limits are generally low for most elements with a typically range of 1 – 100 g/L. Probably the largest advantage of employing an ICP when performing quantitative analysis is the fact that multielemental analysis can be accomplished, and quite rapidly. A complete multielement analysis can be

undertaken in a period as short as 30 seconds, consuming only 0.5 ml of sample solution. Although in theory, all elements except Argon can be determined using and ICP, certain unstable elements require special facilities for handling the radioactive fume of the plasma. Also, an ICP has difficulty handling halogens, special optics for the transmission of the very short wavelengths become necessary.

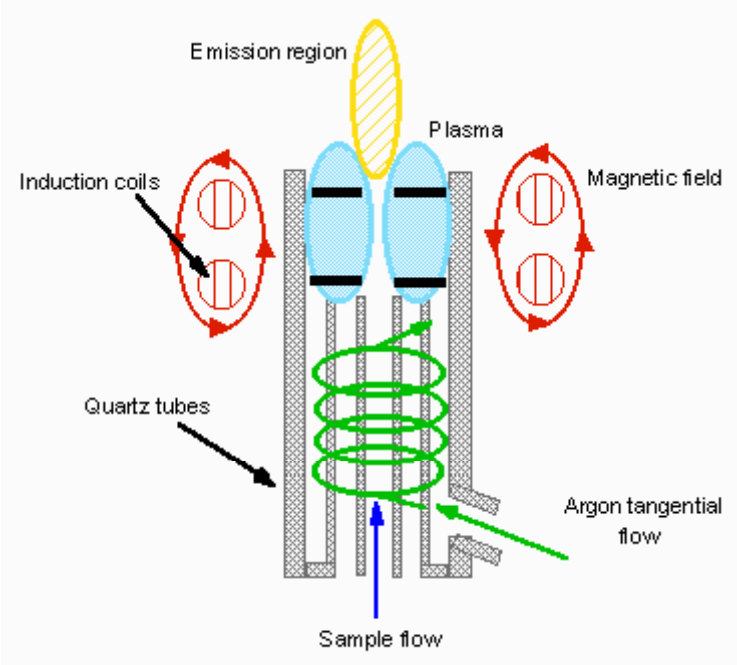


Figure 6.1: Schematic cross-section of an ICP

6.2 Ultraviolet and Visible Adsorption Spectroscopy (UV-Vis)

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Absorption measurements can be at a single wavelength or over an extended spectral range. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels, and UV-Vis spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Vis spectra have broad features that are of limited use for

sample identification but are very useful for quantitative measurements. The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Beer-Lambert law.

In single-beam UV-Vis absorption spectroscopy, obtaining a spectrum requires manually measuring the transmittance of the sample and solvent at each wavelength. The double-beam design greatly simplifies this process by measuring the transmittance of the sample and solvent simultaneously. The detection electronics can then manipulate the measurements to give the absorbance.

6.2.1 Instrumentation

The Uv-Vis spectral range is approximately 190 to 900 nm, as defined by the working range of typical commercial UV-Vis spectrophotometers.

The light source is usually a deuterium discharge for UV measurements and a tungsten-halogen lamp for visible measurements. The instruments automatically swap lamps when scanning between the UV and visible regions. The wavelengths of these continous light sources are typically dispersed by a holographic grating in a single or double monochromator slit width.

The dual-beam optical desing greatly simplifies the process by simultaneously measuring P and P_o (light power of the sample and reference cells, respectively), Figure 6.2.

The detector in single-detector instruments is a photodiode, phototube, or photomultiplier tube. The detection electronics or software program can then manipulate the P and P_o values as the wavelength scans to produce the spectrum of absorbance or transmittance as a function of wavelength.

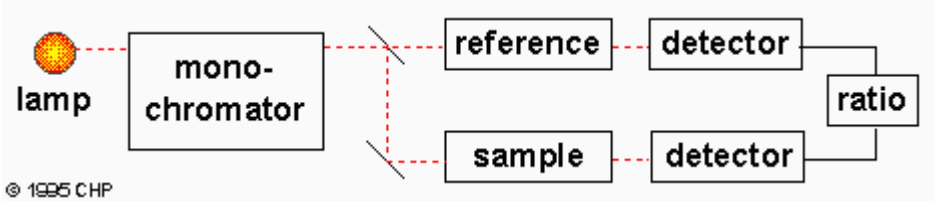


Figure 6.2: Schematic of a dual-beam UV-Vis spectrophotometer

6.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transforms Infrared Spectroscopy (FTIR) is a powerful tool For identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular "fingerprint".

FTIR is most useful for identifying chemicals that are either organic or inorganic. FTIR techniques may be used for qualitative observations or quantitative measurements. It can be applied to the analysis of solids, liquids and gasses.

6.3.1 Physical Principles

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanism, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it adsorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states.

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

6.3.2 Sample Preparation

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate. The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called cast film, and is frequently used for polymer identification.

6.3.3 FTIR Instrument

A simplified diagram of an FTIR instrument is shown in Figure 6.3. The source emits infrared radiation that is sent through the system. A Michelson interferometer (consisting of a beamsplitter, a fixed mirror, and a movable mirror) encodes the radiation by creating a time-dependent, periodic intensity pattern. The movable mirror adjusts the distance between itself and the beamsplitter. When the light from the fixed mirror recombines with the light from the movable mirror, a phase shift between these two beams causes interference in the resulting beam. Therefore, the intensity of the beam exiting the interferometer varies sinusoidally between a maximum intensity value (at a 0º phase difference) and minimum intensity value (at a 180º phase difference). A mirror reflects the beam into the sample compartment.

The sample absorbs some of the infrared radiation at characteristic frequencies according to its bond strength and structure. Atomic mass also affects which infrared frequencies may be absorbed. When infrared radiation is absorbed by a sample, it causes phonon motion (lattice vibrations). Infrared spectroscopy techniques should only be used with materials whose lattice vibrations lead to changes in the dipole moments of the sample molecules. Otherwise, the sample does not absorb infrared radiation and is considered IR inactive.

The transmitted part of the beam then enters a detector for final measurement. The detectors are specially designed for measuring interferogram signals.

Finally, a computer processes the data from the detector. Using Fourier transform methods, the computer breaks down the interferogram into its sinusoidal components, which it then uses to calculate the absorbance values across the spectrum. The final absorbance data is then presented graphically to the user for interpretation.

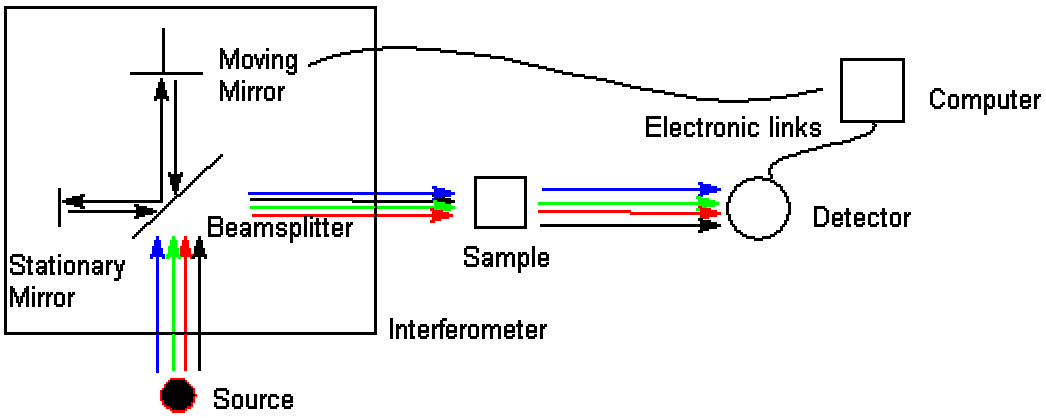
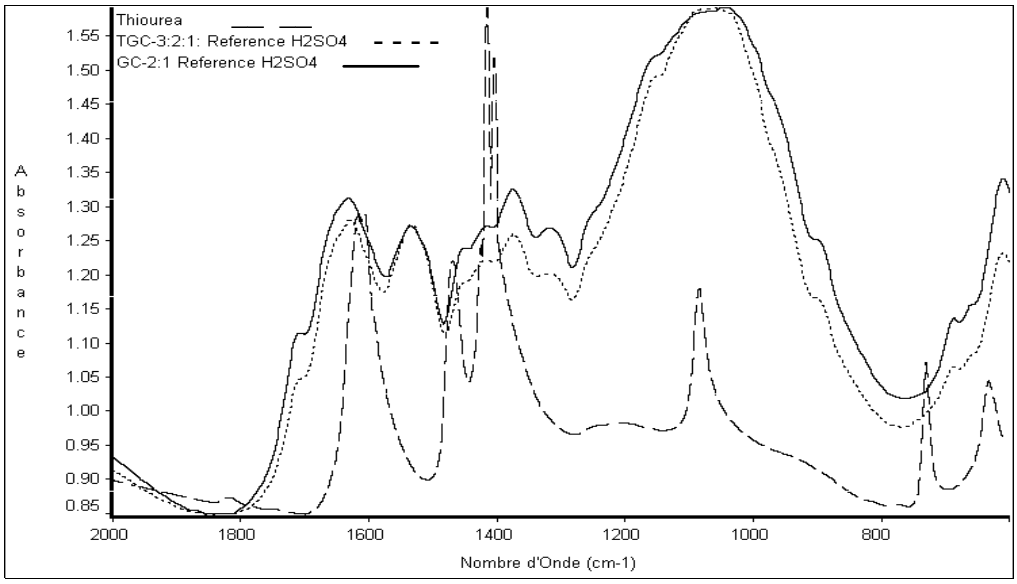


Figure 6.3: Diagram of an FTIR instrument

Figure 6.4 shows some FTIR spectra obtained with glutaraldehyde crosslinked chitosan (GCC) and thiourea derivative of chitosan (TGC).



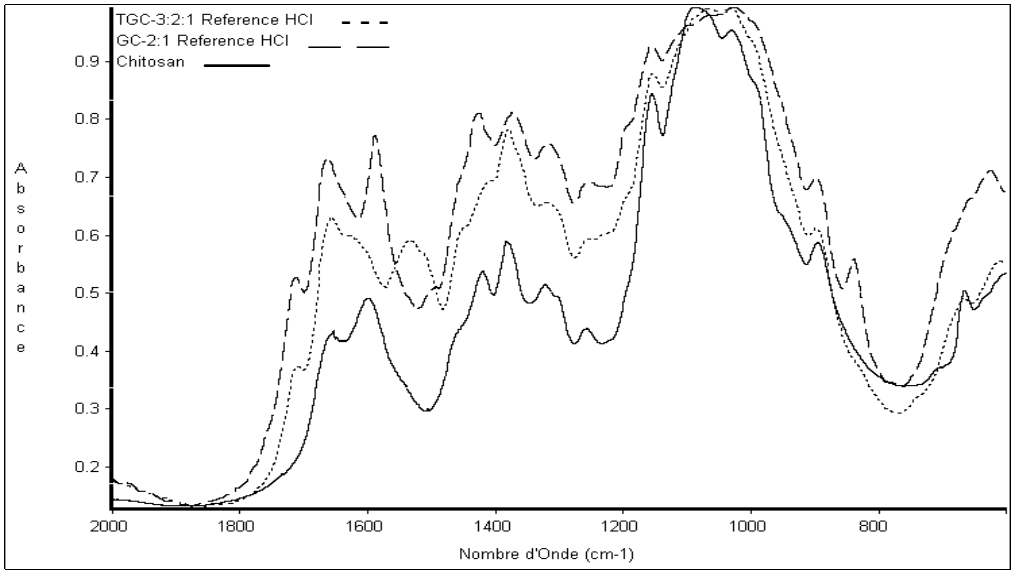


Figure 6.4: FTIR spectra of chitosan, thiourea, GCC-2:1, and TGC-3:2:1 after contact with either HCl or H_2SO_4 (nombre d'onde = wavenumber)

6.4 SEM-EDAX Analysis

6.4.1 Energy Dispersive X-ray Analysis (EDAX)

An energy-dispersive x-ray analyzer (EDAX) is a common accessory which gives the scanning electron microscope (SEM) a very valuable capability for elemental analysis. The electron beam in an SEM has an energy typically between 5000 and 20000 electron volts (eV). The energy holding electron in atoms (the binding energy) ranges from a few eV to many Kilovolts. Many of these atomic electrons are dislodged as the incident electrons pass through the specimen, thus ionizing atoms of the specimen. Ejection of an atomic electron by an electron in the beam ionizes the atom, which is then quickly neutralized by other electrons. In the neutralization process an x-ray with an energy characteristic of the parent atom is emitted. By collecting and analyzing the energy of these x-rays, the constituent elements of the specimen can be determined (Lyman et al. 1990).

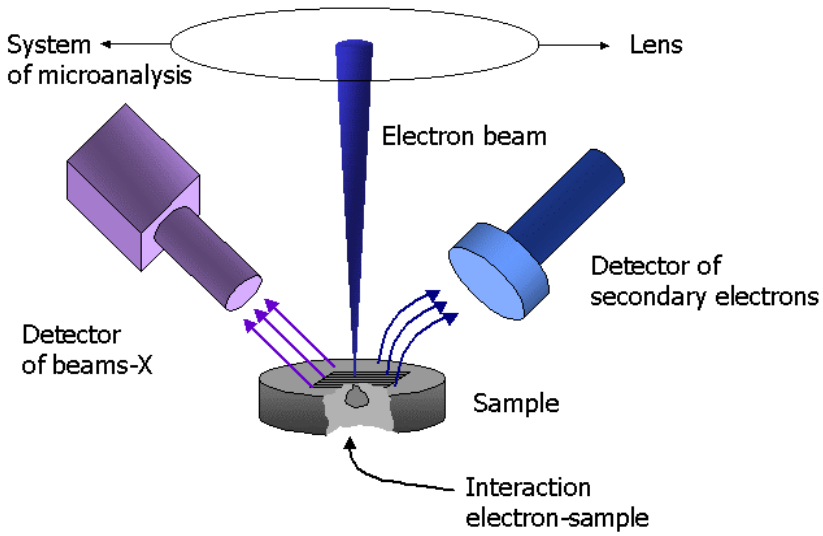


Figure 6.5: Schematic of scanning electron microscope (interaction electron-sample).

Limitations for the quantified analysis:

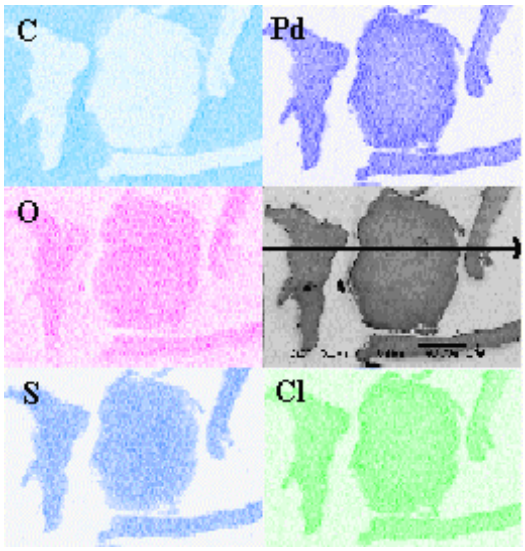
One can work only on samples conductive or made conductive by plating in the carbon. The analysis is quantitative exact only on polished samples and plans. The analysis is possible on rough samples or in powder with a certain error difficult to estimate.

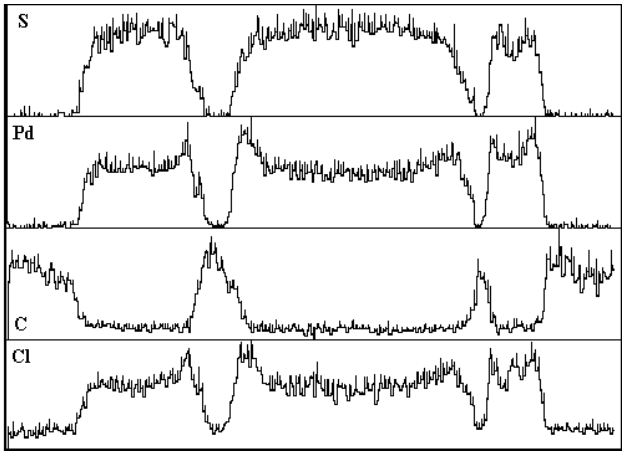
Cartography:

One can acquire the image of the analyzed surface and the simultaneous distribution of 26 individual elements then make in colors of this one. These images can treated in analysis of quantitative image for shown the percentage of distribution of surfaces, the number of grains, the perimeters.

Automatic analyses and profiles:

One can make the automatic purchase in analysis quantified with groups of registered points: either on-line for profiles, or in womb, or chose, or unpredictable.





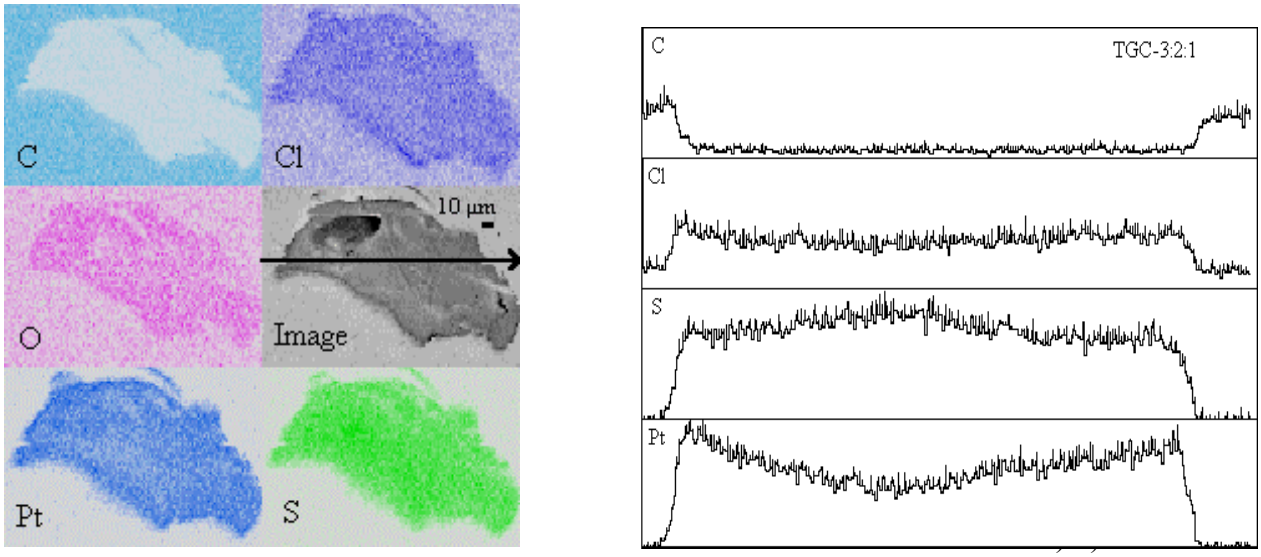


Figure 6.6: SEM-EDAX analyses of thiourea derivative of chitosan after (a) platinum (TGC-3:2:1) and (b) palladium (TGC-1:1:1) sorption.

Figure 6.6 shows the distribution of C, O, S, Cl, and Pd (and Pt, respectively) in TGC satured with Pd (and Pt, respectively) in hydrochloric acid solutions.

6.5 Environmental Scanning Electron Microscope (ESEM)

The field-emission environmental scanning electron microscope (ESEM-FEG) represents several important advances in scanning electron microscopy. Whereas conventional scanning electron microscope requires a relatively high vacuum in the specimen chamber to prevent atmospheric interference with primary or secondary electrons, an ESEM mar be operated with a poor vacuum (up to 10 Torr of vapor pressure, or one seventy-sixth of an atmosphere) in the specimen chamber (Lyman et al. 1990).

In such "wet mode imaging", the specimen chamber is isolated (by valves, pressure-limiting apertures, and a large-diameter by pass tube) from the rest of the vacuum system. Water is the most common imaging gas, and a separate vacuum pump permits fine control of its vapor pressure in the specimen chamber. When the electron beam (primary electrons) ejects secondary

electrons from the surface of the sample, the secondary electrons collide with water molecules, which in turn function as a cascade amplifier, delivering the secondary electron signal to the positive biased gaseous secondary electron detector (GSED). Because, they have lost electrons in the exchange, the water molecules are positively ionized, and thus they are forced/attracted toward the specimen (which may be non conductive and uncoated), serving to neutralize the negative charge produced by the primary electron beam. The field-emission gun produces a brighter filament image (primary electron beam) than either tungsten or lanthanum hexaboride sources, and its accelerating voltage may be lowered significantly, permitting nondestructive imaging of fragile speciments. The ESEM-FEG also retains the capabilities for conventional secondary and backscattered electron detection, and the field-emission source permits very high resolution imaging of coated or naturally conductive samples under high-vacuum and high-voltage conditions. This electrons microscope has light-element X-ray analysis (energy-dispersive spectroscopy), as well as many other options.

Different pictures realized with Field Emission, Philips XL30 ESEM are shown. In figure 6.7 the picture of a bead of chitosan raw material can be observed. The external surface can be seen (at the top) and the inside (botton section) without showing specially different structures.

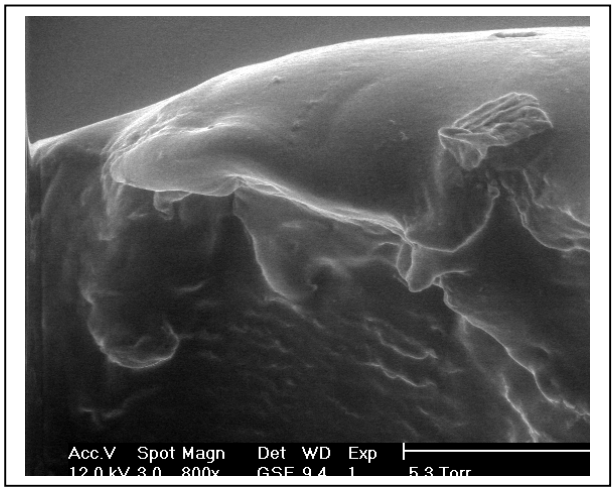


Figure 6.7: Bead of chitosan raw material

Figure 6.8 corresponds to a bead of crosslinked-chitosan. The smooth external surface of the bead (on the left) and the inside (right section, filling all the image), where a solid surface without big conduits or porous, can be seen.

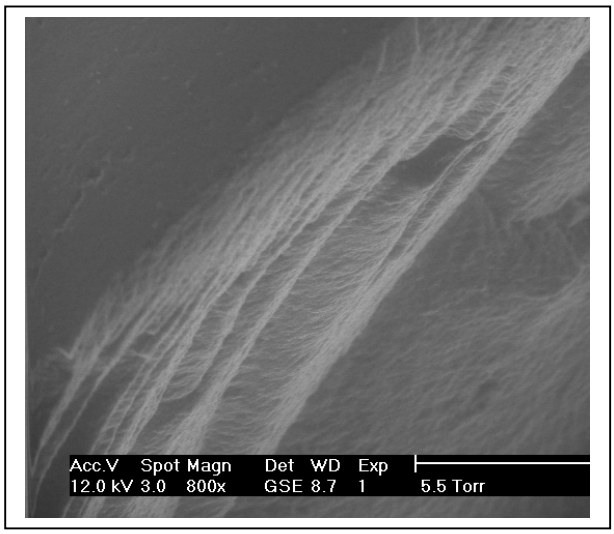


Figure 6.8: Chitosan crosslinked with glutaraldehyde

The last figure, 6.9, shows the external surface of the crosslinked-chitosan bead on which Pd sorption has been realized, but no differences can be observed with beads without Pd.

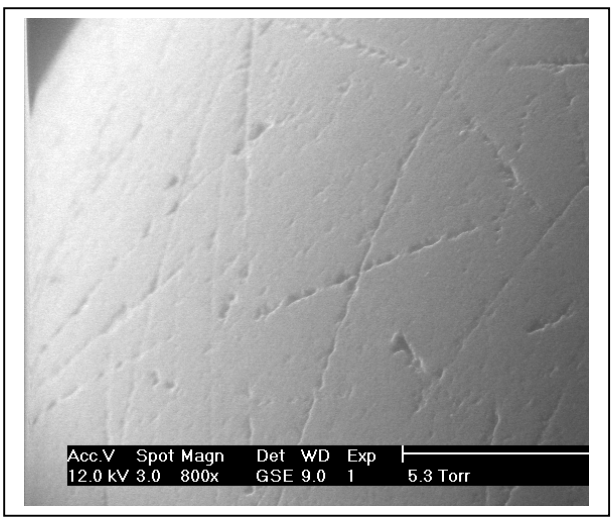


Figure 6.9: Crosslinked-chitosan bead with Pd sorbed