DESIGNING SPECTROELECTROCHEMICAL CELLS: A REVIEW

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Abstract A review on the recent state of use of spectroelectrochemical techniques for multivariate chemical analysis is presented. Starting with a discussion of the advantages of the application of spectroelectrochemical techniques instead of an ex-situ combination of spectroscopic and electrochemical methods, the main part of this review is focused on two topics: practical considerations for obtaining the optimal conditions for spectroelectrochemical measurements according to the spectroscopic or electrochemical technique selected, and considerations for the optimal design and construction of spectroelectrochemical cells with examples. The final outlook is intended to the use of spectroelectrochemical detectors in flow injection analysis (FIA) experiments. More than 300 references are collected covering the main contributions on this subject.

Keywords spectroelectrochemistry; cell design; hyphenated techniques; flow cells; multivariate chemical analysis

1. INTRODUCTION

Electrochemistry is a pervasive scientific discipline, being essential for several generally relevant research subjects in Physics, Chemistry and Biology/Physiology, such as the transformation of materials, the transfer of information, and the conversion and storage of energy[1]. In addition, electrochemical processes constitute a major class of chemical reactions both in the laboratory and on large industrial scale[2].

However, although there is a large number of electrochemical techniques[3,4], they can rarely unequivocally identify electroactive species[5–7]; the molecular identity of a new electrogenerated material is typically inferred from the measured physical properties of a known standard system. In addition, electrochemistry provides only limited and indirect information on structural changes accompanying redox events. This problem limits its application to explore complex electron transfer reactions[8]. In these cases, the information provided by the electrochemical techniques must be supplemented through complementary measures of separation and chemical identification, usually spectroscopic information.

Therefore, although electrochemical measurements are those that provide general information in the investigation of redox processes, it is essential to use spectroscopic techniques for structural details of the electrochemical systems[9].

The application of optical methods in electrochemistry can be divided into two general cases[10,11]:

- *Ex situ methods (off-line):* Realization of the spectroscopic measurement outside the electrochemical cell in an external device. The off-line methods belong to the traditional chemical and instrumental techniques for the study of electrode materials, electrolytes and products of an electrochemical reaction. They are useful for a limited number of electrochemical systems, whose components do not change their properties during or after their transfer from an electrochemical environment to the measuring device.

- *In situ methods (on-line):* Realization of the spectroscopic measurement within an electrochemical experiment at the same electrode system. This coupling is known as spectroelectrochemistry.

Thus, spectroelectrochemistry is a hyphenated technique that combines two classical methods, Electrochemistry and Spectroscopy, to obtain chemical information. An essential feature of this technique is that the two measurements are obtained simultaneously and not sequentially, as in many other hyphenated techniques[12], avoiding misinterpretation of electrochemical results because the real situation is different in the electrode[13].

Since the first publications[14–16], an important development in this technique have been achieved, resulting in some interesting combinations that allows the study of many types of chemical systems[17–19]. So much so that in recent decades a number of articles has been published in which spectroelectrochemical techniques are not only widely used for studies of electronic transfer reactions[20,21], they also provide a promising option for chemical detections in complex environments[22].

1.1.Advantages and disadvantages of spectroelectrochemistry

The spectroelectrochemical techniques have many advantages[10]:

- Direct access to kinetic data of electrode reactions.
- Qualitative and quantitative information on the state of the interface at electrochemical conditions.
- Efficient set of experimental data (under variation of the different parameters) at high scan rates.
- Fast repetition of experiments at different conditions including a computerized evaluation of the data.
- Simultaneous acquisition of data from different methods in a single experiment, which increases the selectivity and sensitivity[23]. This fact is reflected in spectroelectrochemical sensors based on changes in the optical absorption in response to electrochemical changes[22]. Thus, it is possible to distinguish and isolate the overlapping spectra of compounds that cause interferences, so a high selectivity is obtained[24–26].
- Separation of the Faradaic and non-Faradaic contribution of an electrochemical reaction by a quantitative identification of the reaction products at the electrode.

In situ techniques also have some problems and drawbacks which must be considered too[10]. The main disadvantages of in situ methods in electrochemical studies are:

- The low concentration of the electrochemical reaction products at the phase boundary requires a high sensitivity of the in situ spectroscopic method. Otherwise sampling is required, which can be disturbed by irreversible changes at the electrode surfaces. Therefore, concentrations needed for spectroscopy should be higher than the required in electrochemical measurements for reasons of insufficient band intensity. While the desired for adequate spectroscopic response may thus require higher concentrations of up to 0.05 mol dm^{-3}, the comparison with typical CV measurements at 0.001 mol dm^{-3} analyte concentration can lead to inconsistencies, especially for processes involving chemical reactions[1].
- In situ experiments are time consuming with respect to the preparation of the experimental setup, the simultaneous data acquisition and the evaluation of all data.
- For the determination of non-electrical properties of the electrochemical system, special cells are required, the type and size of which are adjusted to the requirements of the spectroscopic method which might contradict the requirements of the

electrochemical methods in terms of electrode geometry, electrolyte composition, volume, etc.

- The selection of solvents, supporting electrolytes and the electrode materials is limited by the requirements of the spectroscopic method. It might be necessary to apply materials with less advantageous electrochemical properties. The choice of solvents is relatively simple for measurements in the UV-VIS region. Most solvents generally used in electrochemistry (water, alcohols, ketones, nitriles, amides, chlorohydrocarbons, cyclic ethers, etc.) can be utilized. On the other hand, strong absorption bands of many electrochemically applicable solvents limit their use especially in the infrared region[1].
- The spectroscopic method applied can cause such an energy consumption of the spectroelectrochemical cell, which results in a change of the electrochemical reaction or the equilibrium at the electrode by structural changes.
- The spectroscopic method applied might require the addition of such materials to the electrochemical system, which could change the electrode reaction.

1.2. Applications of spectroelectrochemistry

Spectroelectrochemical techniques provide in situ insight into the spectroscopic characteristics of electrogenerated compounds, allowing the study of species with short lifetime and knowing the chemical reversibility of these reactions. In addition, these methods provide information about the species that adhere or release of a catalyst or an electrode surface[27]. This fact allows develop, test and refine reaction mechanism providing knowledge of the structure of the intermediates[9], sometimes with the help of computational techniques[28,29].

These techniques are also suitable in other situations where redox processes come into play, as corrosion studies. Some investigations follow in situ the changes occurring during corrosion processes in humid[30] or wet[31] conditions, but reports on the coupling of electrochemically forced corrosion and adequate analytical technique are much less common. Spectroelectrochemical techniques[32–35] are gaining importance, since they enable insight into the corrosion processes that occur either on the surface of metals or in the structure of protective coatings, simultaneously with or immediately after electrochemical treatment.

Nowadays, spectroelectrochemical methods are finding numerous purely analytical applications too, such as the development of spectroelectrochemical sensors for chemical detection. This approach is based on the change of some optical property in response to an electrochemical change, so it is possible to distinguish between different interfering compounds, obtaining a high selectivity[24–26].

The reduction or oxidation of a given analyte can be produced by applying a certain potential. This specie also absorbs or emits a specific wavelength. Thus, setting these two parameters, it is possible to minimize the number of interferences in the measurement.

One of the most relevant contributions to this area has been a group of articles published by Heineman and his research group, which describe various analytical aspects of a spectroelectrochemical sensor[36].

2. GENERAL CONSIDERATIONS FOR SPECTROELECTROCHEMICAL CELL DESIGN

2.1.Electrochemical considerations

In principle, it is possible to couple all interfacial electrochemical techniques with spectroscopic techniques for in situ spectroelectrochemical studies, although, in practice, most studies use only some of them. Even so, it is possible to find some examples of the application of each of these techniques to spectroelectrochemical studies. The election of the electrochemical technique only depends on the information which can provide it.

For example, potentiometric techniques are used for studies of synthesis and characterization of conductive films[37–39], in the development of sensors for proteins and other molecules with biological interest[40,41], and for the electrochemical characterization of systems[42] and new compounds[43].

In the same way, amperometric techniques are primarily used for detection and quantification of different molecules in the area of spectroelectrochemical sensors[44–47].

It is possible to find several examples of using coulometric techniques in spectroelectrochemical studies of electrodes[48] and cells[49,50] characterization or studies of the redox behavior of coordination complexes[51]. Other authors use these techniques for protein determination[52] or to estimate the reduction potential of various organic and biological molecules[53].

Time-dependent electrochemical techniques are widely used for electrosynthesis[54] and electropolymerization[55] studies, and to know the behavior of membranes[56] and films[57,58] acting as electrodes[59], although it is also possible to find some applications of these electrochemical techniques for studying electron transfer reactions[60].

Finally, voltammetric techniques are the most commonly used group in electrochemistry. Similarly, these techniques have found numerous applications in spectroelectrochemistry. Within this group, there are many techniques and different variants, but here only the most used in spectroelectrochemistry will be considered, as linear sweep voltammetry[61–64], cyclic voltammetry[65–68], differential pulse voltammetry[69–71] and stripping voltammetry[27,72,73]. All these techniques have many possible applications in spectroelectrochemistry, as sensors development, electrode and film characterization or mechanistic studies of electrochemical reactions.

To conclude, it should be noted that the design of spectroelectrochemical cells mainly depends on the requirements of spectroscopic techniques, so that, any spectroelectrochemical cell can virtually operate with each and every one of electrochemical techniques.

2.2.Spectroscopic considerations

The most important factor for the choice of the most suitable spectroscopic method is how easily it can be implemented[74]. So, although unpaired electrons in redox intermediates can be characterized by ESR spectroscopy, the availability of this technique and the requirements of the electrochemical systems restrict its applicability to very few experiments.

For this reason, it is necessary to use other spectroscopic methods to detect these intermediates, such as UV-visible or infrared spectroscopy, which besides offer a better resolution.

In addition to the aforementioned spectroscopic methods, there are others that provide more detailed structural information. Among the candidates, the Fourier transform infrared spectroscopy (FTIR) is the most widely used and for which the most efficient cells have been designed, while the nuclear magnetic resonance (NMR) is essential to know structural details of molecules and solids, although it has a low applicability. Furthermore, Raman spectroscopy has become a powerful tool, particularly for the study of nanostructures[10,75].

Light striking a dielectric interface can undergo a number of processes, the most important of which are reflection, absorption and scattering[76]. In a spectroscopic experiment, the intensity of light incident on a surface, I_0, is compared to that which has been transmitted through the medium ($T = I_0/I_T$), scattered from the medium ($S = I_0/I_S$) or reflected from the medium ($R = I_0/I_R$).

The dominant processes in light interaction at an interface are reflection, transmission, and elastic scattering of light, in that order. Inelastic scattering is a much weaker phenomenon but it is very used too, as in the Raman scattering spectroscopy.

IUPAC has classified all spectroscopic methods applied in electrochemistry[77] based on the transmission, reflection or scattering of electromagnetic radiation, including spectroscopic methods based on light polarization, X-ray based techniques, magnetic resonance methods and light emission based techniques too.

Typical spectroscopic methods used in spectroelectrochemistry[1,7,78,79] include absorption spectroscopy in the ultraviolet (UV), the visible (VIS)[80], the near-infrared (NIR)[81] or the infrared (IR)[82,83] regions, Raman scattering spectroscopy (SERS)[84], or magnetic resonance techniques such as electron paramagnetic resonance (EPR)[85]. Whereas the latter is restricted to species with unpaired electrons, the other spectroscopic methods exploit electronic or vibrational transitions.

Less common but also well developed spectroelectrochemical techniques involve nuclear magnetic resonance (NMR)[11,86], X-ray absorption spectroscopy (XAS)[87] and luminescence in the UV or VIS region[88].

Figure 1 shows common optical geometries for transmission and reflectance measurements used in spectroelectrochemistry[89].

(Figure 1)

Optical transmission experiments are the most common optical arrangement. They are based in the measurement of the wavelength-dependent decreased in the intensity of incident light, I_0, following its passage through an absorbing medium[90]. In a conventional absorbance experiment, the optical arrangement minimizes the contribution of scattering and reflection from the sample so that the main contribution to the decrease in I_0 arises from absorption; therefore absorbance is defined as $A = -\log(I_0/I) = -\log T$.

In absorbance or transmission measurements in spectroelectrochemistry, scattering and reflection must be minimized to provide an optimum signal-to-noise ratio. Since the working electrode generally presents a reflective surface, minimizing scattering and reflection can prove challenging and lead to distortions of the optical signal in an absorbance experiment. The use of optically transparent electrodes (OTEs) in which the incident light is perpendicular or normal to the electrode surfaces (Figure 1A) significantly reduces such interferences. An alternative transmission arrangement directs the optical path parallel to the electrode (Figure 1B).

In internal reflection experiments (Figure 1C), the beam is passed through solution and reflected from the electrode surface back through the solution[79]. In contrast, external reflection experiments (Figure 1D) involves introducing the optical beam through the back side of a transparent electrode at an angle greater than the critical angle so that the beam is totally reflected[91]. Spectral changes near the electrode are observable due to the small penetration of the electric field vector into the solution[92]. Sensitivity for both types of reflectance spectroscopies can be enhanced by multiple reflections.

Luminescence and scattering spectroscopic techniques have been coupled with electrochemistry too. In Raman spectroelectrochemistry (Figure 2) the excitation is by a laser beam directed though solution against the electrode and the Raman back-scattering is observed[93].

(Figure 2)

On the other hand, a beam of excitation light can be passed through an electrochemical cell, and the resulting fluorescence of electrogenerated species is observed[94]. In addition, electrochemical cells have been placed in the sample cavities of ESR and NMR spectrometers to record the absorption spectra of electrogenerated species[95,96]. Mass spectroscopy has been coupled to an electrochemical cell too[97].

2.3. Timing between both techniques

Commercial instrumentation available for experiments, both by electrochemical and spectroscopic techniques, often lack facilities for synchronizing measurements with events outside the instrument. This fact becomes even more evident when medium-low range instrumentation is used.

In most cases, synchronization between the two techniques is quite impossible, and when there is any equipment designed for this use, it tends to only consist of an input or output signal, whether analogical or digital, that the researcher should be able to use to achieve the desired synchronization. Furthermore, although both commercial instruments used for the electrochemical and spectroscopic methods have facilities of timing, achieving its protocols is a complicated task, especially if it takes into account that manufacturers of electrochemical instruments rarely engage in the commercialization of spectroscopic instrumentation, and vice versa.

In almost all cases, it is lacking any control system (either programmed or instrumental) that is responsible for synchronizing and it should be specifically designed for the technique and instrumentation used[98].

The timing requirements are highly variable depending on the spectroscopic technique and the treatment that acquired data require later in an attempt to maximize the signal/noise relation and increase the sensitivity of the technique.

The less demanding situation consisting of polarizing the electrode with a suitable potential and make a single spectroscopic experiment while the potential of the working electrode is maintained; but even in this case it is useful to have timing systems to facilitate automation of experiments.

Nowadays, you can only find one commercial instrument designed to spectroelectrochemical studies by combining a source of light, a bipotentiostat/galvanostat and a spectrometer on a single device. This is the SPELEC, an instrument developed by DropSens[99] which includes functions such as experimental control, graph treatment and synchronized processing of optical and electrochemical measurements, among others. Also Metrohm have a spectrophotometer[100] that can work together with all Autolab potentiostat instruments and is supported by the same electrochemical software, so correlation between electrochemical and spectroscopical data is ensured.

3. SPECTROELECTROCHEMICAL CELLS

In this section, it will be shown different spectroelectrochemical cell designs, classifying them according to the spectroscopic technique for which they have been designed and exploring the basic requirements to be met by each of them. Here, it will be cited the best materials for the cell body or the optical windows as well as the best electrode materials that can be used for a correct operation of each of the cells cited.

3.1. Spectroelectrochemical cells for UV-visible spectroscopy

This is probably the most predominant technique used since most of organic compounds and metal coordination complexes show absorption spectra in this region[101]. Generally, any species with a system of alternative double bonds absorbs ultraviolet light, and any colored molecule absorbs visible light, so that this spectroscopic technique is applicable in a wide range of organic, inorganic and biological compounds[80].

The simplest spectroelectrochemical experiment is to direct a light beam through the electrode surface, as shown in Figure 3, and to measure absorbance changes resulting from species produced or consumed in the electrode process. The obvious prerequisite is an optically transparent electrode (OTE)[102,103].

(Figure 3)

Transmission experiments in UV-visible may involve the study of absorbance vs. time as the electrode potential is stepped or scanned, or they may involve wavelength scans to provide spectra of electrogenerated species.

Furthermore, specular reflectance measurements in UV-visible spectroelectrochemistry are attractive for the evaluation of the optical constants of metals and other materials, particularly in the growth of films, whose properties may differ markedly from those of bulk solids[79]. Probably the most important applications of specular reflectance spectroscopy in electrochemistry involve the monitoring of surface films and adsorption layers[104].

All spectroelectrochemical cells for UV-visible are designed to be used in experiments of transmittance or internal reflection[105]. The essential requirement for electrodes is that they must transmit more than 50% of the incident light within the region of the wavelength of interest.

Other prerequisites for materials used as optically transparent working electrodes include, in addition to optical transparency, a wide potential window and chemical and electrochemical stability against the different solvents and electrolytes used.

Generally, OTE can be classified into two groups:

- ***Electrodes formed by conductive thin films***, which can be formed by metals, semiconductor metal oxides, boron doped diamond and conductive polymers or plastics.

Thin metal films are obtained by depositing metals such as Au, Ag or Pt on transparent substrates such as quartz, glass or plastic. In quartz, the optical window ranges from 220 nm to the visible and infrared region, while glass or plastics are only useful in the visible region, and rarely in the infrared.

Deposition of metal films of Pt or Ag requires the previous deposition of a transition metal such as W or Ti to improve the adhesion and to stabilize the conductive film.

Another option for stabilizing the conductive film consists of the substrate functionalization with groups that bind to the metal and stabilize it. This process is especially important in the case of Au, which is vulnerable to friction, resulting in very robust and transparent electrode materials[106].

The metal film must be sufficiently thin (less than 200 nm) for maintaining the optical transparency. A disadvantage associated with this requirement is that the film may have low conductivity.

Transparent thin films of semiconductors and metal oxides such as indium tin oxide (ITO)[107] deposited on transparent substrates are seeing increased their application because it is possible to use due to the transparency of the oxides in the visible region of the spectrum having lower resistance problems that metal films[108] because they can be thicker. The problem of these materials is that they do not transmit ultraviolet light and their use is limited to studies in the visible or near infrared regions. Furthermore, a high amount of dopant can reduce the optical transparency.

To deposit these films described above, it is possible to employ various techniques[109,110], such as chemical vapour deposition, spray pirolysis, pulsed laser deposition, dipping, spinning or sputtering, among others.

Optically transparent diamond electrodes are also finding many applications in spectroelectrochemical transmission studies[111,112]. These electrodes are manufactured in several ways, being the most common technique the chemical vapour deposition. Polycrystalline diamond can be also grown on metal substrates, and then be separated for use as optical window[113]. It is also possible to deposit diamond thin films on optically transparent substrates.

High purity diamond has excellent optical transparency, transmitting from 225 nm to far infrared. However, diamond is not a good conductor and need to be doped, for example with boron, to obtain an useful electrode material[114]. Unfortunately, its optical properties degrade with doping and the wide range of wavelengths and the transparency are greatly reduced. However, doped diamond has a wide potential window, a good resistance and can tolerate several solvents in extreme conditions.

Another possibility is the use of transparent films composed by conductive plastic polymers, such as polypyrrole (Ppy), polyaniline (PANI) or poly(3,4-ethylenedioxythiophene) (PEDOT)[115]. These polymers can be obtained by chemical or electrochemical methods, being the electrochemical one the most used to deposit the polymeric material on a surface[116], since these techniques permit the control of the film morphology.

- ***Mesh electrodes.*** Transparent materials as minigrids or meshes[117] have found many applications in UV-visible and IR spectroelectrochemistry. Some metals have been commercialised in the form of mesh, such as Au (Figure 4), Pt or Pt-Rh alloys. Reticulated vitreous carbon (RVC) and other less common metals and alloys, such as Au amalgamated on Hg, are also widely used[118].

(Figure 4)

The optical transparency of these materials depends on the dimensions of the wires and mesh lattice, but is usually above 50%. The high surface area and high conductivity make these materials suitable for quickly total electrolysis. The dimensions and thickness of the mesh and the pore size are important parameters to determine the diffusive behavior in this type of electrodes[119].

Au meshes are not too strong, which prevents easy handling limiting the use of cells which use this electrode[120]. Trying to solve this problem, complicated cell designs using adhesives or epoxy resins have been developed[102,121]. The problem with these designs is that organic solvents used in electrochemistry usually dissolve gradually both the resin and the adhesive materials, leading to leakage problems or deformation and making necessary to build new cells every few experiments.

Many research groups have published several designs in which a working electrode based on a Pt mesh was used[60,120,122,123]. The problem of these electrodes is that poorly defined voltammetric peaks can be observed. Figure 5 shows a cell design for operate under vacuum, employing a sandwiched double Pt mesh to avoid the use of adhesives and resins.

(Figure 5)

- ***Other types of OTE.*** Other optically transparent working electrodes employed in UV-visible spectroelectrochemistry are microstructured electrodes[7,124], which are prepared by a lithographic galvanic deposition process, like that shown in Figure 6, or by polymerization with ceramic micromolds[125].

(Figure 6)

In recent years, a lot of spectroelectrochemical determinations using screen-printed electrodes as working electrodes are being carried out[126]. This type of electrode is suitable for quantitative studies because they are very easy to modify making them selective, sensitive and rapid in detections. In addition, these electrodes ensure reproducible and suitable surfaces for routine analysis. Figure 7 shows a cell design for internal reflection measures based on this type of electrodes[127].

(Figure 7)

Some spectroelectrochemical transmission cells combine the use of these optically transparent electrodes with the use of thin solution layers (between 10 and 300 μm in width for the sample chamber). Thus, they combine the characteristics of these electrodes with the benefits of rapid electrolysis[90]. This type of cells is very suitable for the study of biological species as vitamins[128], proteins[129–131] or nucleic acids[132,133].

With this configuration it is possible to perform a rapid and exhaustive electrolysis, which can detect species with short life time without interferences[134]. This thin layer configuration is also useful for studying homogeneous chemical reactions of electrogenerated species.

The thin layer design, by necessity, introduces a considerable uncompensated resistance in cell. Also, the auxiliary electrode is typically placed near one of the openings of the thin layer or in a closed compartment. These factors lead to a poor distribution of current between the working and the auxiliary electrodes. When a high uncompensated resistance is combined with a poor distribution of the current, temporal variations in the concentration of redox species on the OTE surface are observed, i.e. in a perpendicular plane to the light path[50]. The practical result of this situation is that, generally, there is a little or no temporal correlation between electrochemical and spectroscopic responses.

Only when the cell reaches equilibrium, a uniform distribution of the electroactive species is achieved. Although in most cases, there is no problem in waiting to reach equilibrium inside the cell, there are some situations where it is desirable to obtain spectra in non-equilibrium conditions, especially when irreversible processes coupled to electron transfer reactions are studied. In these cases, it helps to obtain spectral data resolved in time under conditions where the current is not zero.

Many research groups have focused their efforts on designing spectroelectrochemical cells that minimize the aforementioned problems allowing rapid spectroscopic studies. An example is shown in Figure 8, consisting of a cylindrical sample chamber with small diameter, open and accessible to the solution over the circumference of thin layer. The auxiliary electrode is placed along the edge of the thin layer to establish a geometrical relationship between the working and the auxiliary electrodes.

(Figure 8)

Another requirement of thin layer cells is the need for a short optical path to provide a high optical performance, which is very important to establishing a good signal/noise ratio. When, conversely, it is the starting specie which limits the optical performance of the cell to the desired wavelengths, two options can be considered: to reduce the optical path length or the concentration of this specie[135]. The latter option, despite increasing the optical performance, can reduce the absorbance change produced after electrolysis. In addition, under these conditions of dilution it can be significantly revealed other effects due to impurities or adsorption phenomena.

Many authors reduce the optical path using a light pipe, generally a quartz rod to transmit light at a short distance above the OTE surface without losing optical performance[136,137].

In transmission experiments, however, the light pipe obstructs the passage of current between the counter and the working electrode. With high resistance solutions, or with very short optical paths, this may result in an unequal distribution of potential.

The opposite situation occurs when it intends to carry out quantitative adsorption/desorption or electrocatalytic studies. In this case, cells with long optical paths and large electrode surfaces are needed to maximize the optical sensitivity[138,139]. Figure 9 shows an example of such cells, in which conductive thin metal layers are commonly used as working electrodes.

(Figure 9)

The concept of light pipe is more suitable for external reflection designs, such as that shown in Figure 10. This type of configuration is focused on minimizing the resistance induced by the potential distribution in the sample chamber and on increasing the effective optical path to improve the sensitivity. Most of these cells also employ optically transparent electrodes based on Au mesh[140] or polished metal foils[141]. The advantage of these electrodes is to provide a much longer optical path and offer much less resistance.

(Figure 10)

The total optical path is reduced by using light pipes in this configuration, without obstructing the current passage between electrodes. Furthermore, the absorbance change detected in reflection experiments is much greater than that observed in transmission experiments. On the other hand, when it is necessary the use of more dilute solutions due to the presence of strongly absorbing species, the increased sensitivity of this geometry helps to compensate the small optical changes observed.

Another way to get better results in internal reflection experiments is by using rotating disk electrodes (RDE), since this coupling has a number of advantages over other systems of forced convection. In particular, this type of electrodes generates a well defined diffusion layer with similar characteristics to those of thin film spectroelectrochemical cells[142]. One of the major advantages of this type of cells (Figure 11) is the possibility of reducing the IR drop of OTE, allowing measurements to be made on a smaller time scale. Furthermore, the possibility of working under stationary conditions with the replacement of the studied solution may be beneficial for the study of systems for which the decomposition of electrogenerated species may impair a reliable quantitative analysis.

(Figure 11)

All transmission cells showed use a configuration in which the light beam passes perpendicularly through the electrode surface, so it is necessary the use of an optically transparent electrode. However, it is possible to find cell designs where the incident light passes the solution in parallel to the electrode[143–145]. These designs not only provide high optical sensitivity to monitor species in solution under low diffusion periods but allow the use of opaque working electrodes. Figure 12 shows an example of this type of cells.

(Figure 12)

An unconventional cell design was proposed by the research group of López-Palacios[146,147] allowing the use of a new technique called "bidimensional spectroelectrochemistry" (Figure 13). In this technique it is possible to obtain simultaneously two different optical signals over a single spectroscopic experiment[146,148].

(Figure 13)

A way to minimize the sample volume inside the spectroelectrochemical cell is by using optical fibers and metal capillaries to build such devices[149–151]. An example is shown in Figure 14[152], where a cell with a volume smaller to 100 μL made with a working electrode of carbon nanotubes is shown.

(Figure 14)

Some authors have developed spectroelectrochemical cells for flow measurements[153], and even our group have developed a cell whose design allows working in batch or flow conditions[154], as shown in Figure 15. This cell allows variable configurations for use in a number of analytical situations besides the possibility to use different types of electrodes and materials. The dimensions and format of the cell are suitable for fitting in a standard cell holder for macro cuvettes in commercial UV-visible spectrometers.

(Figure 15)

3.2.Spectroelectrochemical cells for IR spectroscopy

In infrared spectroelectrochemistry (IR-SEC), species are probed at the electrode surface and in a thin layer of solution near the surface: the electrode/solution interface[82,155–157]. These approaches have been especially useful with species that have a high infrared absorption coefficient, like CO[158] and CN^-[159]. In favorable cases, information about the orientation of an adsorbed molecule and the potential dependence of adsorption can be obtained.

When someone designs a spectroelectrochemical cell for measurements in the IR region must have an important consideration in mind: it is necessary to minimize the absorption of incident radiation by the solvent[160]. Given this fact, two configurations have been mainly used to design IR cells[9,83]: external reflectance[82] and transmission[161]. It is also possible to use internal reflectance or attenuated total reflectance[162–165], but this technique is generally not feasible due to the low conductivity of the available elements of internal reflectance.

In the external reflection mode, the infrared radiation passes through a window and a thin layer of solution, reflects off the electrode surface, and is detected[166,167], (Figure 16). In this configuration the width of the solution layer is determined by the relative position of the working electrode and the window. It should be between 1 to 100 μm because most solvent are good absorbers of IR radiation[168]. In most cases, the auxiliary electrode and the reference electrode are placed outside the solution layer studied.

(Figure 16)

Another important factor to consider is the material for the optical window, which must be transparent to IR radiation and, in the same time, insoluble in the working solution.

It is also important that the working electrode diameter matches the diameter of the infrared beam (3-5 mm). The electrode must be made of a material that is highly reflective in the energy range of interest[9]. The most suitable materials are Au and Pt, however, has been shown that the glassy carbon is sufficiently reflective in the infrared region to be suitable for these techniques. Generally, the working electrode is wrapped in an inert insulator, such as glass or Kel-F.

These techniques not present too many operational difficulties. Therefore a variety of articles have been published including strategies for studying air sensitive compounds[80,169] and studies in a wide range of temperatures[7,170–172], and/or pressure[173]. They are also widely used to study a variety of electrodes, such as massive electrodes or single crystal metal electrodes[174].

External reflectance cells are suitable for the study of solutions with electroactive species or for electrode corrosion studies[175]. These cells, which are been used for more than three decades[176], have suffered a great evolution during this time.

One of the first designs of these cells is shown in Figure 17. In it, an IR transparent window is mounted on one end of the cell. This window should be flat or bevelled to minimize losses by reflection[160]. The working electrode, usually a polished metal foil, is placed near the window.

(Figure 17)

There are generally two types of assemblies: cells based on external reflectance elements which act as electrodes (as in the case of Ge[177]), or cells based on a small sheet as transparent electrode deposited on the surface of a reflective element[178], which is usually a non-conductive material. This is the case of screen-printed carbon electrodes[179], metal electrodes modified with ions[180], or nanomaterial modified electrodes[181].

However, for applications where the solution within the cell is studied, the electrode is positioned such that a small film of solution is between the same and the window. This is the so called thin layer configuration, where the external reflectance geometry minimizes the absorption of IR radiation by the solvent, while maximizing efficiency of absorb the analytes present in the diffusion layer near the electrode.

The choice of materials for optical window depends on the spectral region of interest. CaF_2[182], silica or ZnSe are used for applications in the medium IR, while polyethylene or Mylar windows are used for measurements in the far IR.

The cell body can be composed of inert materials such as glass, Teflon or Kel-F. It is important that this material will be inert, so the solution is not contaminated. The electrode is placed at the end of a glass coated metal rod, so the metal is isolated from the solution. This rod is inserted into the cell body, placing the working electrode in a correct position. A reference microelectrode is situated near the working electrode. The auxiliary electrode, typically a Pt wire, is placed behind the working electrode, in a configuration that minimizes the resistance of the solution. This electrode is circular, resulting in a uniform current distribution to the working electrode (Figure 18)[183,184].

(Figure 18)

However, when these thin layer cells are used to study adsorption or desorption processes on the electrode surface, it is difficult to interpret the obtained spectra due to the change in concentration of species adsorbed on the solution layer[185]. Another problem is the small volume of solution in the layer, which results in a small amount of analyte present in the vicinity of the electrode[186], with a poor mass transport from the solution outside the thin layer.

To solve these problems, cells with forced convection of the electrolyte through the thin layer of solution are employed. It has been used some cells using a radial flow from the side of the electrode to the center thereof[187], wherein the solution is removed from the layer through a hollow in the electrode or window. The other possibility is a configuration that employs a channel electrode where the solution flows through[165,188].

Furthermore, this type of flow cells (Figure 19)[189] provides the possibility of altering the mass transfer rate to eliminate the polarization effects over the concentration.

(Figure 19)

On the other hand, transmission cell designs are based on thin layer configuration. These cells use optically transparent electrodes in a sandwich arrangement, in which the working electrode is placed between two transparent windows. These designs have several drawbacks, such as high sensitivity to leakage or difficult purge[190]. However, the most relevant difficulty when designing a spectroelectrochemical transmission cell for IR spectroscopy is maintained the electrochemical performance while the spectroscopic one is maximized[191]. It is therefore crucial that the passage of light through the cell is as short as possible with the least number of components placed inside the path.

One problem is that materials commonly employed to separate physically the electrodes typically absorb IR light. There have been some cell designs, such as that of Figure 20, used to study cathodic processes, in which an electrode (here the anode) is placed outside the optical path, so it is not necessary to put any physical separation that fully covers electrodes.

(Figure 20)

Transmittance cells have the advantage that they can be placed directly into the sample chamber of most of conventional IR spectrometers[98]. External reflection cells, however, generally require additional instrumentation allowing the IR beam incises directly on the electrode surface. This additional instrumentation is placed outside the sample chamber or, within the same if it has been appropriately modified. This fact presents three disadvantages:

Firstly, the optical performance of the system decreases, since the light beam should be reflected in at least two mirrors, so many losses due to reflection occur. Secondly, the alignment of the beam is much more difficult in a configuration of external reflection than in transmission. Finally, an economic cost should be added to the design if additional commercially available instrumentation is necessary.

Figure 21 shows one of the first designs for IR transmission cells[192]. These cells are similar to those used in UV-visible and avoid the use of adhesives and resins that may cause leakage problems or contamination. Furthermore, these cells are reusable and robust, and are relatively inexpensive to manufacture. In all cases it is essential to employ a three-electrode configuration, since it is crucial that the resistance of the thin layer solution is minimized.

(Figure 21)

Generally, the transmittance percent of IR cells employing optically transparent electrodes is greater than 50%, representing a high yield.

Both transmission and external reflectance configurations have many problems in obtaining spectral information of molecules with limited stability[193], especially when thin film cells are employed. For example, transmittance cells employing transparent electrodes suffer large IR drops, leading to errors in the control of potential and significant distortions in the voltammogram of the of electrolysis products[178,194]. These disadvantages limit the use of these cells for studies of slow chemical reactions coupled to an electronic transfer.

Trying to solve these drawbacks, Shaw published a cell design based on the use of an optic fiber[195,196], shown in Figure 22. This cell has several advantages, including the precise control of applied potential, the ability to quantitatively monitor the progress of electrolysis, a good performance at low temperature and a good elimination of air present in the electrolysis solution.

(Figure 22)

Finally, there are many designs of spectroelectrochemical cells employing a configuration of internal reflectance or attenuated total reflectance (ATR) (Figure 23), although, as discussed above, this is the configuration less used in IR spectroelectrochemistry, as it is much less sensitive than transmission settings[197].

(Figure 23)

This configuration, however, is more suitable for the study of solid-liquid[198] or solid-gas interfaces. In this geometry, the thickness of the solution layer is not limited, which facilitates obtaining a uniform distribution of current density[199].

Most spectroelectrochemical cells with this configuration use transparent electrodes based on a thin metal film deposited on an internal reflectance element[102]. Other cells employ thin sheets pressed on a reflectance prism, such as a diamond film doped with boron on a silicon wafer[200]. Another possibility is the use of a porous spiral electrode[201], as it is shown in Figure 24.

(Figure 24)

ATR configuration can also be used with Surface-Enhanced IR Absorption (ATR-SEIRAS) to obtain spectra on polarized electrodes whose surface has a specific microstructure to enhance the SEIRAS effect[202]. Such techniques enable to observe only the interfacial species because the SEIRA is a very short-term effect, so the adsorbed species and how they are joined to the electrode surface can be detected. The electrodes used are usually thick films of metals (~ 20 nm) vacuum evaporated on the ATR prism, whose surface must be conditioned under strict cleaning conditions[203].

3.3.Spectroelectrochemical cells for RAMAN spectroscopy

Raman spectroscopy provides molecular vibrational information complementing that of IR spectroscopy. Because it is carried out with excitation and detection in the visible region of the spectrum, it can be employed in electrochemical cells with glass windows and aqueous solutions, both of which are strongly absorbing in the IR region.

Since Raman experiments always involve the measurement of small energy shifts on the order of 100 to 3000 cm^{-1} from the excitation energy, a monochromatic source is essential. Since high intensity is also required, lasers are universally used. A high-resolution double or triple monochromator is employed to separate the Raman lines from the intense Rayleigh line.

In electrochemical situations, measurements are usually made on species within the operating cell[204]. Dissolved species or those adsorbed on an electrode surface can be monitored[205]. Thus this technique is a powerful tool for the study of lithium batteries[206,207], fuel cells[208,209] and other molecular devices[210]. In addition, it has become an important analytical technique in many other fields of science, such as chemistry, medicine and other life sciences[211,212]. More specifically, in the last decade, Raman spectroscopy has found numerous applications in studies of carbon structures[7,10] as fullerenes, nanotubes or graphene due to the particular Raman spectra of these materials[213], which depends on the laser excitation energy, number of carbon layers, doping or applied potential. The most common device for Raman spectroelectrochemistry is one in which the surface of the working electrode is placed near the optical window, which is usually made of glass or silica, and the light beam is incident thereon at an angle of about 60 °. In this case, it is achieved a thin layer of solution between the electrode and the optical window to minimize absorption and scattering of light by the electrolyte[214]. Figure 25 shows an example of this type of thin layer cells[215,216].

(Figure 25)

However, when it is intended to conduct studies in electronic materials which exhibit a strong absorption at the wavelength of study, cells with rotating working electrodes are used[217], as shown in Figure 26. This electrode serves to minimize local effects due to heat in the vicinity of the light beam, while avoiding the decomposition of the sample.

(Figure 26)

An alternative to this configuration is producing the electrolyte solution flow on the surface of the working electrode in a flow cell such as that shown in Figure 27[218–222].

(Figure 27)

On the other hand, there are cells in which, instead of a rotating electrode, the sample is rotated[223–225], as shown in Figure 28. The advantages of this type of cells with respect to those employing rotary electrodes are: mechanical simplicity, versatility because the electrode house may have various geometries, and a wide range of temperatures, including the possibility of studying frozen samples.

(Figure 28)

There are many other designs of spectroelectrochemical cells for Raman studies. An example was published by Schwab[226], wherein the input beam is incident at an angle close to 90º on the surface. This cell also employs an optical fiber to collect the scattered light, maximizing the coupling between the cell and the spectrometer.

It is also possible to find some spectroelectrochemical cells for routine analysis, as the portable cell based on screen-printed electrodes published by Robinson[227].

3.4.Spectroelectrochemical cells for X-ray

X-ray absorption spectroscopy provides information about some basic considerations and symmetry on the electronic structure of active atomic orbitals of different materials[228,229], as bond lengths and angles, identity of neighbor atoms or oxidation states[230,231]. Recently, this technique has been employed in spectroelectrochemical studies about corrosion processes[232,233], electrodeposition[234], ionic adsorption[235] or yields of fuel cell anodes[236], among others.

However, the application of X-ray methods to electrochemical studies is still in its infancy. The need for synchrotron radiation, rather than sophisticated cells, and elaborate data interpretation has strongly limited the use of these techniques. But the atomic-level structural information that these methods provide is rivaled only, perhaps, by the scanning probe methods.

When X-ray spectroelectrochemical cells are designed, it must be taken into account various points[87,237,238]: the need for a total electrochemical conversion of the analyte of interest, the need to minimize the resistance of the cell to achieve analyte conversion in a reasonable time and the need for materials which result in good optical signals being transparent to X-rays.

Extended X-ray Absorption Fine Structure (EXAFS) spectroelectrochemical cells can be divided into three groups: solution cells[239], polymer film cells[240] and metal or metal oxide film cells[241–243].

Solution cells use thin layer configuration for rapid and complete electrolysis and also for minimizes solvent absorption. The first cell of this type[244] was based on a gold mesh acting as transparent electrode. A subsequent design employs a reticulated glassy carbon electrode[245], as shown in Figure 29. This design reduces the conversion time, which is important when synchrotron sources, that are available for a limited period of time, are used.

(Figure 29)

Cells based on conductive films use polymer modified electrodes. This configuration has the advantage that the substance of interest is confined in a layer in a region adjacent to the electrode surface. It is therefore possible to minimize the amount of solution in contact with the X-ray beam, either by employing a thin layer compartment for the solution or by removing most of the electrolyte after electrolysis of the species electroactive in the conductive film. An example of such cells is shown in Figure 30. This cell made of Teflon uses Ru and Os vinylpyridine polymers acting as a working electrode, placing at the end of the cell and coated by a film which allows the contact of only a thin layer of solution[246].

(Figure 30)

Meanwhile, spectroelectrochemical studies of X-rays on metal or semiconductor surfaces supported on metal electrodes have the same advantages as in the case of polymer films: the electrolyte layer can be reduced, resulting in less attenuation of the X-ray beam.

There are several designs for this type of cells. One of them, published by IBM researchers[247], is based on a working electrode located on a bracket that is attached to another swivel bracket, allowing the correct alignment of the sample. An Ag/AgCl electrode is used as reference electrode, while a Pt wire acts as auxiliary electrode.

This cell has the advantage that the deposition of the layer of interest is performed while the electrode is exposed to a large amount of electrolyte solution, while for data collection a thin layer configuration is achieved by using a capillary.

Long[248] used a similar concept in the design of his cell. In this case, the interior of the cell was placed over a piston which is removed during electrolysis time and turned to place to perform subsequent studies in a thin layer configuration. The three electrodes were placed on an inert resin support so that were coplanar. The working electrode was prepared by depositing the sample on a glass surface.

Hoffman published two designs for spectroelectrochemical cells used in the study of electrochemical interfaces[237,249]. The first one, shown in Figure 31, is known as “bag cell". Here, the sample is deposited on an Au substrate, which is used as working electrode. The auxiliary electrode, a wire of Au, is separated from the working electrode by a Teflon spacer. An adsorbed oxygen Pd electrode is used as reference electrode.

(Figure 31)

When electrolysis is carried out, the bag is released to allow a large volume of electrolyte around electrodes. When the electrolysis is completed, the auxiliary electrode is placed outside the X-ray beam and the volume of the bag is reduced by joining the bag walls.

The second design, shown in Figure 32, uses a rotating disk working electrode, with only half of it in contact with the electrolyte solution. While, the other half is exposed to a He atmosphere where X-ray measurements are developed.

(Figure 32)

Another example of this type of cells is that published by McBreen[250], which is a transmission cell of two electrodes, as shown in Figure 33. The cell consists of two acrylic pieces at the ends, each one with an optical window. The cell components include a NiO_2 working electrode and a counter electrode, separated by three layers of filter paper soaked in electrolyte. Each component is mounted on a PTFE support, and all these supports are screwed together.

(Figure 33)

In recent years there have been other EXAFS cells based on composite electrodes[251,252]. These cells show the same advantages as those designed previously for polymer films or metal electrodes.

So far, we have seen several examples of spectroelectrochemical cells for EXAFS, but there are also some designs of cells for X-ray Absorption Near-Edge Structure (XANES). An example is published by Soderholm[253], shown in Figure 34, which is based on the use of a working electrode consisting of a U-shaped network of Pt.

(Figure 34)

On the other hand, some spectroelectrochemical cell designs have been described for their use in X-ray scattering studies. These cells, with a very thin solution layer (~ 100 μm) between a window (an organic thin film of Mylar or polypropylene) and the electrode surface, were used in reflection geometry.

This geometry, although has some advantages such as reducing the absorption by the solvent, also has some disadvantages for the electrochemical performance as insufficient control of potential or poor current distribution along the film of electrolyte. For this reason, working electrodes based on single crystal disk geometry have been employed, where in addition to the thin layer of study; only one of the electrode faces is in contact with the electrolyte solution. In this configuration it is possible to determine the precise current which flows at the single crystal face. An example of this type of cells is shown in Figure 35[254].

(Figure 35)

Finally, it must be noted that numerous cell designs can be used for both absorption or scattering measurements of X-ray. An example of this is shown in Figure 36[232]. This cell consists of three parts: first, the PVC body, the main portion of the cell containing the electrolyte circulation chamber and the calomel reference electrode. The second part is a PVC piston which controls the thickness of the solution layer, and is designed to introduce therein a Pt electrode serving as the counter electrode. The third part of the cell is a conductive metal piece, which is detailed in Figure 36B.

(Figure 36)

The working electrode consists of a thin layer of graphite mixed with the sample. This paste is set in an amorphous carbon plate using Ag conductive paint to make the electrical contact.

3.5.Spectroelectrochemical cells for NMR

NMR, one of the most suitable tools for absolute elucidation of chemical structures, was associated with electrochemistry for the first time in 1975, with the design of the first spectroelectrochemical liquid NMR cell[95]. Since then, the number of publications on spectroelectrochemical NMR experiments has increased considerably due to the increasing need to know quickly the structure of electrogenerated compounds[11]. In fact, this is the favorite technique for determining the finer structural and electronic changes[255,256].

The application of NMR to spectroelectrochemistry has many limitations, especially due to changes to be made to the geometry of the NMR tube to introduce electrodes, and the interaction of metals with the magnetic field, that difficult to carry out such measures[257]. A device as simple as the use of two Pt wires as cathode and anode in a NMR tubes causes a great influence on the homogeneity of the magnetic field, making it impossible to perform simultaneous measurements of electrolysis and RMN spectroscopy[258].

Therefore, it is still possible to find numerous publications on electrochemistry employing NMR as in ex situ technique, where a metal powder acts as electrode in the electrochemical cell. After the electrochemical experiment, this powder is transferred, usually along with the electrolyte, to an NMR tube for his study[259–262].

In fact, in recent decades, there are very few publications devoted to the manufacture of spectroelectrochemical NMR cells[95,257,263–266]. These cells, suitable for the introduction into the NMR detector, are useful for identifying the structure of electrogenerated species or for monitoring unstable intermediates before other chemical reactions consume them[267].

Most spectroelectrochemical NMR studies are focused on identifying electrogenerated species by electrolysis[86,268]. However, there are only a few references about the study of the electrode/solution interface, due mainly to the low sensitivity of this technique.

The detection limit for a single observation is 10^{18} protons, being one or two orders of magnitude higher if the average of the signals of several measures is taken. The sensitivity for the detection of other nuclei, such as C^{13}, is even smaller. If it is necessary to study a surface covered with adsorbed species, it is required to employ several m^2 of it. However, it is possible to use NMR to study surfaces if finely divided powder is used[168,269].

The first attempt to design a spectroelectrochemical cell for NMR was realized in 1975[95] and is shown in Figure 37. With this design it was proved that it was possible to detect some unstable intermediates. Other authors propose flow cells with electrodes located outside the radiofrequency field in order to achieve a good fit of the elements[257,258].

(Figure 37)

Other examples of NMR spectroelectrochemical cells for batch experiments have been published. They are based on a three-electrode configuration[267]. Compared with flow cells, these one require a smaller amount of volume, minimizing the use of deuterated solvents[266].

The use of cells based on Au coated NMR tubes has obtained good analytical results for flow and batch cells, showing that this configuration minimizes the width of the NMR signals[264,266]. An example of these cells is shown in Figure 38. Other configurations employ carbon fibers as working electrodes, being able to work in a broad frequency range[268].

(Figure 38)

3.6.Spectroelectrochemical cells for microscopy

Due to the large number of variants that can present the coupling of different microscopy techniques with electrochemical methods[23,270–275], it can be concluded that there is no a general spectroelectrochemical cell design for this purpose. For this reason, in this section some examples of cells that have been published until now will be shown.

The first example was published by Schröder[276]. The body of this cell, shown in Figure 39, is made of acrylic. It has a three-electrode system, consisting of an Ag/AgCl reference electrode, a Pt wire as counter electrode, and a paraffin impregnated graphite working electrode.

(Figure 39)

This device is used for the study of immobilized particles on the electrode surface. Once deposited on the surface thereof, the electrode surface is placed parallel to the optical cell window, which allows observation under a microscope in a configuration of internal reflection.

Another example is published by Komorsky-Lovric, who has designed a cell working in transmission mode. This device has been used for studies of electron transfer reactions in three-phase electrodes[277].

Gyurcsányi published a cell for spectroelectrochemical microscopy with a thin layer configuration for studying selective membranes[270]. This cell, whose scheme can be seen in Figure 40, consisted of a Plexiglas body with two inlets and two outlets, and two connections for Ag/AgCl electrodes, because a set of four electrodes is used, instead of the usual three.

(Figure 40)

The most important elements of this cell are the membrane and the spacers, and their adequate fusion for obtain a proper thickness of the membrane.

Recently, Surface Plasmon Resonance (SPR) has been used in a spectroelectrochemical configuration[278] because the nature of metallic surface where plasmon is propagate strongly depends on the application of an electrical potential if such metal is used as working electrode.

3.7.Spectroelectrochemical cells for luminescence

Luminescence spectroscopy is a more sensitive technique than UV-visible absorption spectroscopy, and enables the independent control of excitation and emission wavelengths. Judicious choice of these wavelengths therefore allows selective monitoring of individual groups responsible to light absorption in a polymer film[279]. These groups, called chromophores, provide a certain color to a molecule.

When luminescence spectroscopy is coupled with electrochemical techniques[280], this provides the opportunity to detect some properties of electrogenerated chromophores which are in their excited state[281]. However, this technique has received relatively little use as spectroelectrochemical method, even despite its high sensitivity vs. other absorption methods.

The main reason for that can be attributed to lack of versatile spectroelectrochemical cells that meet the detection requirements of electroluminescence measures.

Many articles have been published on the use of cells with optically transparent electrodes in spectroelectrochemical luminescence measurements[281–286] in a transmission configuration. To accommodate the detection of the emitted light, these cells are displaced 45° with respect to the excitation and emission slits. In general, the advantage of small electrolysis time with these cells compensates the interferences caused by scattering of the radiation by the components of the cell. It is possible to find publications showing spectroelectrochemical cells based on a thin layer configuration using transparent electrodes[88], as shown in Figure 41.

(Figure 41)

To minimize the inherent difficulties in this type of configuration, some authors have reported cells with large optical paths[287], which allow the detection of light emitted at an angle of 90°. This cell employs a reticulated glassy carbon electrode as the working electrode. The narrow optical channels have been drilled through the electrode to provide optimum detection at 90º with minimal interference. This design presents a number of advantages such as ease of coupling in a conventional spectrometer, ease of construction and assembly and chemical resistance thereof, plus it requires small volumes of solution.

It is also possible to find several publications on the development of spectroelectrochemical sensors for fluorescence measurements[288,289].

As mentioned, articles about use of fluorescence spectroelectrochemistry are relatively scarce. There have been some based on the study of liquid-liquid interface under controlled potential[290,291]. Other publications use rotating electrodes to study fluorescence on electrochemically active films[279]. There are also some based in fluorescence microscopy[292] and hydrodynamic spectroelectrofluorometric voltammetry[293].

More generally, luminescence spectroelectrochemistry[294] is very suitable for the study of molecules having luminescence, which are useful in the development of chemical sensors[295,296], storage optical devices[297], smart doors[298], live images[299] and screens[300]. This technique is also used to study mechanisms of redox reactions including chromophores[282,301] and electrochemiluminescence studies[88,302]. It is also widely used in the development of spectroelectrochemical sensors[303,304].

3.8.Spectroelectrochemical cells for EPR

Electron Spin Resonance (ESR), also known as Electron Paramagnetic Resonance (EPR), is used for the detection and identification of electrogenerated products or intermediates that contain an odd number of electrons; that are radicals, radical ions, and certain transition metal species[74].

This technique has found extensive application to electrochemistry because ESR is a very sensitive method, allowing detection of radical ions at about the 10^{-8} M level under favorable circumstances, and because it produces information-rich, distinctive and easily interpretable spectra[305,306]. Also, electrochemical methods are particularly convenient for the generation of radical ions; thus they have been used frequently by ESR spectroscopists for the preparation of samples.

In a classic experiment of ESR spectroelectrochemistry, radicals are produced within the cell which, in turn, is placed inside the microwave detector[307]. Therefore, it must keep in mind that polar solvents and glass windows are not suitable for this technique, because they absorb in the microwave region. Therefore, small volume flat cell made of quartz are used[52,308].

Most electrochemical ESR cells contain a large-area working electrode, with smaller auxiliary and reference electrodes positioned as fully as possible outside of the sensitive region[309–312]. Such cells allow experiments in which the ESR signal and the electrolysis current can be monitored simultaneously as functions of potential or time. An example of such cells is shown in Figure 42.

(Figure 42)

However, this type of cells is unsuitable when trying to study a large volume of electrolyte solution[313]. For this type of analyses it is necessary to used modified cells, in which the working electrode is also one of the reflecting surfaces of the microwave resonator. In practice, this is achieved using a wire wound in a helix as working electrode, and placing the other two electrodes inside this helix. This geometry allows the use of a larger volume of solution in the cell, substantially reducing the risk of depletion of electroactive material, while the sample volume that can be detected in microwave is maximized.

Furthermore, these designs are not suitable when Q or W bands are used, due to space limitations of commercial spectrometers. In these cases, the diameter of the sample tube is between 0.5 and 1 mm, respectively. An example of cell for spectroelectrochemical measures in these bands is shown in Figure 43[307]. The device is constructed from a standard quartz sample tube. A system of three electrodes based on metal wires has been placed inside this tube. The working electrode is Teflon coated Pt wire, the quasi-reference electrode is an Ag wire, and the auxiliary electrode is a Pt wire.

(Figure 43)

In general, ESR is very useful to identify not only the presence of a radical on an electrochemical reaction[314,315], but is also suitable for studying the temporal evolution of a radical undergone various potential stages[53,316] or even further radical deterioration when applying current is interrupted and calculate their lifetime. A more detailed analysis of the ESR spectrum provides information on the distribution of the spin density in the radical and ion-pair formation, solvation or internal restricted rotation processes.

It is possible to perform comparative measurements of the same radical species in different media[65,317,318], since the ESR spectrum is very sensitive to the environment. ESR has also been widely used to measure electron transfer rates between the radical ion and the initial compound, by no concentration effects on line widths[3].

If the lifetime of the electrogenerated radical is very small, it is possible to detect them using “spin traps”[319,320], which are chemical compounds that react with the electrogenerated radical forming a more stable radical, giving a characteristic ESR spectrum. Obviously, these traps should be stable over the range of potential used in the analysis.

3.9.Other spectroelectrochemical cells

This section will go over some cell designs for other analytical techniques less used in spectroelectrochemistry as atomic absorption spectroscopy or optical impedance spectroscopy.

In the literature there are several designs similar to Figure 44 for spectroelectrochemical cells used in atomic emission spectroscopy[61,321,322]. This cell consists of two compartments in which the working electrode is exposed to a flow of electrolyte in a cell of small volume, whose composition is continuously monitored by ICP-OES (inductively coupled plasma optical emission spectrometer). This flow channel has the input in the bottom and the output at the top so that gas is not generated within the cell during the experiment. The other compartment is separated from the working electrode by a porous membrane that allows ion flow from one compartment to another while preventing mixing of the two electrolytes. This secondary compartment is for the reference and the auxiliary electrode.

(Figure 44)

As cells for optical impedance spectroscopy measures will be noted that shown in Figure 45. This cell comprises an ITO working electrode connected to a Pt wire to connect with the potentiostat, an Ag/AgCl pseudo-reference electrode and a Pt wire as auxiliary electrode[323].

(Figure 45)

This technique is based on the application of a modulated electrical potential for altering the oxidation state of the adsorbed species on the electrode surface and on the use of a fiber optic signal for monitoring the spectral changes occurring during the application of this potential. Next, the optical data experimentally obtained are mathematically converted to determine several electrochemical properties of the system.

4. FIA AND SPECTROELECTROCHEMISTRY

At this point, it must be noted that although there is a certain amount of spectroelectrochemical flow cells[153,185,220,222], in the vast majority of cases, this system is used only to facilitate the introduction or renewal of the solution under study within the sample chamber.

Moreover, the use of spectroelectrochemical detectors in FIA systems has been very limited in recent years, only two groups: the Daniel and Gutz group[46,324] and our group[154,325] have published something about it in the first decades of 21th century, despite that there are evident analytical advantages offered by having a sensor element capable of simultaneously recording multiple properties of a continuously flowing solution.

In general, the use of spectroelectrochemistry in FIA experiments is aimed to develop methods of analyte detection and quantification based on the simultaneous analysis of several properties getting self-validated results, which greatly enhances the selectivity of the method avoiding much of the interferences. It is also possible the simultaneous detection of multiple analytes, since it is possible to register multiple properties simultaneously. Even an improvement in the sensitivity of the FIA method can be achieved if the electrochemical measure affects to spectroscopic results, increasing the signal, or if the application of electromagnetic radiation (radiant energy) modifies the redox reactivity.

5. CONCLUDING REMARKS

Although the first articles dealing with spectroelectrochemistry were published in the mid-20th century, and afterwards this combination of techniques has been used in numerous works, most of them use spectroelectrochemistry to study what happens on the electrode-solution interface during an electrochemical process.

The use of a spectroelectrochemical cell as multimode detector in an analytical device is rather scarce yet, despite the evident new opportunities that having two techniques applied at same place and time offer to get more analytical selectivity and sensibility. Such multivariate detectors should be explored in deep to enhance the performance of new analytical devices. This fact could open new chances to study more complex samples, getting quality results while using simpler and more compact devices.

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Figure Caption

Figure 1. Common optical configurations for spectroelectrochemical cells showing path of incident light (thick line) and detected light (thin line) in (a) transmission mode normal to the electrode and (b) transmission mode parallel to the electrode, internal (c) and external (d) reflectance modes. The dashed line represents the electrode solution interface. Adapted from[76].

Figure 2. Common optical configuration for Raman spectroelectrochemical cells showing path of incident light (thick line) and detected light (thin line). The dashed line represents the electrode solution interface. Adapted from[92].

Figure 3. Schematic view of the experimental arrangement for transmission spectroelectrochemistry. Adapted from[3].

Figure 4. Schematic drawing of the Au-μ-mesh coated with a PANI layer[96].

Figure 5. Schematic illustration of a vacuum-tight thin-layer spectroelectrochemical cell with a double platinum gauze working electrode. The front view shows the vacuum operation while the side view shows the cell with regular nitrogen deoxygenation. The frit arm is not shown in the left side view. Parts of the cell are as follows: (a) width and (b) length of gauze working electrode; (c) thin-layer chamber; (d) thickness of the thin-layer chamber; (e) glass frit (Pt tipped for vacuum operation, asbestos tipped for regular operation); (f) photo window; (g) gauze working electrode; (h) stainless steel foil; (i) TEFZEL film protection; (j) light shelter for photo window; (k) magnetic stirrer[120].

Figure 6. Schematic view of a microstructured Au electrode[124].

Figure 7. Scheme of a spectroelectrochemical cell using a screen-printed electrode (SPE; RE = reference electrode, WE = working electrode, CE = counter electrode). The spectroelectrochemical cell has been drawn in proportion to its actual size[127].

Figure 8. Schematic diagram of an optically transparent thin-layer electrochemical cell. The thin-layer, windows, and cells walls have been exaggerated for clarity[50].

Figure 9. Schematic diagram (not to scale) of a thin-layer cell. (a) An exploded side view of all components down the optical axis of the cell including the plate assembly, thickness spacers (ts), back plate (bp), electrode positioning foot (f), positional spacer (ps), thin film electrode (tfe), and a compression spring. (b) Top view showing all components, including the reference (RE) and auxiliary (AE) electrodes, assembled inside the cuvette[138].

Figure 10. Details of a cell for internal reflection spectroelectrochemical experiments[135].

Figure 11. Schematic diagram of a experimental setup for near-normal incidence UV-visible reflection absorption measurements at a rotating disk electrode[142].

Figure 12. Schematic view of a parallel incident spectroelectrochemical cell. (a) auxiliary electrode, (b) reference electrode, (c) working electrode, (d) methacrylate bracket, (e) saturated KCl solution, (f) quartz cell, (g) optical path, (h) light beam height[143].

Figure 13. Schematic diagrams of a bidirectional thin-layer spectroelectrochemical cell: (A) 3D view: (a) platinum sheet electrode; (b) Ag/AgCl/KCl reference electrode; (c) spacers; (d) epoxy pieces containing the platinum working electrode; (e) inert epoxy wall. (B) Side view: (f) platinum wire counter electrode[146,148].

Figure 14. Schematic image of an experimental long-optical-pathway spectroelectrochemical cell. CE, counter electrode; RE, reference electrode; WE, working electrode; SWCNT, single-walled carbon nanotubes[152].

Figure 15. Diagram of the multi-configurational spectroelectrochemical cell designed by our group[154].

Figure 16. Diagram of the external reflectance configuration for IR-SEC. Adapted from[3].

Figure 17. Configuration of an external reflectance cell for IR spectroelectrochemistry[161].

Figure 18. Drawing showing a cross section of the assembled cell and electrode assembly (upper). Lower drawings show the back and front views of the cell with window and retaining flange removed[184].

Figure 19. Simple diagram of a flow thin layer cell for external reflectance spectroelectrochemical measurements in IR[189].

Figure 20. A diagram of an in situ transmission FTIR spectroelectrochemical cell. I_{IN} and I_{OUT} refer to the intensity of the infrared beam before and after passing through the cell, respectively[191].

Figure 21. (1) side view and (2) front view of a thin film spectroelectrochemical transmission cell for IR measurements. A, hole for the working electrode; B, holes for reference and auxiliary electrodes; C, silica window; D, Teflon piece; E, incident beam direction[192].

Figure 22. Schematic representation of a sampling probe head at the end of the fiber-optic cable. The portion shown is immersed in the electrolysis solution, and solution enters the sample chamber through holes in the stainless steel probe wall[196].

Figure 23. Schematic view of a IR spectroelectrochemical cell with attenuated total reflectance configuration[197].

Figure 24. Spiral gold electrode with nanoscale pores made by anodization at different pH values[201].

Figure 25. Diagram of a thin layer spectroelectrochemical cell for Raman spectroscopy[216].

Figure 26. Diagram of a Raman spectroelectrochemical cell with rotating disk electrode. A, nylon body; B, joint; C, hole for the rotating electrode; D, axis for the electrode rotation; E, balls; F, PTFE seal; G, working electrode; H, ring; I, carbon brush; J, motor connection[217].

Figure 27. Scheme of a spectroelectrochemical flow cell for Raman. WE, working electrode; C, electrical contact to the working electrode; SP, flow pump; M, magnet; CE, counter electrode; PE, potentiometric electrode; RE, reference electrode; PV, vycor to isolate the electrodes; V, valve; FO, fiber optics; FL, lens; W, quartz window; RC, capillar[222].

Figure 28. Device for in situ Raman spectroelectrochemistry with an eccentric rotation of the electrochemical cell. The working electrode is positioned out of the motor axis (dashed-dotted line) using the eccentric holder[223].

Figure 29. Spectroelectrochemical cell based on a reticulated glassy carbon electrode for X-ray measurements[245].

Figure 30. Spectroelectrochemical cell for surface X-ray studies on modified electrodes. A, working electrode (Pt disk); B, Pt auxiliary electrode; C, hole for the

reference electrode; D, holes for electrolyte; E, disk; F, Teflon body; G, goniometer; H, optical window[246].

Figure 31. Spectroelectrochemical cell for X-ray measurements. A, working electrode; B, auxiliary electrode; C, reference electrode; D, separator; E, polyethylene bag; F, assembly; G, X-ray beam[237].

Figure 32. Spectroelectrochemical cell based on a rotating disk electrode. A, rotating disk working electrode; B, auxiliary electrode (Au wire); C, reference electrode (Pd-H); D, X-ray beam; E, assembly for working electrode[249].

Figure 33. Transmission cell for X-ray spectroelectrochemical studies. A, working electrode; B, auxiliary electrode; C, reference electrode; D, current collector; E, separator; F, joints; G, window; H, electrolyte[250].

Figure 34. Spectroelectrochemical cell for XANES experiments. The working electrode (W) is a Pt mesh, while the auxiliary electrode (A) is a Pt wire. The reference electrode (R) is an Ag/AgCl electrode. The cell has a N_2 input for facilitate the mixing[253].

Figure 35. Schematic view of a cell for X-ray dispersion studies. A, single crystal disk working electrode; B, Pt auxiliary electrode; C, Ag/AgCl reference electrode; D, optical window; E, electrolyte solution; F, input for electrolyte solution; G, output for electrolyte solution; H, cell body; I, micrometer; J, electrode house; K, exterior chamber[254].

Figure 36. (a) Photograph of the electrochemical cell with the piston, the body and the metallic conductive part and, (b) zoom on the electrochemical cell, to see the saturated calomel electrode (SCE) reference electrode, the platinum wire turned around the piston and the working electrode on the 500 μm thick graphite window (mix of reference powder + graphite). Arrows point the electrolyte circulation in the cell. A gasket is placed between the body cell and the piston to avoid electrolyte leakage[232].

Figure 37. Electrochemical flow cell for insertion in NMR probe[95].

Figure 38. Coaxial three-electrode assembly inserted in normal 10-mm NMR sample tube: (a) RE capillary, (b) cylindrical Pt-mesh CE, (c) pinholes connecting CE/WE compartments, (d) Teflon plugs, (e) tubular WE, (f) receiver coils. Reproduced with permission from[86].

Figure 39. Scheme of a cell employed for spectroelectrochemical studies of microscopy with an internal reflectance configuration[276].

Figure 40. Thin-layer electrochemical cell for microscopic studies. (A) top view; (B) cross-sectional view. Right: photographic image of the placement of the membrane strip-spacer ring assembly over the surface of the polished plexiglass cell block. The two compartments on the two sides of the membrane strip are equipped with pairs of Ag/AgCl electrodes and solution inlet and outlet ports[270].

Figure 41. Schematic diagram of the thin-layer spectroelectrochemical cell. (A) Perspex blocks; (B) polyethylene membrane; (C) quartz glass; (D) Pt mesh working electrode; (E) valve; (F) outlet; (G) screw; (H) thin layer; (I) solution reservoir; (J) rubber stopper; (K) reference electrode; (L) Pt counter electrode; (M) Pt connecting wire[88].

Figure 42. Spectroelectrochemical cell for EPR measurements[310].

Figure 43. Schematic diagram of Q/W band EPR in situ spectroelectrochemical cell[307].

Figure 44. Functional diagram of a electrochemical cell (left) and a computer image of a cell as constructed (right); wec, working electrode compartment; cec, counter electrode compartment; j, o-ring; m, membrane; we, working electrode; ce, counter electrode; re, reference electrode; s, spring; ss, spring support. Dashed arrows indicate the direction of the solution flow[61].

Figure 45. Schematic representation of a spectroelectrochemical cell for optical impedance spectroscopy. The insert shows the distribution of the electric field on the structure[323].

Figure 1

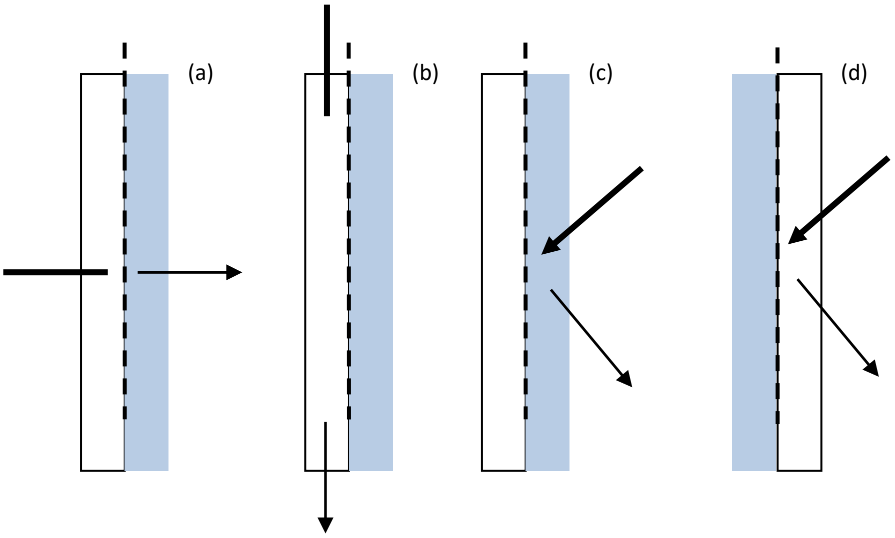


Figure 2

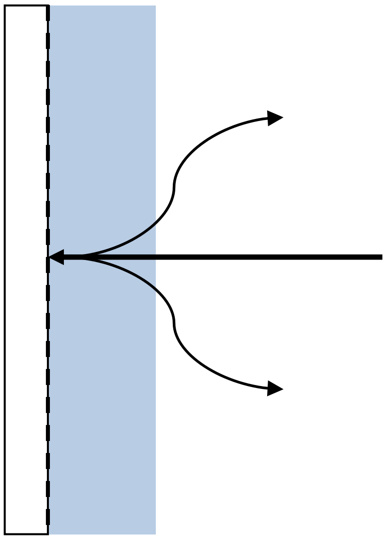


Figure 3

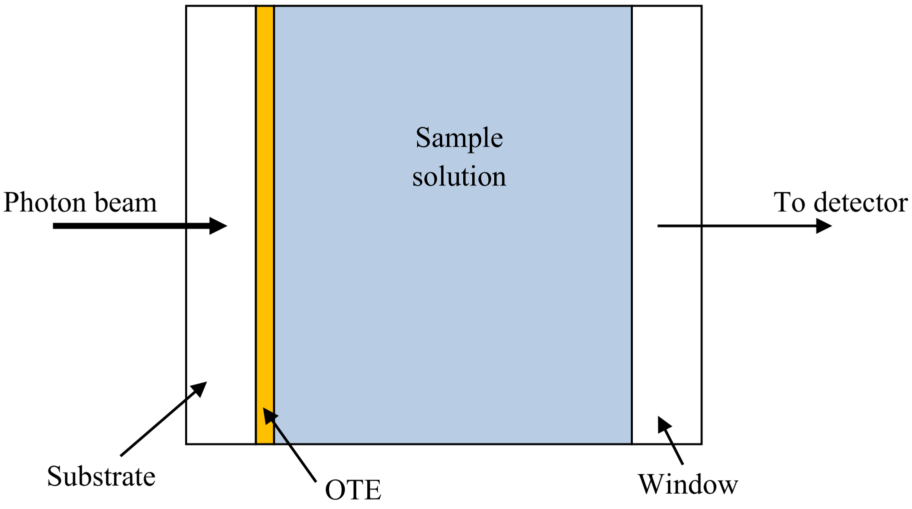

Sample
solution
Photon beam
To detector
Substrate
OTE
Window

Figure 4

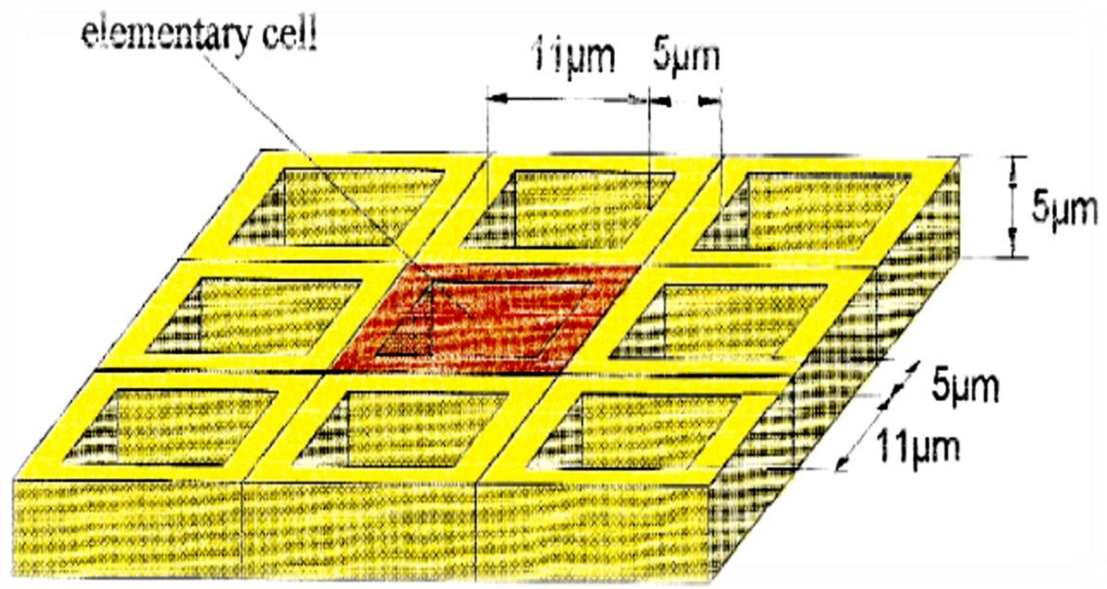


Figure 5

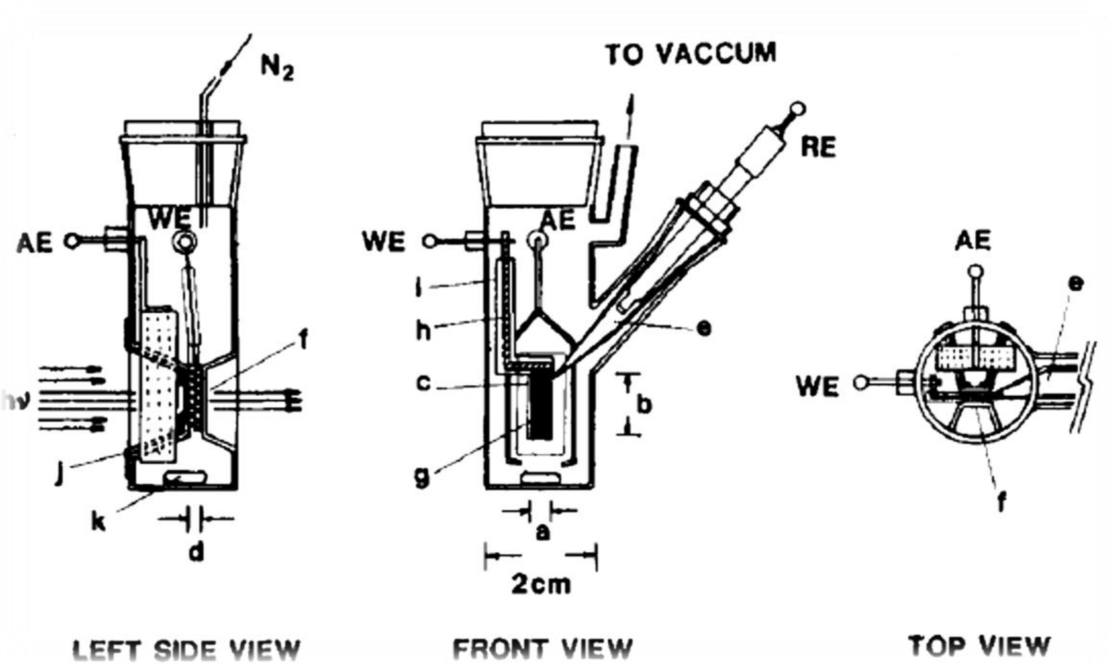

N2
TO VACCUM
RE
AE
WE
AE
WE
AE
WE
hν
f
j
k
d
i
h
c
g
e
b
a
2cm
e
f
LEFT SIDE VIEW
FRONT VIEW
TOP VIEW

Figure 6

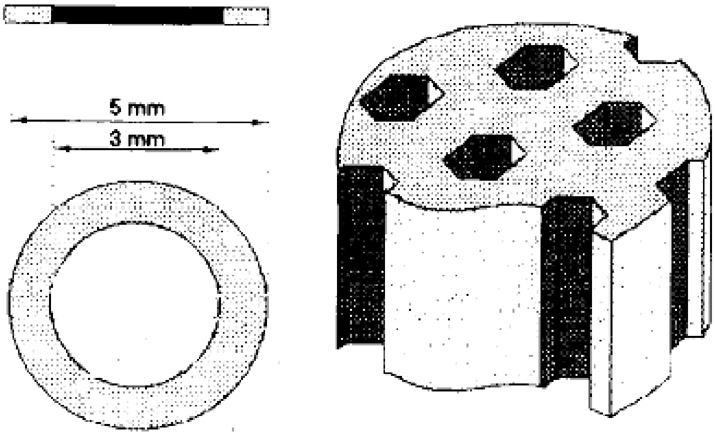


Figure 7

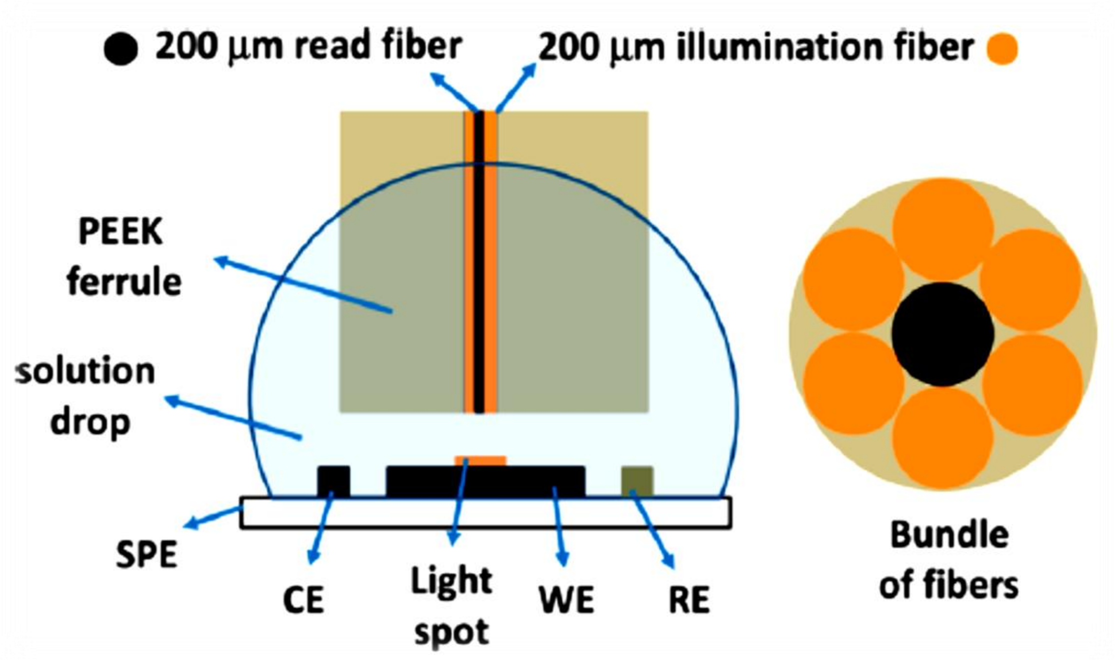

● 200 μm read fiber
200 μm illumination fiber ●
PEEK ferrule
solution drop
SPE
CE
Light spot
WE
RE
Bundle of fibers

Figure 8

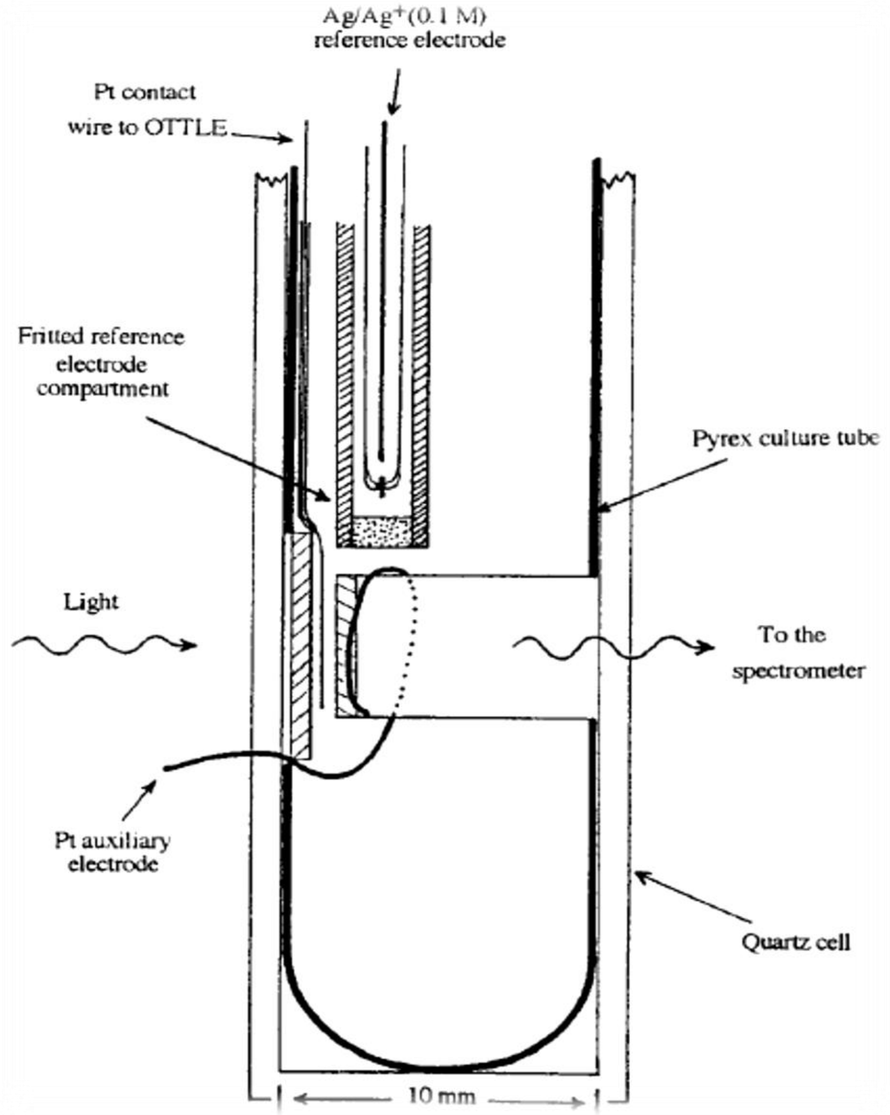

Ag/Ag$^+$(0.1 M)
reference electrode
Pt contact
wire to OTTLE
Fritted reference
electrode
compartment
Pyrex culture tube
Light
To the
spectrometer
Pt auxiliary
electrode
Quartz cell
10 mm

Figure 9

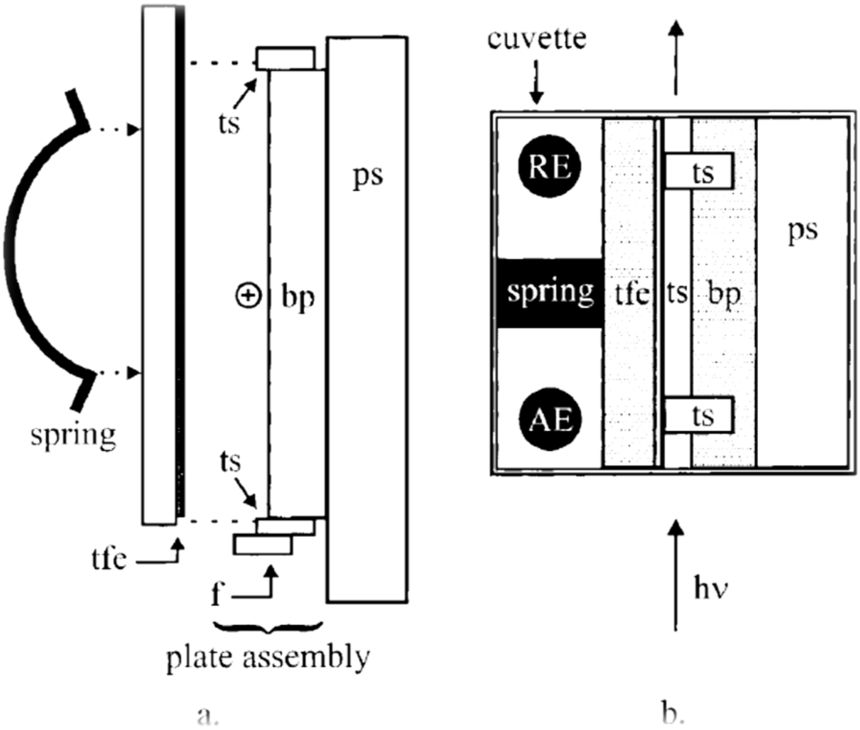
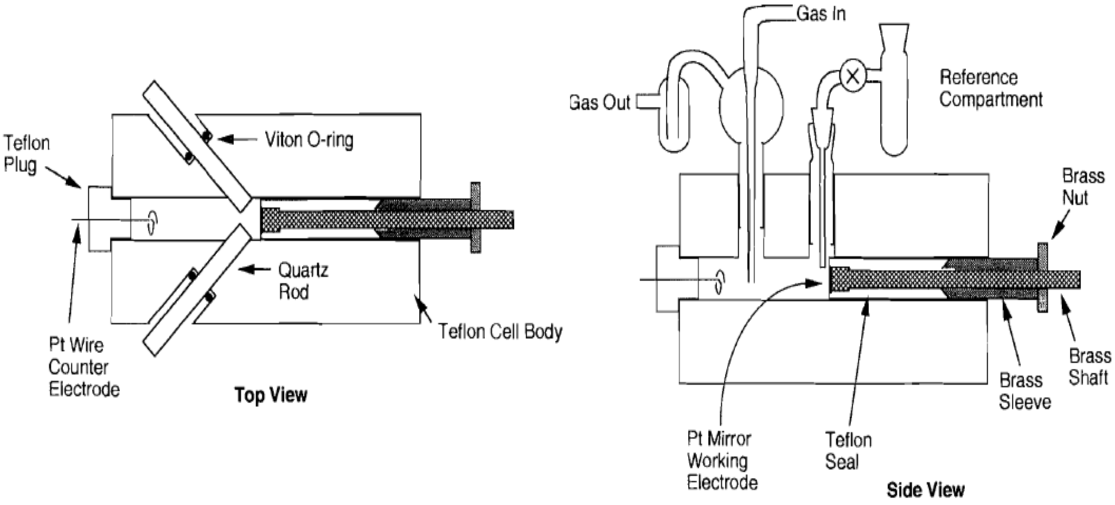

spring
tfe
ts
ts
f
⊕ bp
ps
plate assembly
a.
cuvette
RE
ts
ps
spring
tfe
ts
bp
AE
ts
hν
b.

Figure 10



Top View

Side View

Figure 11

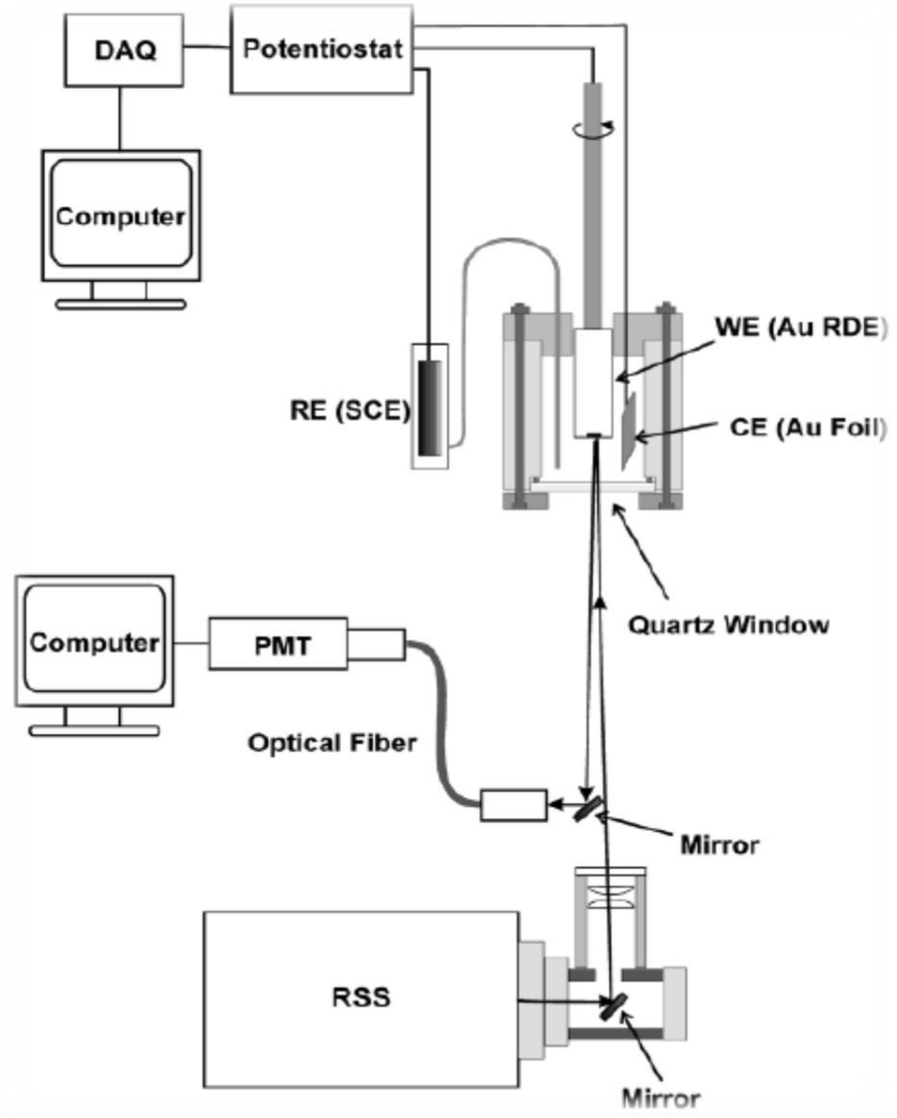

DAQ
Potentiostat
Computer
WE (Au RDE)
RE (SCE)
CE (Au Foil)
Quartz Window
Computer
PMT
Optical Fiber
Mirror
RSS
Mirror

Figure 12

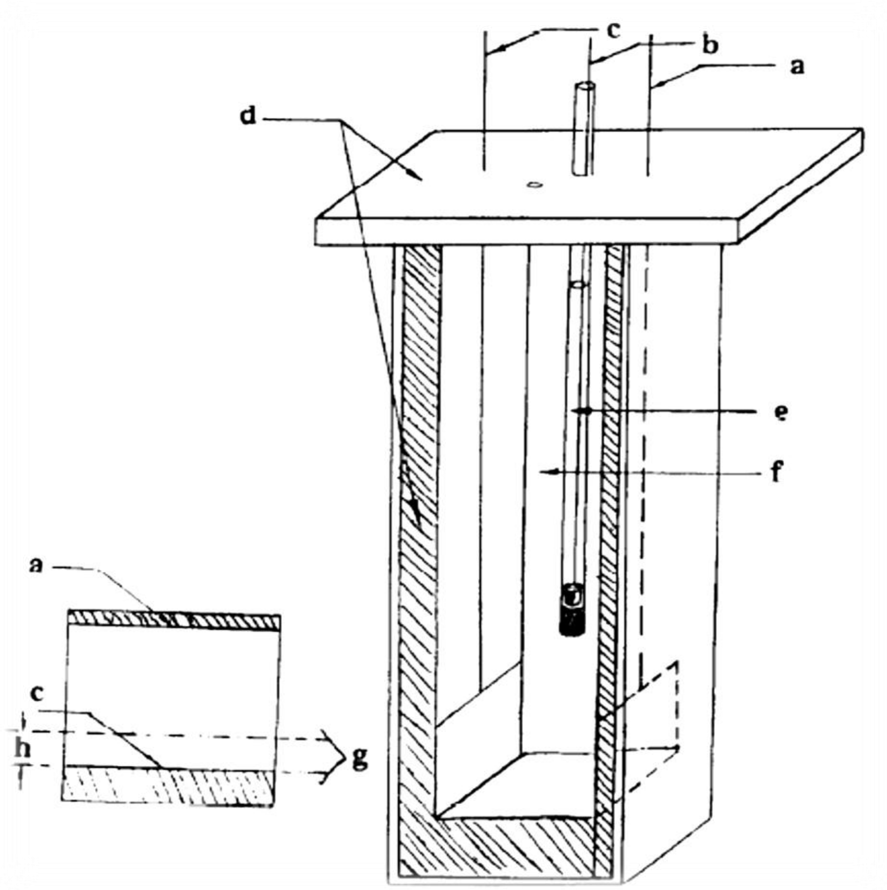


Figure 13

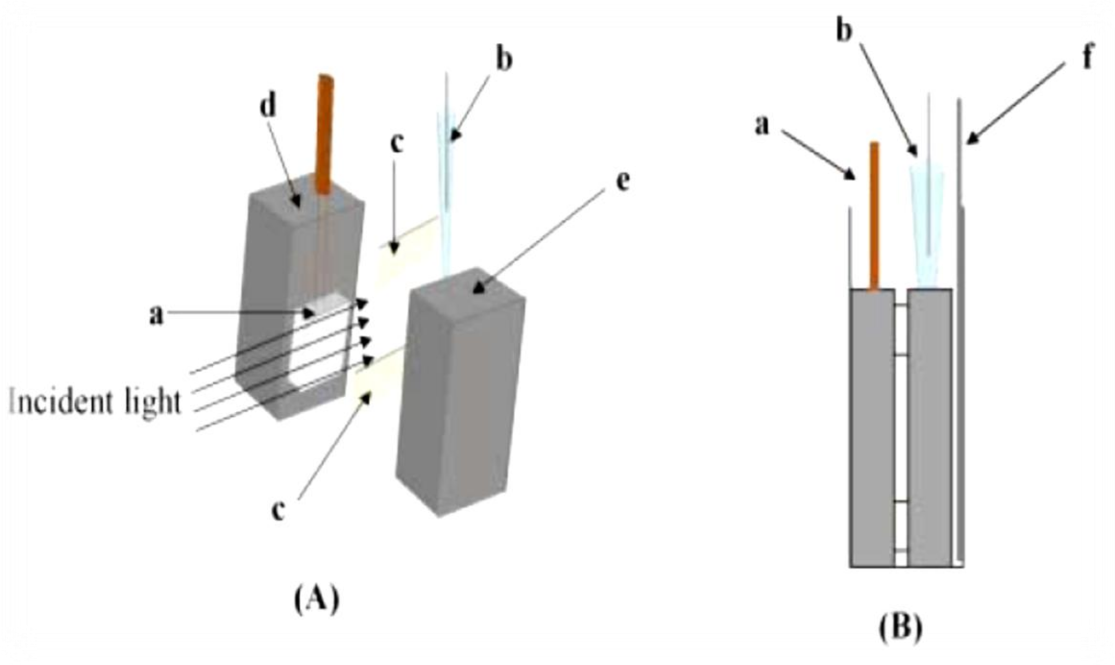


Figure 14

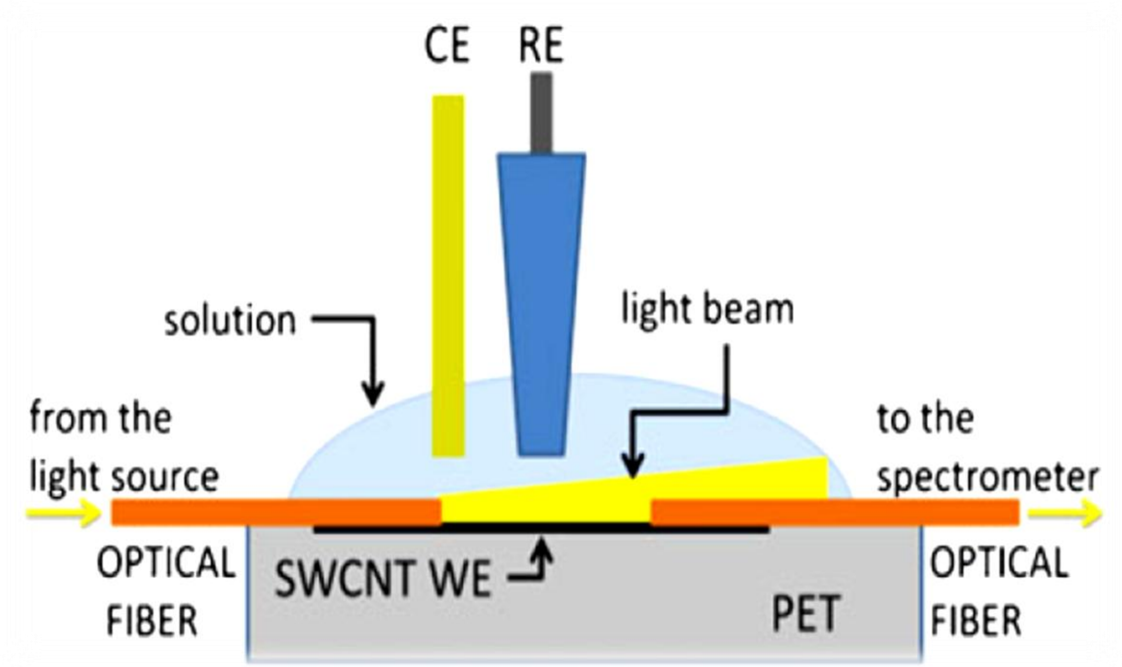

CE
RE
solution
light beam
from the
light source
to the
spectrometer
OPTICAL
FIBER
SWCNT WE
PET
OPTICAL
FIBER

Figure 15

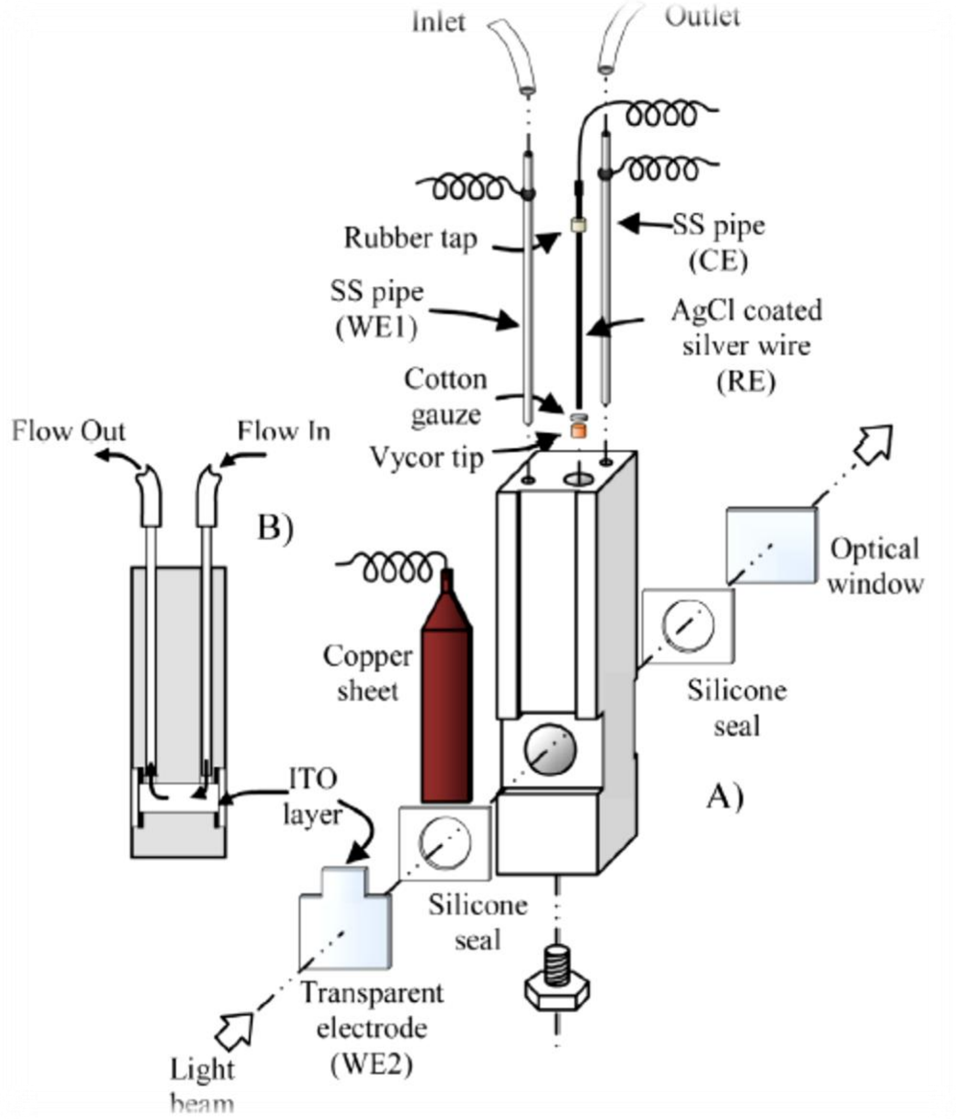

Inlet
Outlet
Rubber tap
SS pipe (CE)
SS pipe (WE1)
AgCl coated silver wire (RE)
Cotton gauze
Vycor tip
Flow Out
Flow In
B)
Optical window
Copper sheet
Silicone seal
ITO layer
A)
Silicone seal
Transparent electrode (WE2)
Light beam

Figure 16

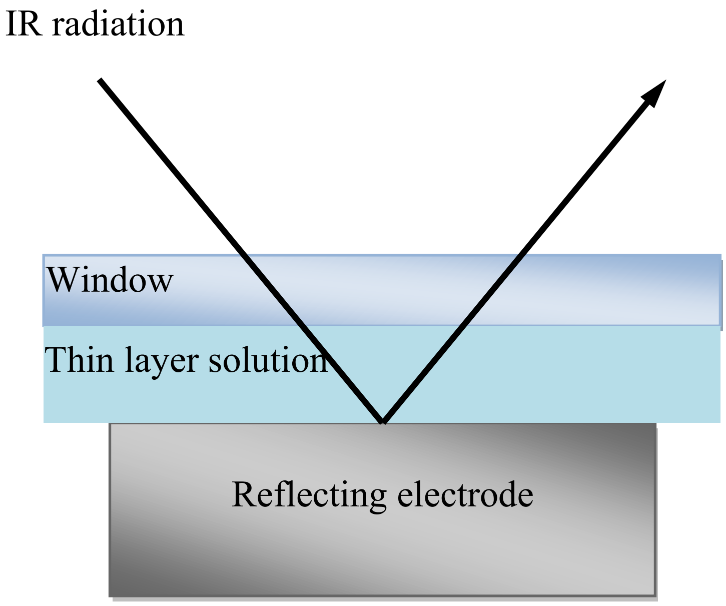

IR radiation
Window
Thin layer solution
Reflecting electrode

Figure 17

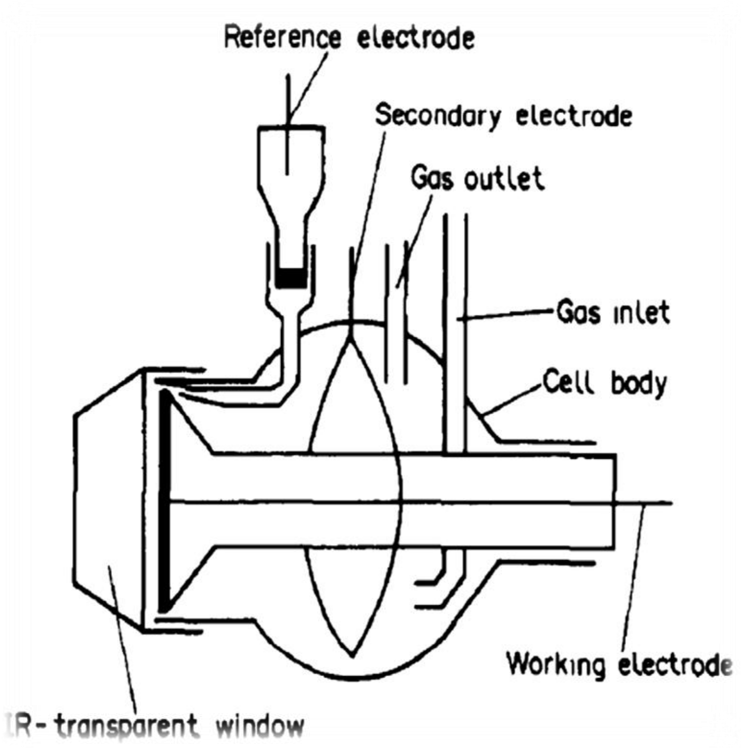

Reference electrode
Secondary electrode
Gas outlet
Gas inlet
Cell body
Working electrode
IR-transparent window

Figure 18

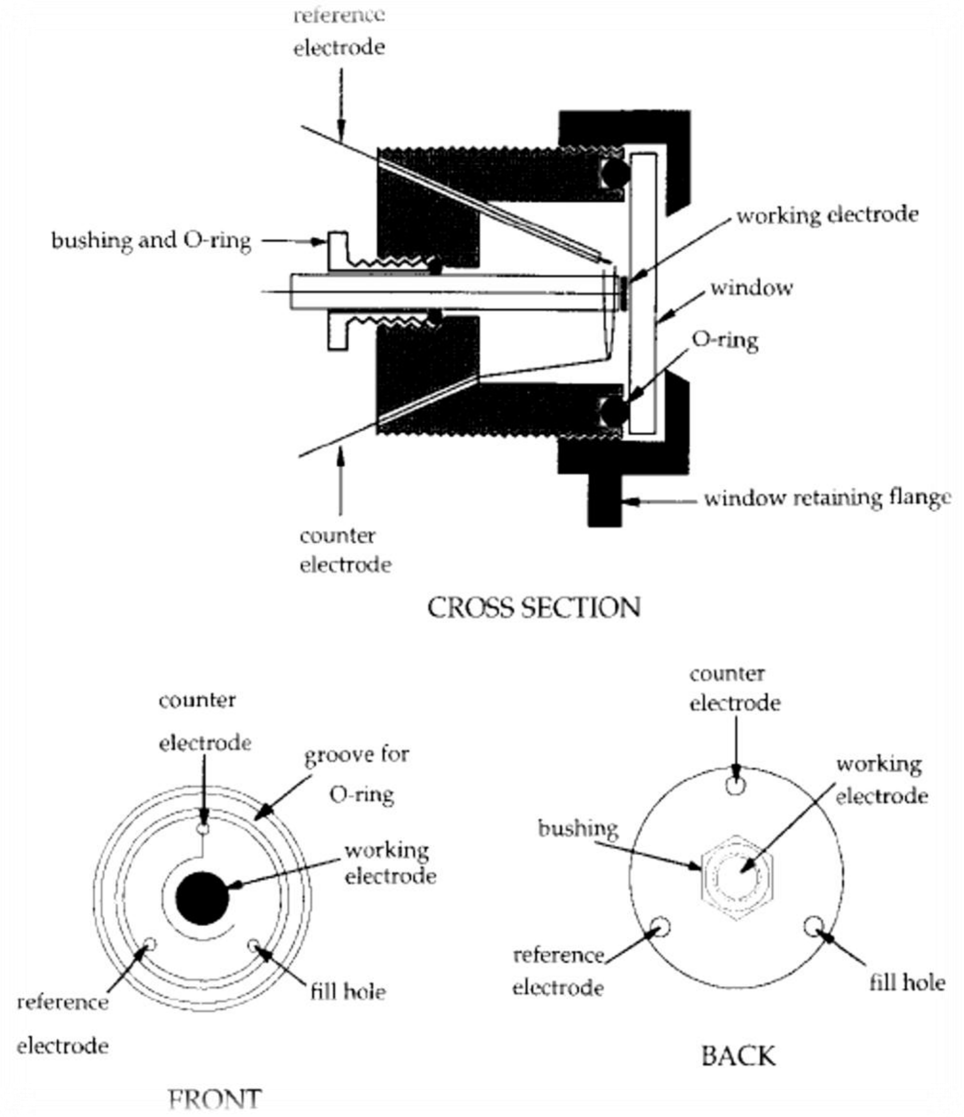

reference electrode
bushing and O-ring
working electrode
window
O-ring
window retaining flange
counter electrode
CROSS SECTION
counter electrode
groove for O-ring
working electrode
reference electrode
fill hole
FRONT
counter electrode
working electrode
bushing
reference electrode
fill hole
BACK

Figure 19

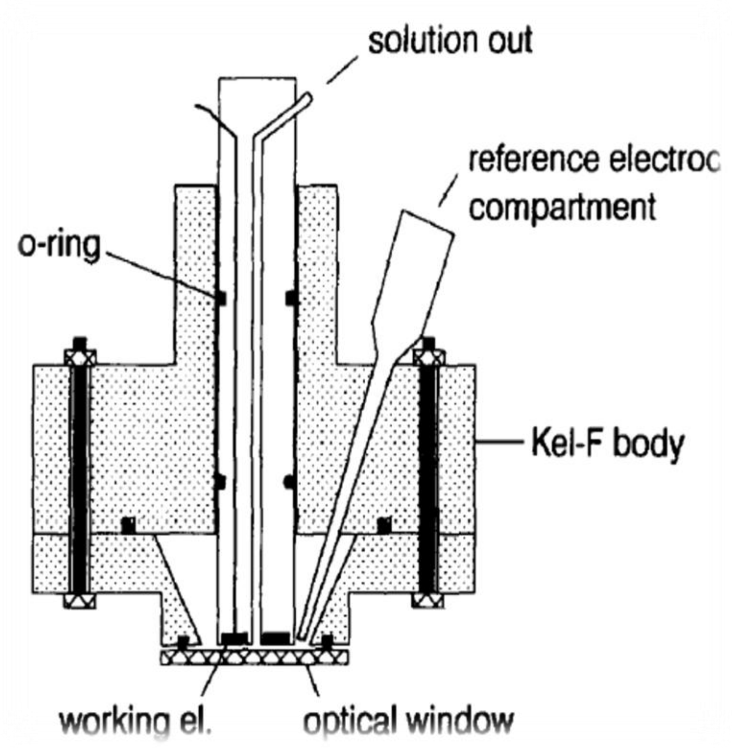

solution out
reference electroc
compartment
o-ring
Kel-F body
working el.
optical window

Figure 20

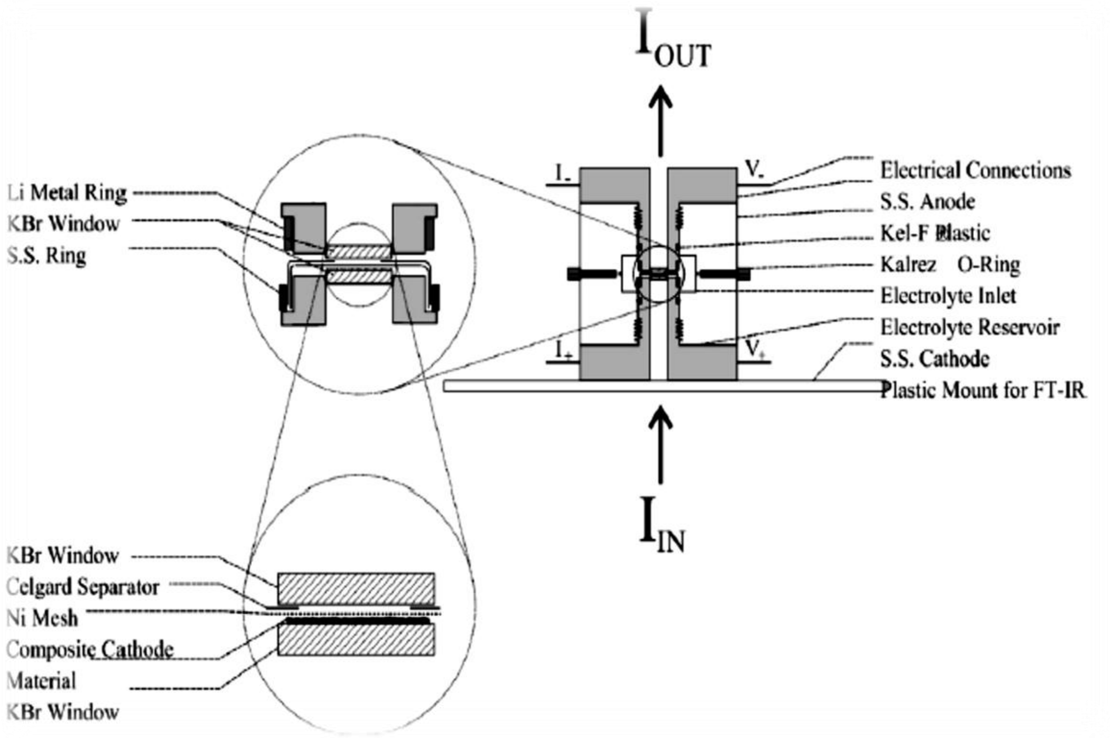

I_{OUT}
Li Metal Ring
KBr Window
S.S. Ring
I₋
V₋
I₊
V₊
Electrical Connections
S.S. Anode
Kel-F Plastic
Kalrez O-Ring
Electrolyte Inlet
Electrolyte Reservoir
S.S. Cathode
Plastic Mount for FT-IR
I_{IN}
KBr Window
Celgard Separator
Ni Mesh
Composite Cathode
Material
KBr Window

Figure 21

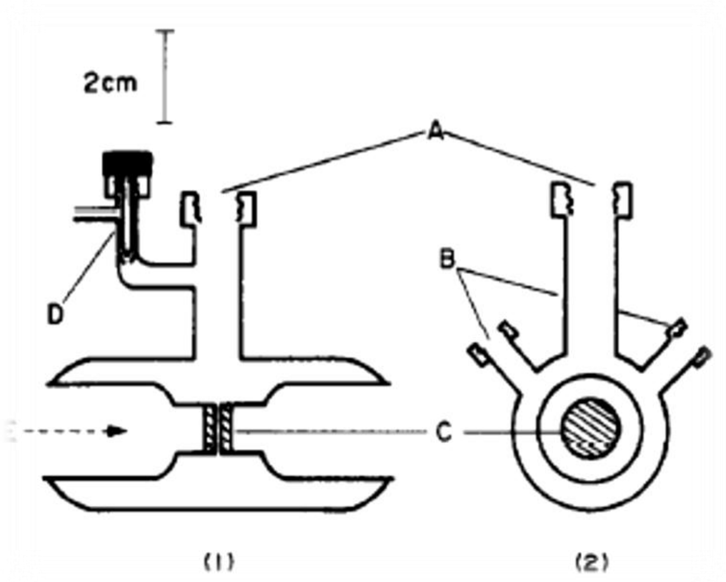


Figure 22

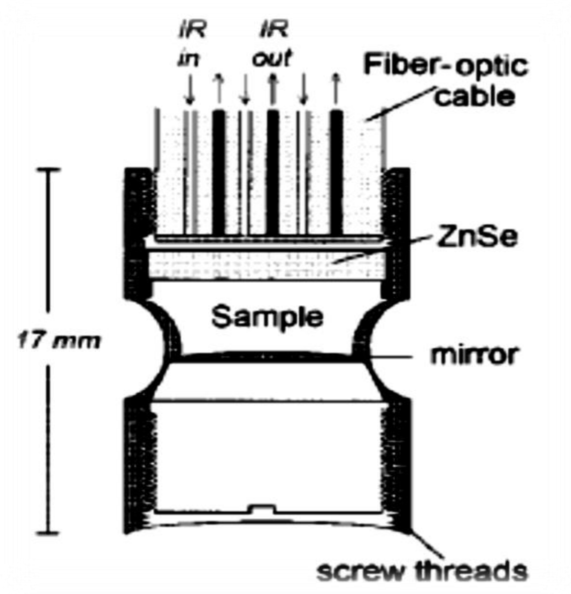

IR
in
IR
out
Fiber-optic
cable
ZnSe
Sample
17 mm
mirror
screw threads

Figure 23

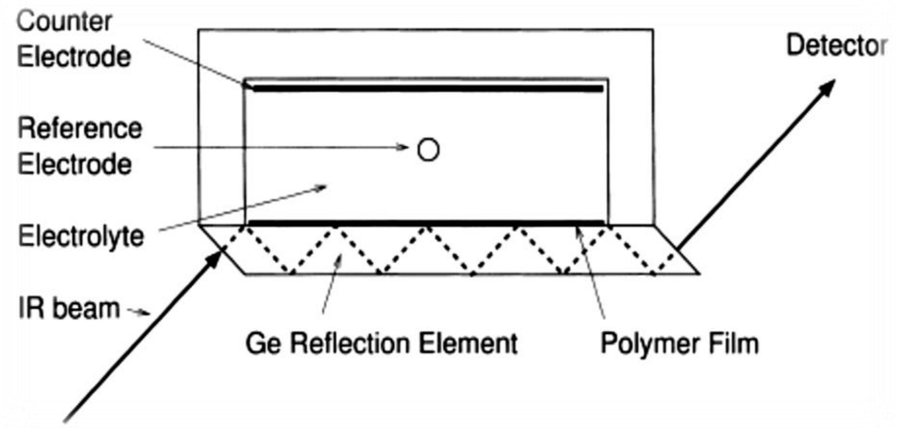

Counter Electrode
Reference Electrode
Electrolyte
IR beam
Detector
Ge Reflection Element
Polymer Film

Figure 24

Figure 25

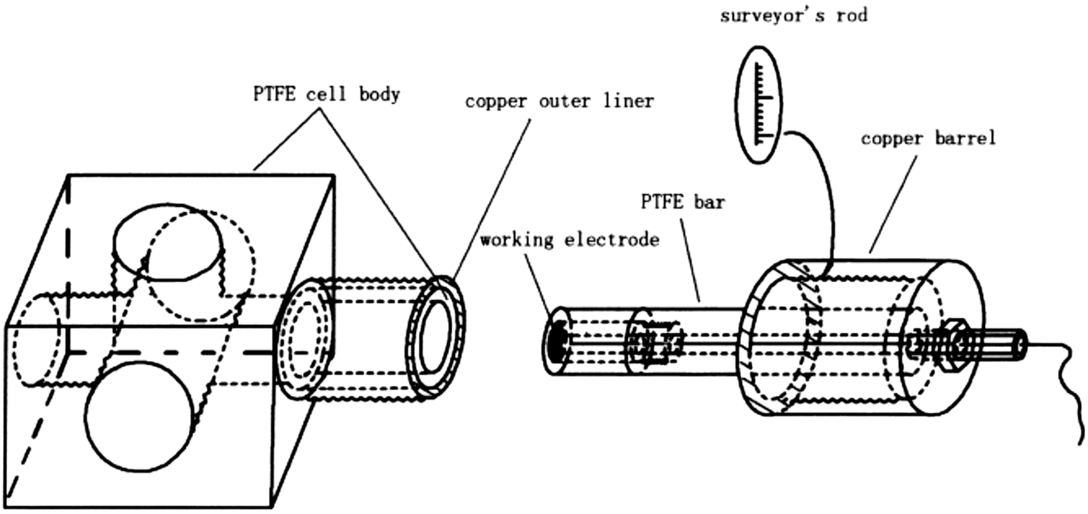

surveyor's rod
PTFE cell body
copper outer liner
copper barrel
PTFE bar
working electrode

Figure 26

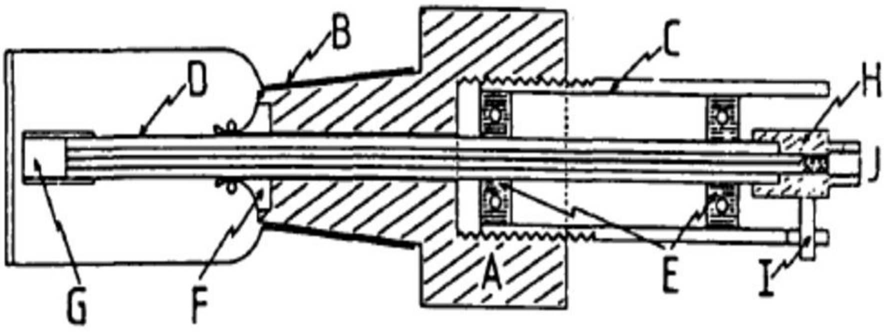


Figure 27

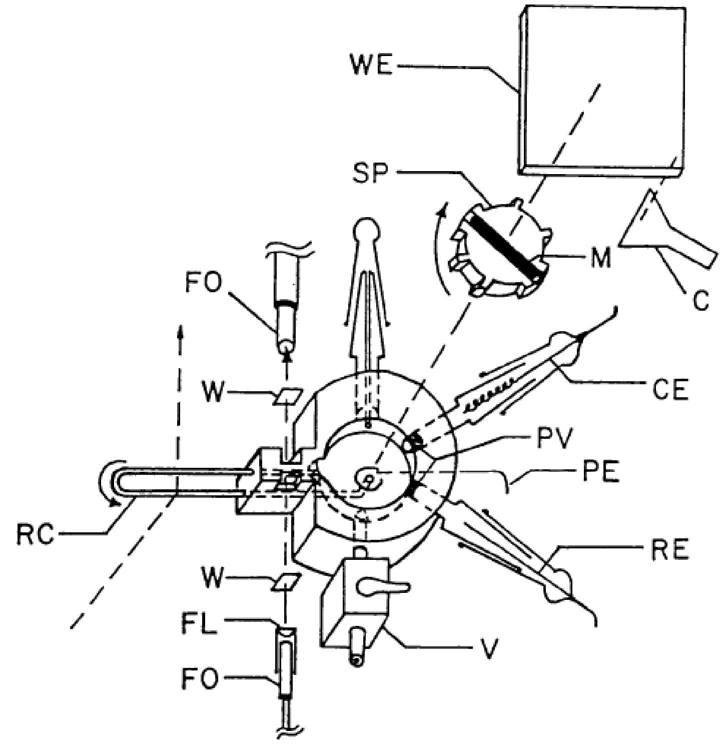


Figure 28

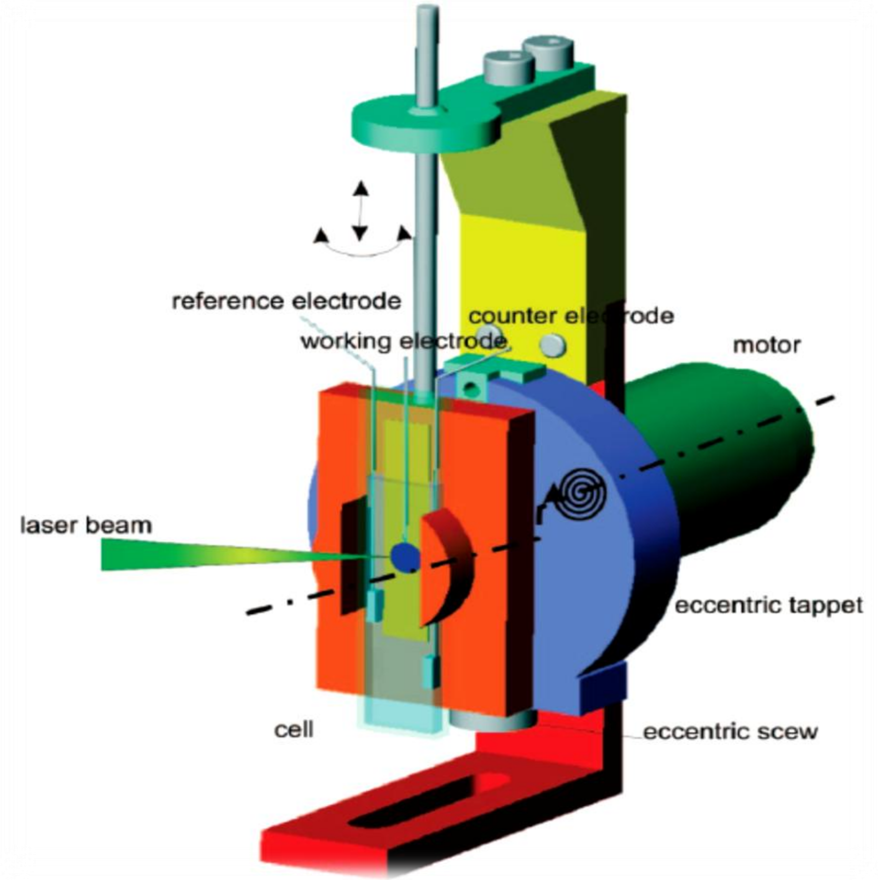

reference electrode
working electrode
counter electrode
motor
laser beam
eccentric tappet
cell
eccentric scew

Figure 29

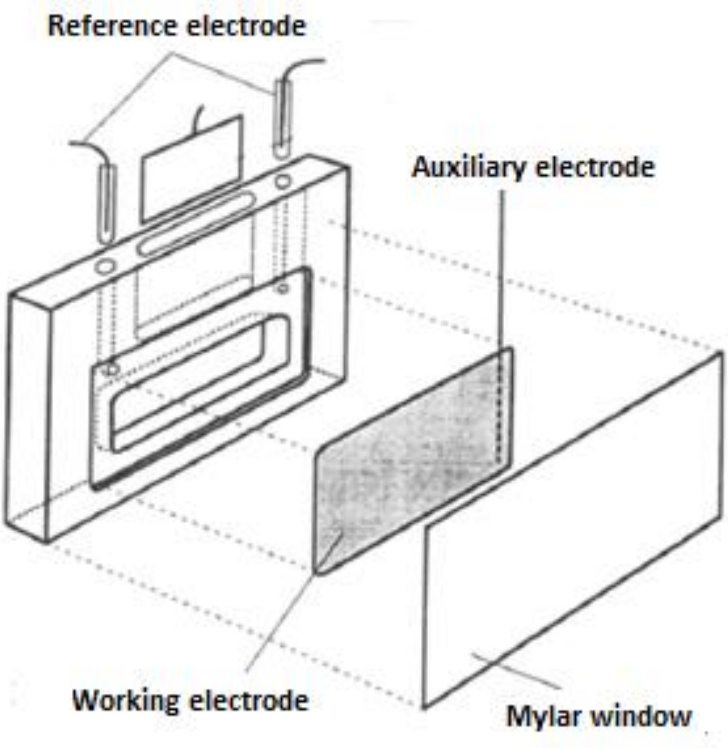

Reference electrode
Auxiliary electrode
Working electrode
Mylar window

Figure 30

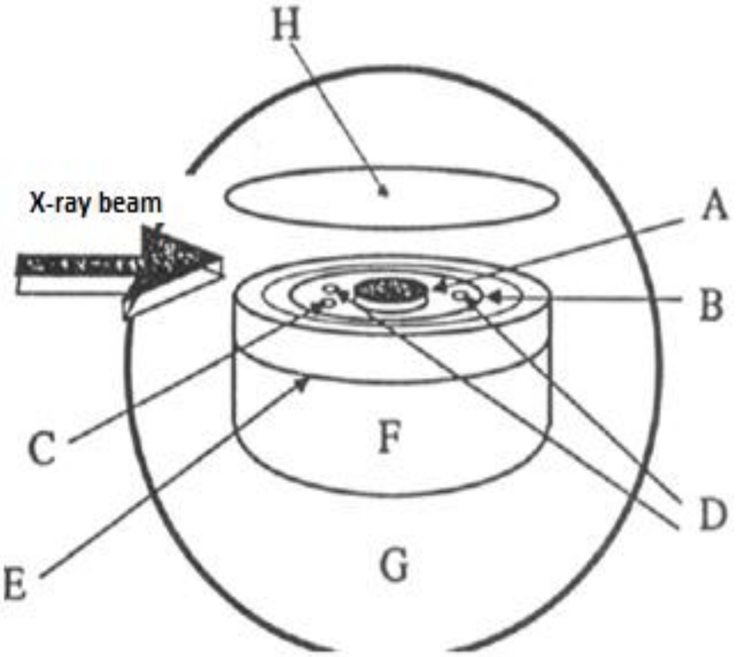


Figure 31

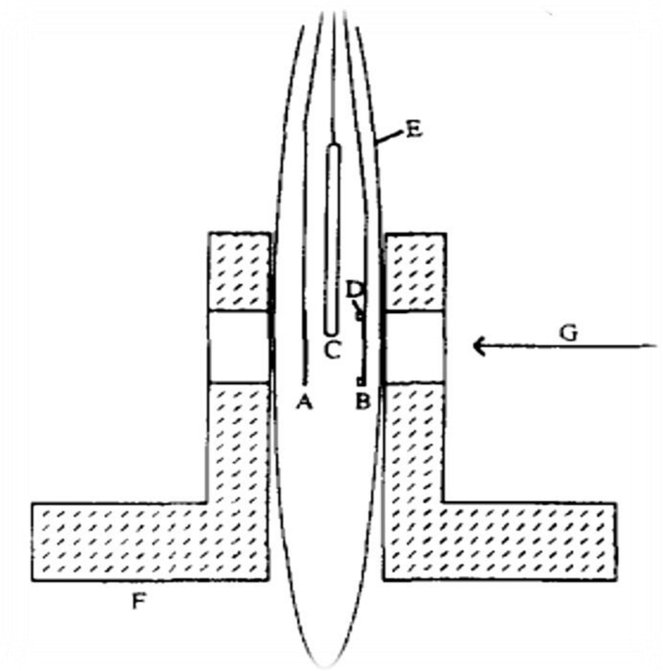


Figure 32

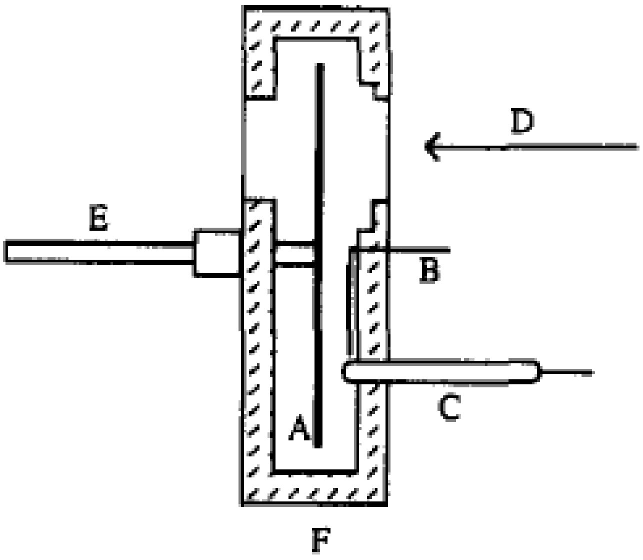


Figure 33

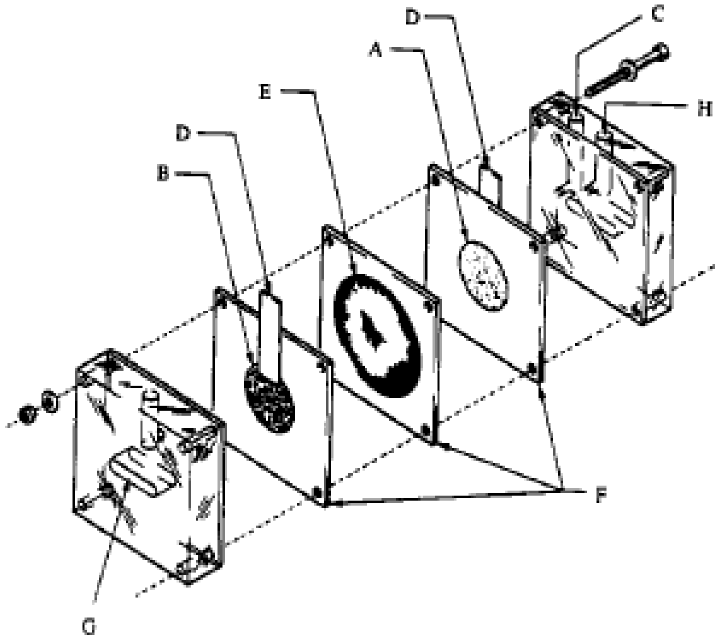


Figure 34

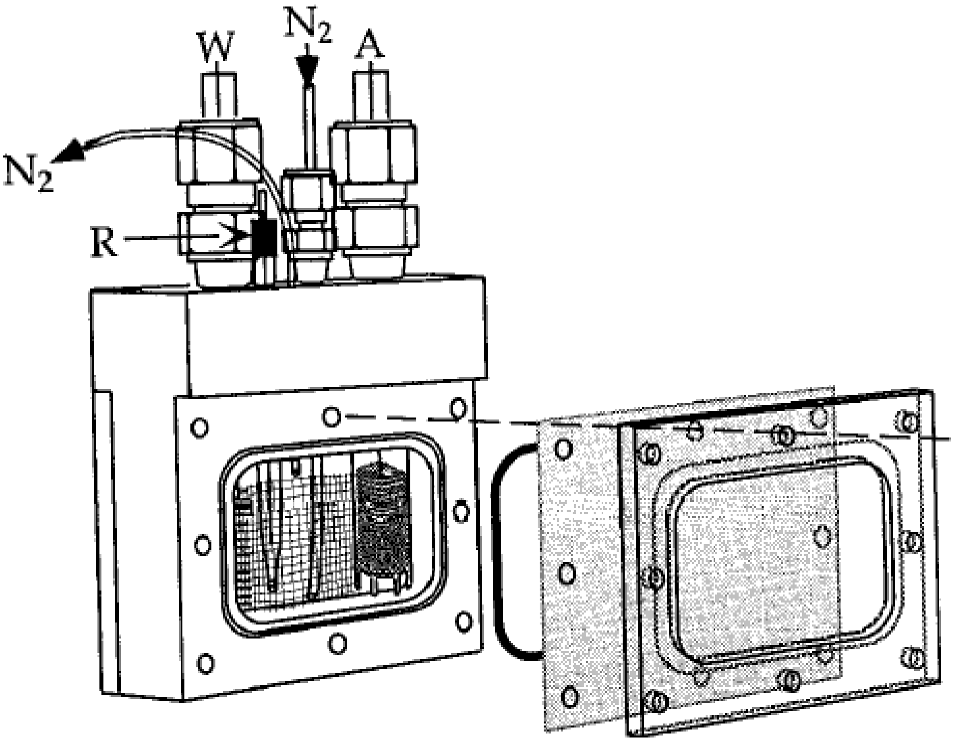


Figure 35

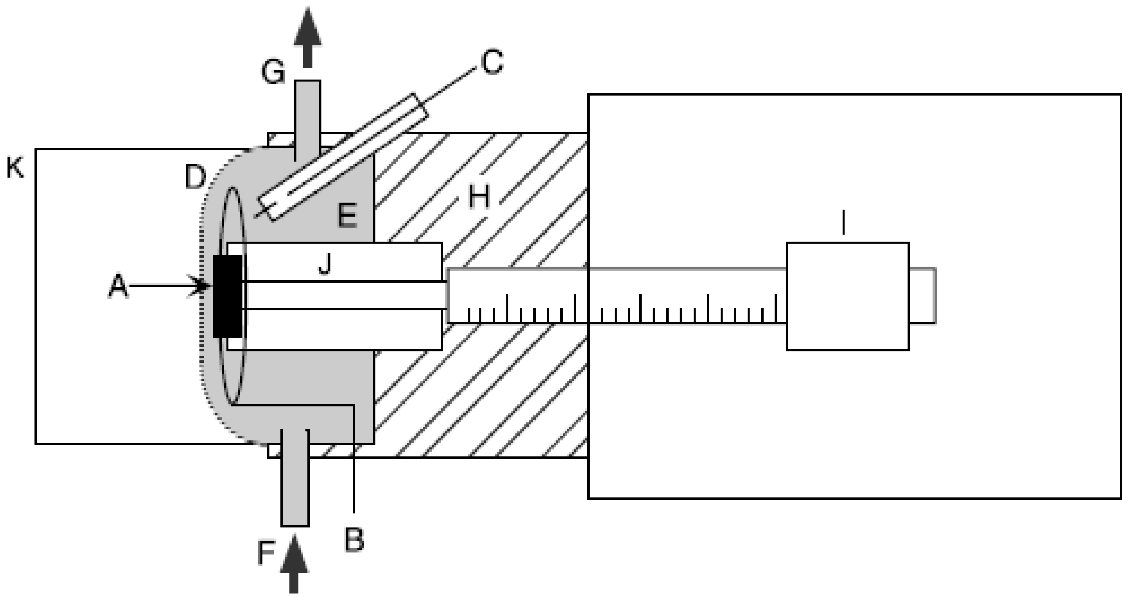


Figure 36

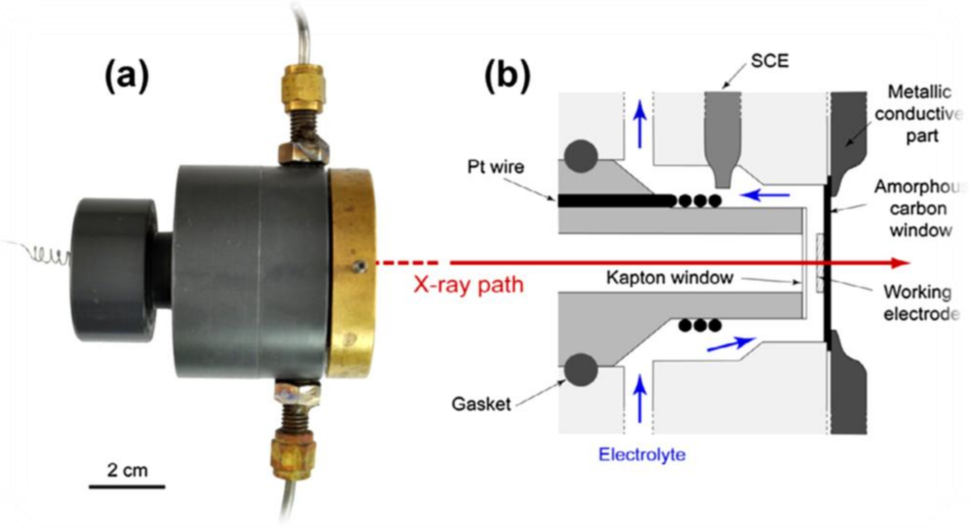

(a)
2 cm
(b)
SCE
Metallic
conductive
part
Pt wire
Amorphou
carbon
window
X-ray path
Kapton window
Working
electrode
Gasket
Electrolyte

Figure 37

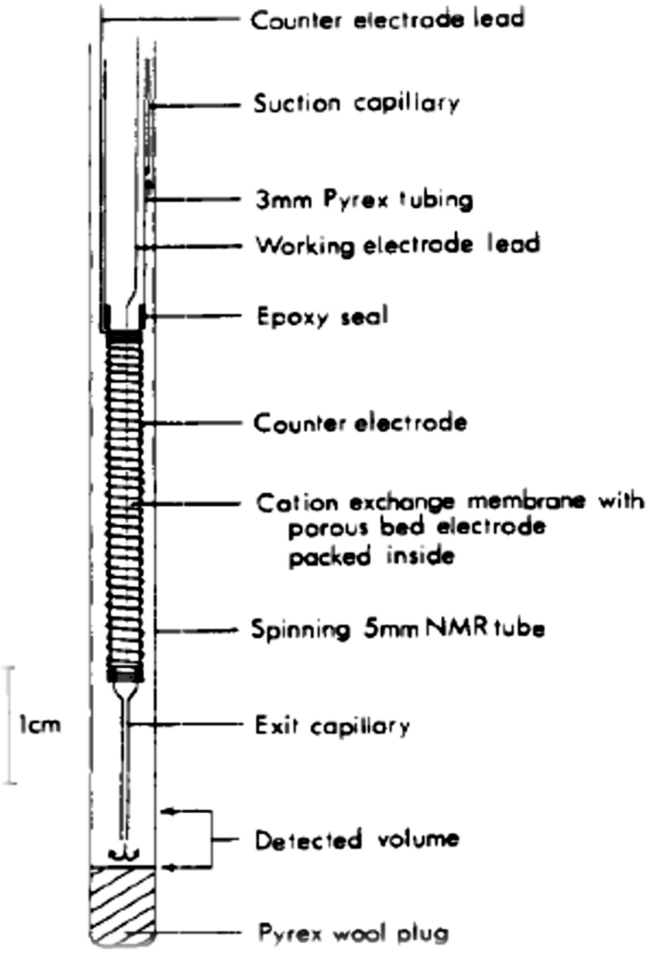

Counter electrode lead
Suction capillary
3mm Pyrex tubing
Working electrode lead
Epoxy seal
Counter electrode
Cation exchange membrane with porous bed electrode packed inside
Spinning 5mm NMR tube
1cm
Exit capillary
Detected volume
Pyrex wool plug

Figure 38

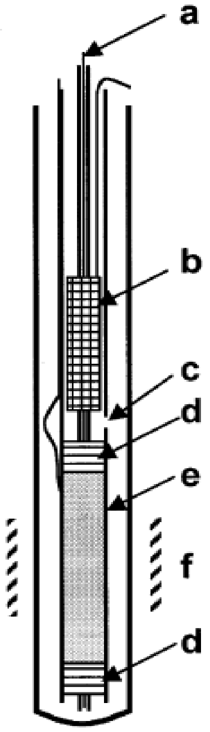


Figure 39

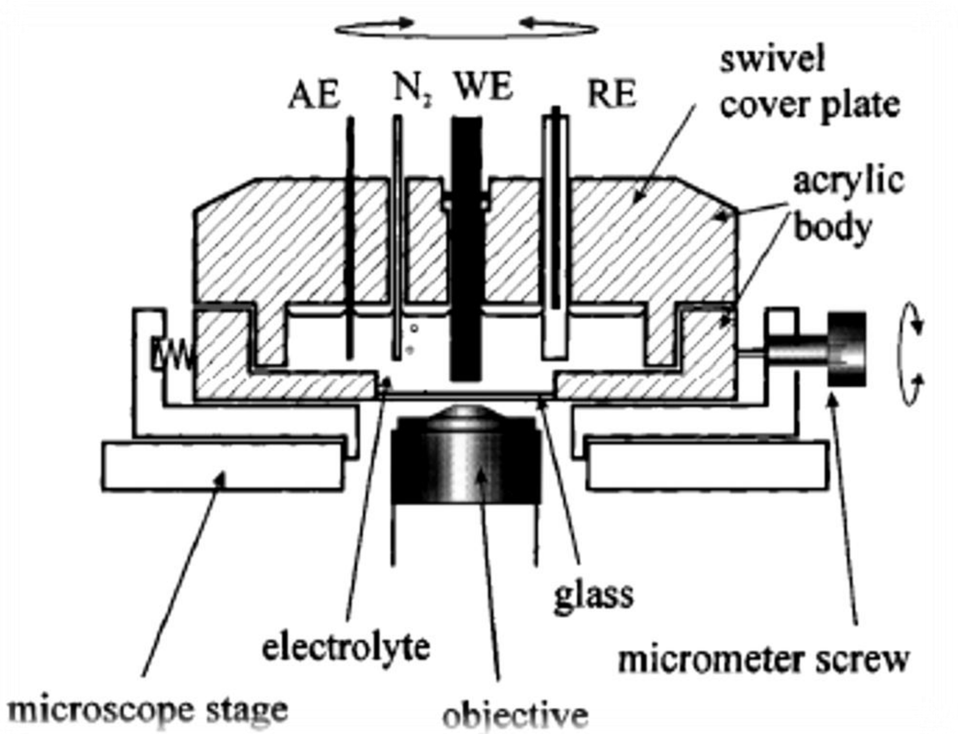

AE
N₂
WE
RE
swivel cover plate
acrylic body
glass
electrolyte
micrometer screw
microscope stage
objective

Figure 40

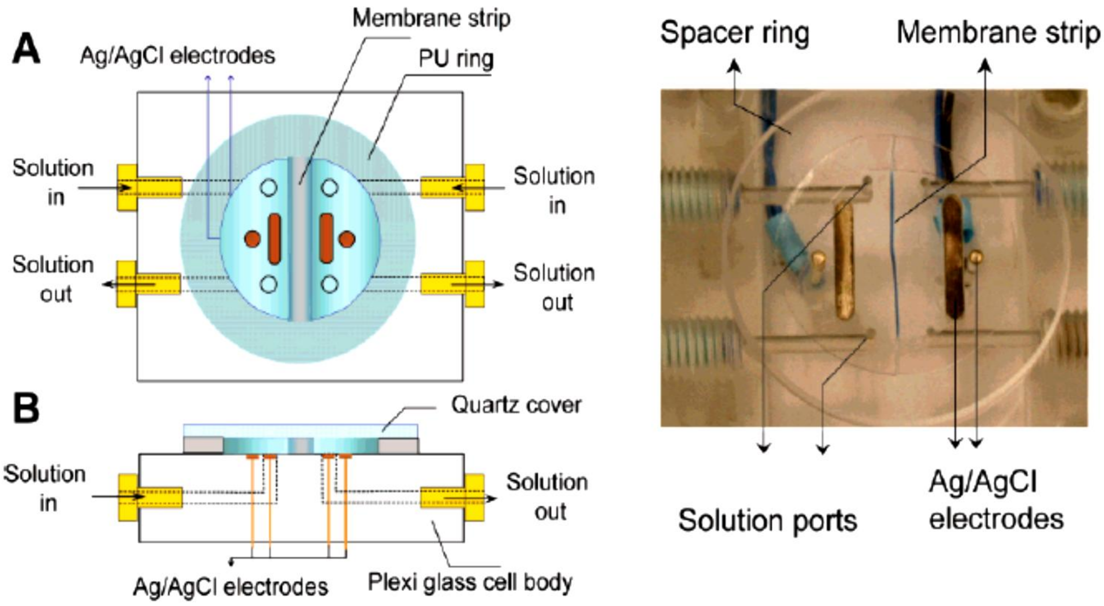

A
Ag/AgCl electrodes
Membrane strip
PU ring
Solution in
Solution in
Solution out
Solution out
B
Quartz cover
Solution in
Solution out
Ag/AgCl electrodes
Plexi glass cell body
Spacer ring
Membrane strip
Solution ports
Ag/AgCl electrodes

Figure 41

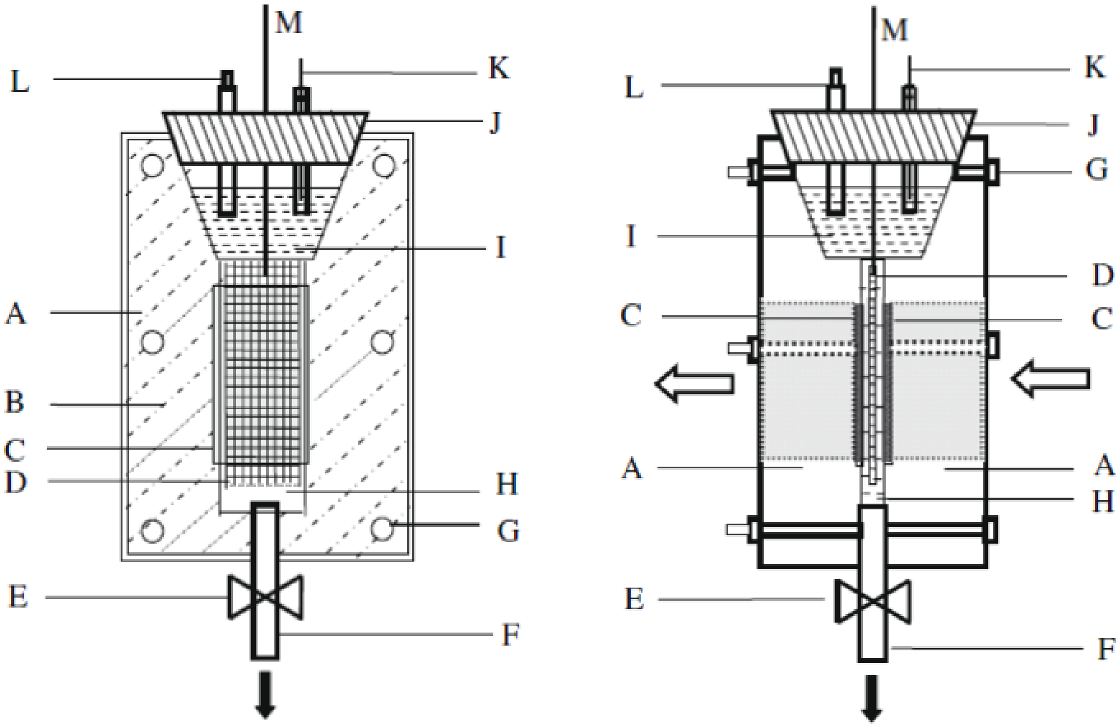


Figure 42

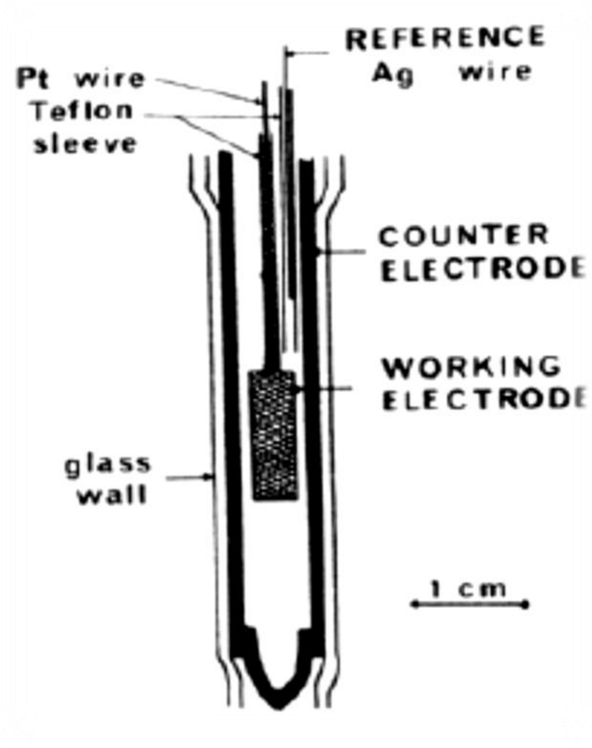

REFERENCE
Ag wire
Pt wire
Teflon
sleeve
COUNTER
ELECTRODE
WORKING
ELECTRODE
glass
wall
1 cm

Figure 43

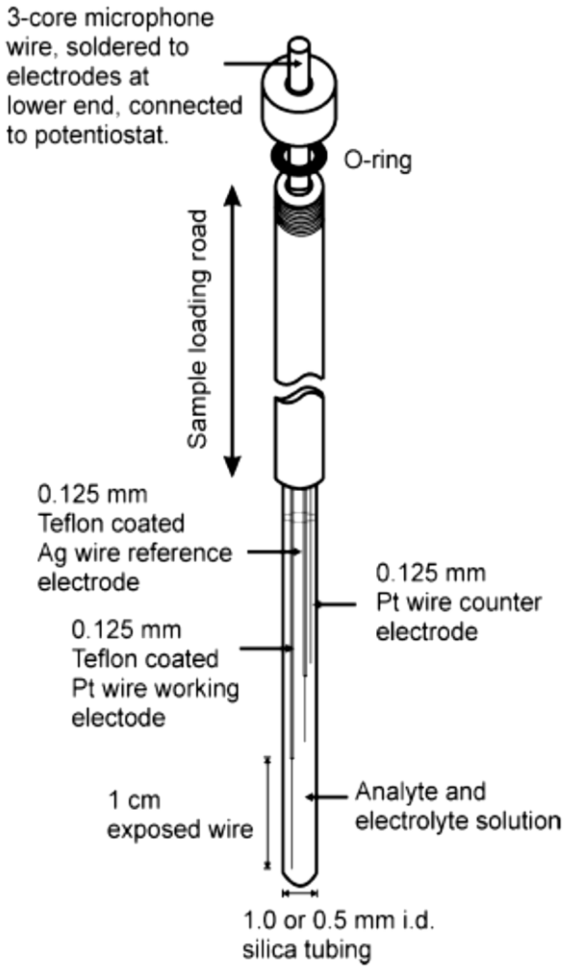

3-core microphone wire, soldered to electrodes at lower end, connected to potentiostat.
O-ring
Sample loading road
0.125 mm Teflon coated Ag wire reference electrode
0.125 mm Pt wire counter electrode
0.125 mm Teflon coated Pt wire working electode
1 cm exposed wire
Analyte and electrolyte solution
1.0 or 0.5 mm i.d. silica tubing

Figure 44

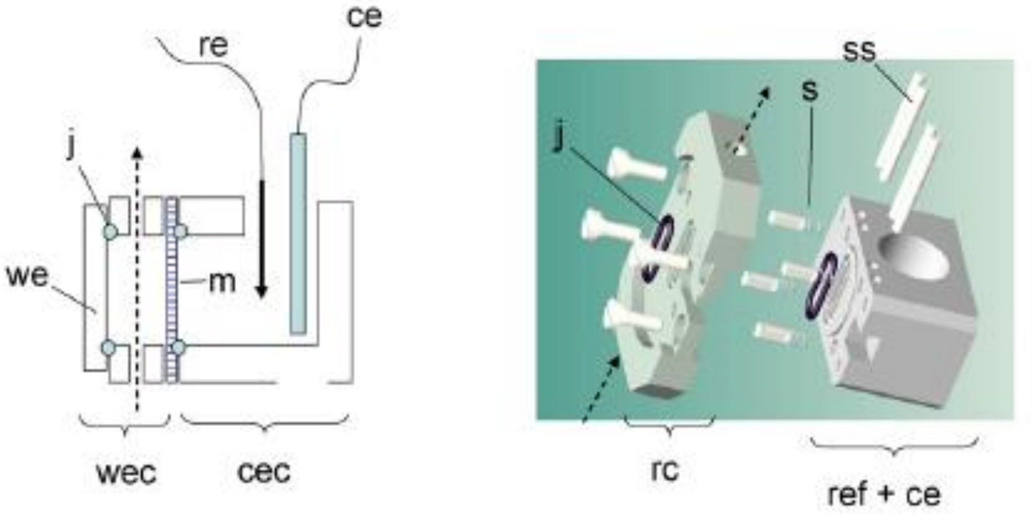
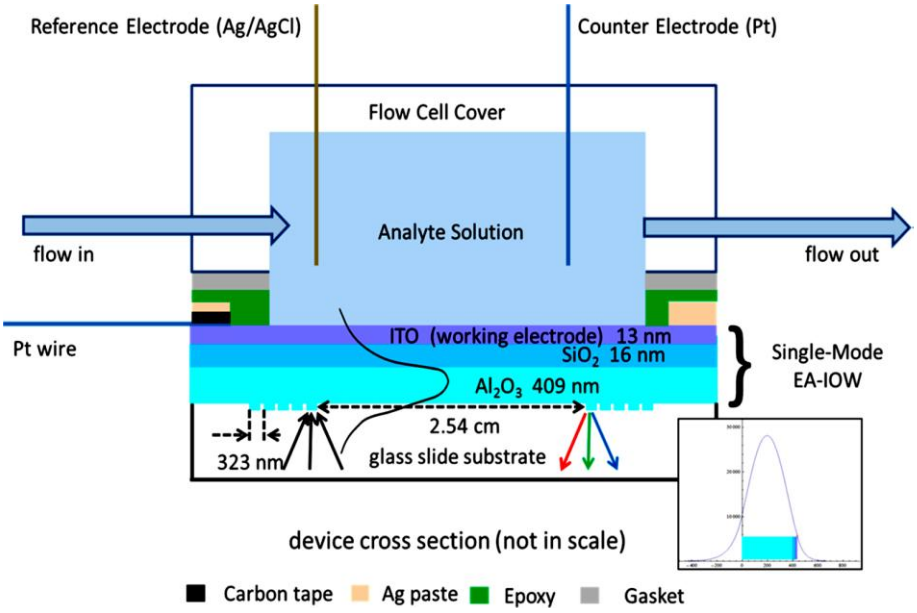


Figure 45


Reference Electrode (Ag/AgCl)
Counter Electrode (Pt)
Flow Cell Cover
flow in
Analyte Solution
flow out
Pt wire
ITO (working electrode) 13 nm
SiO_2 16 nm
Al_2O_3 409 nm
Single-Mode
EA-IOW
2.54 cm
323 nm
glass slide substrate
30 000
20 000
10 000
-400
-200
0
200
400
600
800
device cross section (not in scale)
■ Carbon tape
■ Ag paste
■ Epoxy
■ Gasket