

A Review on Advance in Chemiluminescence, Principle and Application

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ABSTRACT: This paper provides a general review on principle of chemiluminescent and their recent applications in drug analysis. The structural requirements for chemiluminescent reactions and the different factors that affect the efficiency of analysis are included in the review. Chemiluminescence application in immunoassay is the new version for this review. Practical considerations are not included in the review since the main interest is to state, through the aforementioned applications, that chemiluminescence has been, is, and will be a versatile tool for pharmaceutical analysis in future years.

I. INTRODUCTION

It is well known that the first application of chemiluminescence as an analytical tool was developed in the early 1950s, employing several substances such as luminol, lophine, and lucigenin as volumetric indicators (1). In the following years, many researchers have focused on chemiluminescence analysis and brought significant progress, such as the innovation of instrumentation, the development of theoretical concepts, and the creation of methodologies. Owing to the simple measuring devices and the high versatility for the determination of a wide variety of species, chemiluminescence was usually acknowledged to be one of the most highly sensitive and most useful analytical techniques and can now be routinely used to solve diverse qualitative and quantitative analytical problems. However, the development of new or enhanced analytical methodologies based on the use of chemiluminescence phenomenon is still a very active area of current research.

Luminescence is the most conveniently defined as the radiation emitted by a molecule, or an atom, when these species return to the ground state from the excited state. According to the source of excitation, luminescence phenomenon could be classified as photoluminescence (fluorescence and phosphorescence) when the excitation source is energy from absorbed light, chemiluminescence—energy from chemical reactions and bioluminescence energy from biologically catalysed reactions. An excited molecule has the same geometry and is in the same environment as it was in ground state. In this situation it either emits a photon from the same vibrational level to which it was excited initially or it undergoes vibrational relaxation prior to emission of radiation [1, 2]. For an isolated molecule in the gas phase, the only way to lose vibrational energy is to emit an infrared photon, which is less probable than undergoing an electronic transition to return to the ground state. Therefore, one tends to see photon emission from higher vibrational levels of excited states in gas phase spectra at low pressure. In a solution, however, thermal relaxation of a vibrationally excited molecule is quite rapid through transfer of excess vibrational energy from the solute molecule to the solvent. In fact, this process is so efficient that all the excess vibrational energy of the excited state is lost, and this process occurs in 10^{-13} to 10^{-11} sec. This means that before an excited molecule in a solution can emit a photon, it will undergo vibrational relaxation, and therefore photon emission will always occur from the lowest vibrational level of an excited state [3, 4].

Once a molecule arrives at the lowest vibrational level of an excited singlet state, it can do a number of things, one of which is to return to the ground state by photon emission. This process is called fluorescence. The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-7} sec and therefore the decay time of fluorescence is of the same order of magnitude. The quantum efficiency of fluorescence is defined as the fraction of molecules that will fluoresce. In addition to fluorescence, one also encounters radiationless process where molecules in an excited singlet state may return to the ground state without the emission of a photon, converting all the excitation energy into heat: the process called internal conversion. Generally, internal conversion is an inefficient process and is probably only a small fraction of the total excitation energy in most molecules. Although population of triplet states by direct absorption from the

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Vol. 6, Issue 11, November 2017

ground state is insignificant, a more efficient process exists for population of triplet states from the lowest excited singlet state in many molecules. This process is referred to as intersystem crossing and is a spin-dependent internal conversion process. A molecule in excited triplet state may not always use intersystem crossing to return to the ground state. It could lose energy by emission of a photon: the process called phosphorescence. A triplet-singlet transition is much less probable than a singlet-singlet transition. The lifetime of the excited triplet state can be up to 10 sec, in comparison with 10^{-5} s to 10^{-9} s of average lifetime of an excited singlet state. Emission from triplet-singlet transition can continue after initial irradiation [5, 6].

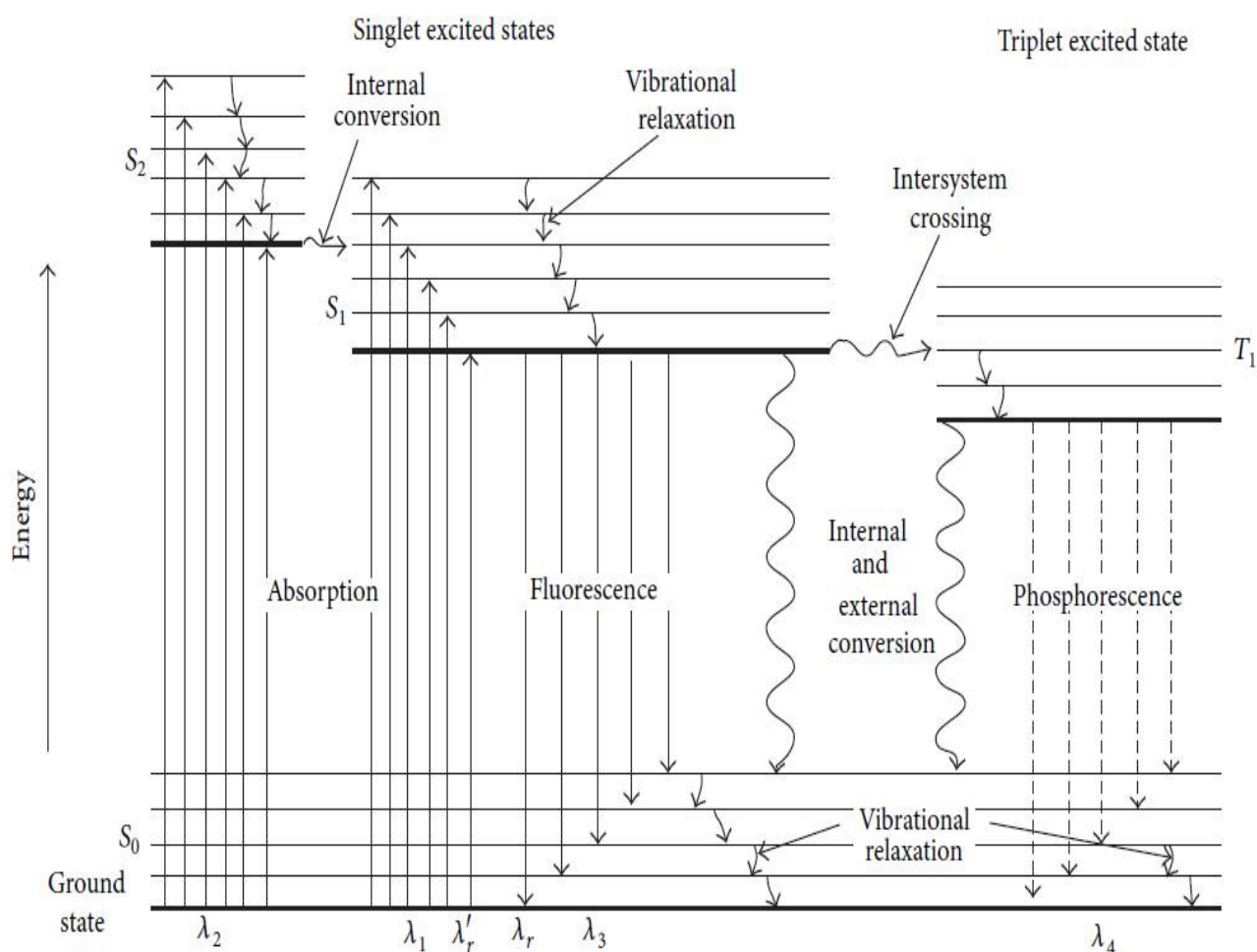


Figure 1: Jablonski diagram describing the electronic levels of common organic molecules and possible transitions between different singlet and triplet states. (M. Sauer, J. Hofkens, and J. Enderlein. Handbook of Fluorescence Spectroscopy and Imaging).

II. ELECTROCHEMILUMINESCENCE

Electrochemiluminescence (ECL) is the process whereby a chemiluminescence emission is produced directly as a result of electrochemical reactions. Unlike conventional CL, commercial ECL instrumentation is not available. Compared to the basic instrumentation, a conventional electrode system used for the electrolytic system must be included. Three main electrode configurations have been used in ECL work: rotating ring-disk (RRD) and dual (19) and single

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electrodes. The materials used for the working electrode where the ECL reaction takes place include platinum (20), gold (20), aluminum (21, 22), glassy carbon (23), paraffinimpregnated graphite electrode (PIGE) (24), carbon paste (25), indium tin oxide (ITO) (26), and silicon (27). One important area in ECL is that of surfactants, such as X-100 (polyethylene glycol tert-octylphenyl ether), which can change the property of the surface of the working electrode. Richter et al. (20) found increases in ECL efficiency and TPrA oxidation current due to the adsorption of surfactant on the electrode surface. Compared with Triton X-100, its hydrocarbon analogue (Zonyl FSN) not only rendered the electrode surfaces more hydrophobic but also significantly retarded the growth of the electrode oxide layers. As a result, oxidation potential and ECL signal change. Another important area in ECL is modified electrodes. ECL properties of the working electrodes modified with poly(4 vinylpyridine) (PVP)-bound Ru(bpy)₂Clp (where bpy ¹/₄ 2,2-bipyridine), clay nanoparticles/Ru(bpy)₃ 2p (28), negatively charged SiO₂ nanoparticles/positively charged (Ru(bpy)₃ 2p) (29), polyelectrolyte complex (30), CdSe nanocrystal (24), RuDS nanoparticles/ Ru(bpy)₃ 2p (31), nickel(II) tetrasulfophthalocyanine (NiTSPc)/Nafion (32), zeolite Y (25), and Fe₃O₄ magnetic nanoparticles/Nafion (33) have been studied in detail. It is found that ECL signal can be enhanced greatly with the modified electrodes, thus improving the sensitivity. Carbon nanotube (CNT) has received considerable attention in various fields because of its unique properties such as high electrical conductivity, physical rigidity, and chemical stability. Based on the composite films of single-wall (SWCNT) and Nafion, Dong's group reported on the preparation and characterization of the Ru(bpy)₃ 2p ECL sensor (34). The ECL sensor based on the SWCNT-Nafion composite films exhibited enhanced ECL sensitivity compared to that based on pure Nafion films. Two years later, a new and simple method for the fabrication of CNT-based Ru(bpy)₃ 2p ECL sensor using sol-gel-derived titania-Nafion mesoporous composite films was first reported (23). The proposed ECL sensor showed better long-term stability without signal loss for four months.

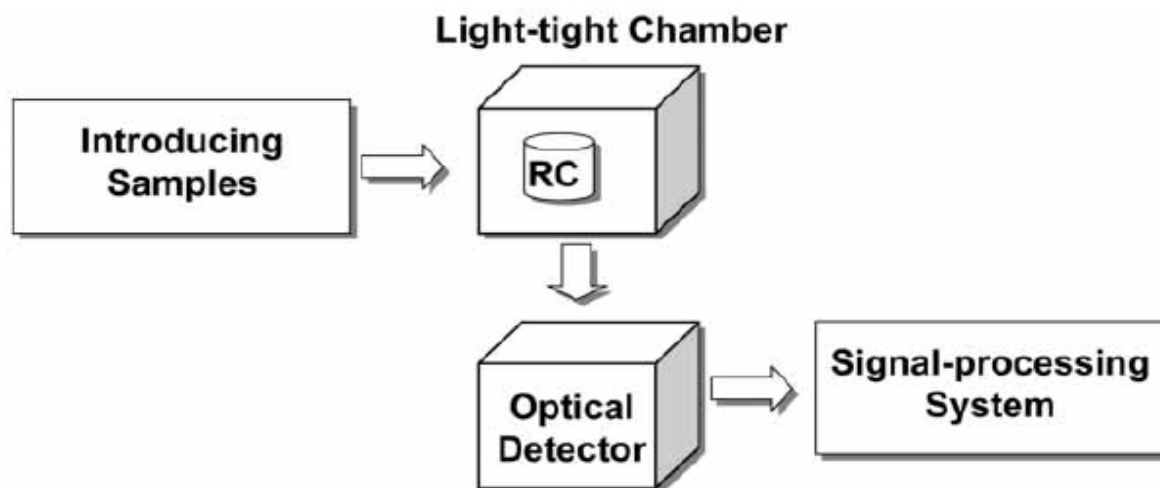


Figure 2: The basic instrumental diagram of CL

III. CHEMILUMINESCENCE BASED ANALYSIS

Because the reaction rate is function of the chemical concentration, CL techniques are suitable for quantitative analysis. The usefulness of CL system in analytical chemistry is based on some special characteristic.

- i. As the technique simultaneously comprises kinetic and luminescence features, it provides highly sensitive and wide dynamic ranges. Excellent detection limits, in the range of femtomoles, can be reached if $\dot{\phi}$ CL is high enough. As an example, in the gas phase, typical detection limits are 10 pmol NO using ozone and 0.1 pmol for sulfur compounds using a hydrogen flame followed by ozone, in the liquid phase down to 1 fmol of the fluorophore may be detected using the peroxyoxalate CL system and 0.1 fmol peroxidase when using luminol.

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Vol. 6, Issue 11, November 2017

- In comparison to other spectrometric techniques, in general, CL is approximately 105 times more sensitive than absorption spectrometry and at least 10³ times more sensitive than fluorimetry.
- ii. Compared to photoluminescence process, no external light source is required, which offers some advantages such as the absence of scattering or background photoluminescence signal, the absence of problems related to instability of the external source, reduction of interferences due to a nonselective excitation process, and simple instrumentation.
 - iii. Selectivity and linearity are most dependants on the reaction conditions chosen. As for photoluminescence process, absorption or emission radiation by the analyte, products, or concomitants can cause nonlinearity or spectral interference.
 - iv. The technique is versatile for determination of a wide variety of species that can participate in the CL process, such as CL substrates or CL precursors responsible for the excited state; the necessary reagent for the CL reaction (usually an oxidant); some species that affects the rate or efficiencies of CL reaction, activators such as catalyst (enzymes or metal ions) or inhibitors such as reductants that inhibit the CL emission; fluorophores in the case of sensitized CL, some species that are not directly involved in the CL reaction but that can react with other reagents in coupled reactions to generate a product that is a reactant in the CL reaction, species that can be derivatized with some CL precursors or fluorophores being determined by direct or sensitized CL
 - v. Depending on the nature of the analyte and the CL reaction the increase or decrease of CL intensity will be directly related to the analyte concentration.
 - vi. CL reactions can be coupled as a detection technique in chromatography, capillary electrophoresis, or immunoassay, providing qualitative and/or quantitative information on a large variety of species in the gas and liquid phases.
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IV. INSTRUMENTATION

The instrumentation employed for chemiluminescence measurements basically consists of a mixing device and a detection system. Three approaches have been used to measure the intensity of emitted light. The first approach involves the use of static measurement system in which the mixing of reagents is performed in a vessel held in front of the detector. The chemiluminescence reagent is added to the analyte in a cuvette held in a dark enclosure, and the intensity of the light emitted is measured through an adjacent photomultiplier tube. In this static system, the mixing is induced by the force of the injection. This simple reagent addition system without a mixing device is of limited usefulness in measuring fast chemiluminescent reactions with precision. The procedure is also rather cumbersome, requiring separate cuvettes for each measurement as well as repeated opening of the light-tight apparatus, which necessitates special precautions to protect the photomultiplier tube.

The second approach is the two-phase measurement system. In this system, the chemiluminescent reagents are immobilized on a solid support such as filter paper, and the analyte is permitted to interact with the immobilized reagent by diffusion or convection. The light emitted is measured using a micro liter plate reader or by contact printing with photographic detection. The chemiluminescent intensity of these systems is influenced by both the kinetics of the reaction and the efficiency of the mass transfer process bringing the reactants together. The principal advantages of this system lie in the conservation of reagents and the convenience of measurement. The third approach involves the use of flow measurement systems. The flow injection approach has been described as the most successful of the methods. It involves injection of the analyte into a stream of appropriate pH, remote from the detector, and the chemiluminescent reagent flows in another stream. The two streams meet at a T-junction inside a light-tight enclosure, then flow through a flat coil placed immediately in front of a photomultiplier tube. This compact assembly provides more rapid and reproducible mixing, resulting in reproducible emission intensities and permitting rapid sample throughput. The design of the mixing device and the means of retaining the emitting solution in view of the detectors are of important consideration. Mixing is reported as being the most effective at a T-piece or a Y-junction, although some have used a conventional FIA in which sample is injected into the surrounding flowing reagent to achieve mixing. This approach is

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reproducible but reported as not producing a rapid mixing. In flow measurement system, the chemiluminescence signal has to be measured during the mixing: as a result, only a section as opposed to the whole intensity-time curve is measured. An additional feature of these systems is that the shape of the curve now depends on both the kinetics of the chemiluminescent reaction and the parameters of the flow system. Chemical variables such as reagent concentration and pH, and physical parameters such as flow rate, reaction coil length, sample size, and the limitations of experimental apparatus all affects the performance of flow injection procedures. The effects of these on the observed analytical signal are not necessarily independent, as interactions can and probably do occur [15, 16].

V. CONCLUSION

Owing to the advantages of high sensitivity, wide linear range, simple instrumentation, and fast dynamic response, CL has continually received more and more attention in the last two years. CL has been used in various fields, including environmental, biological, clinical, food, and pharmaceutical analysis. Nevertheless, compared to other conventional, well-established, and commercial modes of detection such as UV, CL detection is a developing technique and further research is needed in order to implement CL routinely as a mode of detection.

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