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Comparison of two methods for selegiline determination: A flow-injection chemiluminescence method using cadmium sulfide quantum dots and corona discharge ion mobility spectrometry

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ABSTRACT

Two analytical approaches including chemiluminescence (CL) and corona discharge ionization ion mobility spectrometry (CD-IMS) were developed for sensitive determination of selegiline (SG). We found that the CL intensity of the $KMnO_4–Na_2S_2O_3$ CL system was significantly enhanced in the presence of L-cysteine capped CdS quantum dots (QDs). A possible CL mechanism for this CL reaction is proposed. In the presence of SG, the enhanced CL system was inhibited. Based on this inhibition, a simple and sensitive flow-injection CL method was proposed for the determination of SG. Under optimum experimental conditions, the decreased CL intensity was proportional to SG concentration in the range of 0.01 to 30.0 mg L^{-1}. The detection limit (3σ) was 0.004 mg L^{-1}. Also, SG was determined using CD-IMS, and under optimum conditions of CD-IMS, calibration curves were linear in the range of 0.15 to 42.0 mg L^{-1}, with a detection limit (3σ) of 0.03 mg L^{-1}. The precision of the two methods was calculated by analyzing samples containing 5.0 mg L^{-1} of SG (n = 11). The relative standard deviations (RSDs%) of the flow-injection CL and CD-IMS methods are 2.17% and 3.83%, respectively. The proposed CL system exhibits a higher sensitivity and precision than the CD-IMS method for the determination of SG.

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1. Introduction

Selegiline hydrochloride (SG), [(R)-N-methyl-N-(2-propinyl)-1-phenyl-2-propylamine] hydrochloride, belongs to a group of pharmaceuticals called phenethylamines [1,2]. Table 1 illustrates the structure and properties of SG. It is a potent and irreversible inhibitor of type B monoamine oxidase, which is exclusively used in the treatment of Parkinson's disease [1,3]. This pharmaceutical is also utilized in veterinary medicine for the treatment of Cushing's disorder, and is used at high doses relative to humans [4]. The daily recommended dosage of SG is a maximum of 10 mg for a human. An excessive dosage can lead to the nonselective inhibition of monoamine oxidase, which may cause toxicity and symptoms such as dizziness, hypotension, and hallucination [1,3]. Therefore, monitoring residual SG in bulk and in pharmaceutical formulations is very important in order to prevent side effects in patients under treatment. Moreover, pharmaceuticals can be accumulated in aqueous systems through inappropriate disposal and discharge of hospital and chemical industry wastes to the
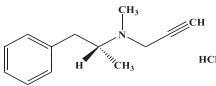
wastewater treatment plants [5,6]. Most of these compounds are resistant to natural removal and bio-removal, so they can remain in the environmental water resources for a long time and cause serious health problems [7]. Due to the aforementioned considerations, monitoring of SG in environmental water samples is very significant. To date, a few analytical methods have been used for the determination of SG, including high performance liquid chromatography–mass spectrometry (HPLC/MS) [8–10], gas chromatography–mass spectrometry (GC/MS) [3,11], potentiometry [12], and spectrophotometry [4]. Although each reported analytical method has its advantages, the HPLC/MS and GC/MS methods still involve laborious and require sophisticated instrumentation [13,14]. Also, spectrophotometric methods lack sensitivity and selectivity. Hence, the development of new analytical approaches for the determination of SG in environmental water samples and pharmaceutical products is important.

The analytical applications of chemiluminescence (CL) technique have received considerable attention in recent years [15–18]. Simplicity of detection, low detection limit, high sensitivity, rapidity, wide dynamic range, and inexpensive instrumentation are some of the characteristics which make the method attractive [19–21]. Since CL emission is usually generated from fast chemical reaction, owing to irreproducible mixing of the reagents and samples, which leads to inaccurate determinations.

Table 1
Characteristics of selegiline hydrochloride.

Chemical structure	Molecular formula	Mw (g mol^{-1})	Therapeutic group	Solubility in water (mg mL^{-1})
	$C_{13}H_{17}N \cdot HCl$	223.74	Monoamine oxidase inhibitors	25

Therefore, the combination flow injection analysis approaches with CL detection technique, flow-injection CL, can supply an automated, reproducible tool for rapid measurements, and enhance the precision of the obtained results [21,22].

Over the past several years, in order to improve the sensitivity and the stability of diverse CL reactions, nanomaterials have drawn considerable interest as signal amplifier in CL-based systems, due to their unique size and physicochemical attributes [16,19,23]. Among nanomaterials, quantum dots (QDs) have attracted substantial attentions due to their exceptional photophysical properties and well-controlled nanosurface which result in probable application in a broad range of fields such as bio-labeling, bio-imaging, and multicolored photoluminescent probes [24]. Hence, traditional CL systems have low quantum yield, incorporation of QDs because of their brightness and tunable band gap can enhance the quantum yield in these kinds of CL reactions [18]. Direct CL of QDs occurs when an electron is injected into the conduction band and a hole is injected into the valence band of QDs after direct oxidation. When the excited state of the QDs returns to its ground state, CL emission is produced [24–26]. QD-catalyzed CL systems were also studied, and their application in analyte detections was demonstrated [18,27–29]. The oxidation of Na_2SO_3 and $Na_2S_2O_3$ in acidic solutions using Ce(IV) or $KMnO_4$ produces a very weak CL emission [30]. The enhancing effect of some fluorescent compounds such as terbium(III) [31] and europium (III) [32] on $KMnO_4$–Na_2SO_3 CL reaction has been studied.

Ion mobility spectrometry (IMS) is a gas phase analytical technique. In this approach, an ambient pressure ion separation tool identifies chemical compounds by gas phase mobilities of ions based on differences in factors such as their collision cross-section, reduced mass and charge via their interaction with the drift gas under weak electric fields [33,34]. The ionization process in the IMS method occurs according to the electron or proton affinity trait of substances [35]. Several ionization sources such as ^{63}Ni radioactive source [36], photoionization [37], and corona discharge (CD) [35,38] have been applied for ionization in IMS. Corona discharge ion mobility spectrometry (CD-IMS), due to its high sensitivity and fast response, has been utilized for the determination of a wide range of compounds including drugs, explosives, illegal drugs, and environmental pollutants [36,39].

In the present work, sensitive and simple flow-injection CL and CD-IMS methods have been developed for the determination of SG in spiked environmental water samples and pharmaceutical formulation. The possible mechanism of the CL system was studied. Also, the obtained analytical results from the proposed CL and CD-IMS methods for the determination of SG were compared. To the best of the authors' knowledge, there are no reports in the literature about the determination of SG by CL and CD-IMS methods.

2. Experimental section

2.1. Materials and solutions

All the used chemicals and reagents were of high purity, analytical grade, or equivalent and purchased from Merck Co. (Germany). SG hydrochloride was provided from Zahravi Pharmaceutical Co. (Tabriz, Iran). All aqueous solutions were prepared with double-distilled water. Fresh stock standard solution of 100 mg L^{-1} SG was prepared daily by dissolving 10 mg of SG into 100 mL of double-distilled water.

This solution was stored in a refrigerator and protected from the light when not in use. H_2O_2 working solutions were freshly prepared by dilution of 30% (w/v) H_2O_2 reagent.

2.2. Apparatus

CL measurements were performed on a CL detector, luminometer (FB12, Berthold Detection Systems, Germany). CL data was acquired with data processing by FB12 software. Ultraviolet–visible (UV–vis) spectra were taken on an UV–vis spectrophotometer (S2000, WPA Lightwave, England). The X-ray diffraction (XRD) spectrum was measured on Siemens X-ray powder diffractometer (D5000, Siemens, Germany) using Cu Kα as the exciting source (λ = 1.54056 Å) at room temperature. The average crystalline size of the as-prepared samples was calculated using the Debye–Scherrer formula [40]. The general morphology and surface structure of the as-prepared CdS QD sample were recorded on a Mira3 FEG scanning electron microscopy (SEM) (Tescan, Czech Republic) and a Cs-corrected transmission electron microscopy (TEM) (JEM-2200FS, JEOL, Japan). Moreover, the obtained SEM and TEM images were analyzed by Nahamin microstructure distance measurement software (Nahamin Pardazan Asia Co., Iran) to determine the size distribution of the obtained samples. The Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets on an IR-spectrometer (Tensor 27, Bruker, Germany). The photoluminescence (PL) spectra were performed with a spectrofluorometer (FP-6200, Jasco, Japan). Furthermore, an ion mobility spectrometry (IMS) equipment (model 200, TOF Tech. Pars Co., Iran) by source type of corona discharge ionization was implemented in the positive mode. This device was equipped with an IMS cell, a thermostatic oven, a needle to produce the corona, power supplies, a pulse generator, an analog to digital converter (PicoScope, UK), and a computer for processing of the data.

2.3. Procedures for chemiluminescence assay

The configuration of the laboratory-made flow-injection CL detection system used in this work is represented in Fig. 1. All the solutions were continuously propelled into the flow cell by a peristaltic
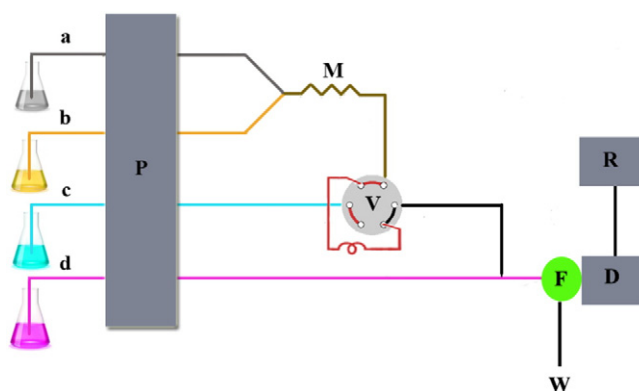

Fig. 1. Schematic diagram of flow-injection CL system; (a) mixture of acid solution and $Na_2S_2O_3$, (b) sample or standard solution of mixture of SG and L-cysteine capped CdS QDs, (c) H_2O as the carrier, (d) $KMnO_4$ solution, (P) peristaltic pump, (M) mixing tube, (V) injection valve, (F) flow cell, (W) waste, (D) detector (luminometer) and (R) recorder (personal computer).