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Analytical Use of Luminescence Induced Ultrasonically in Solution. I. Sonic Chemiluminescence of Luminol for Determination of Cobalt(II) at Sub-pg Levels by Flow Injection and Continuous Flow Methods

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Ultrasonic irradiation of alkaline luminol solution produces intense light emission (sonic chemiluminescence) as a result of the reaction of luminol with reactive species which are generated ultrasonically from water molecule. For the analytical application of ultrasound-induced luminescence, the sonic chemiluminescence of luminol is first utilized for the determination of ultratraces of cobalt(II) by flow injection and continuous flow methods. This novel method is based on the measurement of sonic chemiluminescence enhanced by the presence of cobalt(II); it provides analytical characteristics comparable to those for the conventional luminol chemiluminescence method using hydrogen peroxide as an oxidizing agent. The limit of detection is 0.06 pg(10-μl sample injection) or 0.06 pg ml^{-1} (continuous sample flow), the linear dynamic range is 3 orders of magnitude (10-μl sample injection), the sampling rate is 120 h^{-1}, and the relative standard deviation is 3.9% for 6 pg Co(II) ($n=10$). The method is successfully applied to real samples. Possible explanation of sonic chemiluminescence is also presented; the mechanism involving superoxide anion radical is proposed for the cobalt(II)-catalyzed sonic chemiluminescence.

Ultrasound is widely used in various fields, e.g., diagnosis and therapy, disintegration of biological materials, metal processing, cleaning, etc. Recently, the chemical uses of ultrasound have received considerable attention because of its chemical effects like redox-action and acceleration of chemical reaction.[1–7] Such chemical effects arise from acoustic cavitation which occurs when high intensity ultrasound (>3.5 kW m^{-2}) is propagated through a liquid medium. The acoustic cavitation is a three-stage process consisting of the formation, growth, and collapse of gas or vapor-filled bubbles suspended in the liquid phase; the presence of dissolved gas reduces the liquid strength and hence favors the initiation of cavity formation.[8] The most striking characteristics of the acoustic cavitation is the liberation of a high energy through the process; the collapse generates transient hot-spots with local temperatures and pressures of several thousand K and hundreds of atmospheres.[4] This leads to the thermal decomposition of the cavity contents and the formation of free radicals. For example, in aqueous solutions the primary reaction in the cavitation of water gives hydrogen atoms and hydroxyl radicals in the absence of any volatile solute.[1]

It is known that the cavitation is frequently accompanied by a faint light emission called sonoluminescence (SL).[9,10] The intensity and spectrum of SL depend on the nature of liquid, the nature of dissolved gas, the liquid temperature, the presence of solute, and the ultrasonic intensity.[11] In air-saturated water, the SL spectrum consists of characteristic bands based on OH*, H_2O*, NO_2^*, and radiative recombination (HO_2+H) which are overlaying a broad continuum arising from the radiative recombination (H+OH).[10] The presence of inorganic species like metal ions sometimes provides their characteristic emissions.[12–14] On the other hand, in an alkaline aqueous solution of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) containing dissolved oxygen the cavitation causes an intense light emission (sonic chemiluminescence, SCL) which is essentially luminol chemiluminescence, in addition to the SL.[9,15,16] Our attention has been focused on the introduction of these luminescence phenomena into the field of analytical chemistry. We already made it clear in the preliminary works that the SL and SCL were likely to be usable as analytical tools. That is to say, the SL and SCL techniques permit the determinations of water in methanol with no use of reagents[17] and of traces of cobalt(II) by monitoring the cobalt(II)-catalyzed SCL of luminol,[18] respectively. Our ultimate goal is to evaluate the utility and limit in the analytical use of the ultrasonically induced luminescence. In this paper, we describes the details of the luminol SCL for the determination of cobalt(II) at sub-pg levels, namely, further exploration of the SCL technique, its analytical characteristics, the comparison with the conventional luminol chemiluminescence (CL), and the mechanistic study of the cobalt(II)-catalyzed SCL.

Experimental

Apparatus. A schematic diagram of the flow system is given in Fig. 1. It is basically as before,[18] except that a flow line R_2 is newly placed. An aqueous solution containing luminol and sodium hydroxide is supplied through a flow line R_1. R_2 represents a carrier stream for cobalt(II) and other species. This is an aqueous cobalt(II) solution for the continuous flow method, or pure water or surfactant solution when cobalt(II) and other species are injected by means of a 10-μl rotary valve injector S (injection method). The streams are delivered by peristaltic pumps P_1 and P_2. The alkaline luminol solution is sonicated in a glass sonication cell C

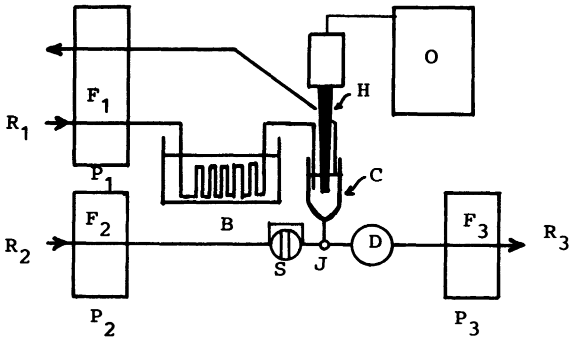


Fig. 1. Flow diagram for sonic chemiluminescence (SCL) method (for key, see text).
Recommended conditions: $R_1=5\times10^{-5}$ M luminol, 0.16 M NaOH, $R_2=0.03$ M SDS; Flow rates (ml min^{-1}) $F_1=1.3$, $F_2=1.6$, $F_3=2.8$.

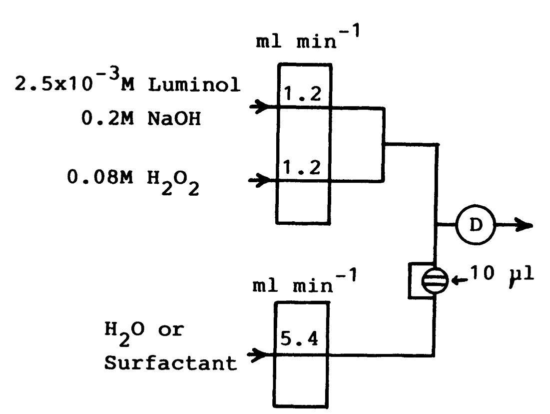


Fig. 2. Flow diagram for conventional chemiluminescence (CL) method.
Recommended conditions are specified in the figure.

by means of an exponential horn H (cross section: 0.05 cm^2) directly immersed in the solution, oscillated with an oscillator O (Tomy Seiko Co., Handy Sonic Model UR-20P; 28 kHz, max. 20 W). The luminol solution within the sonication cell is kept to be a constant volume (ca. 1.3 ml) during sonication by use of the pump tubes for the pump P_1 with different diameters. In order for adequate and stable cavitation to occur continuously, the luminol solution is cooled in an ice-water bath B before sonication. The luminol solution sonicated is drawn by a peristaltic pump P_3 and mixed with R_2 at a Y-joint J to be a flow line R_3. The cobalt(II)-catalyzed SCL is monitored at a spiral flow cell D ca. 15 cm apart from J, the minimum distance which can be achieved. Flow lines and a light-detecting device including the spiral flow cell have been described elsewhere.[19] In the system, there is no oxidizing agent intentionally added.

For the comparison of the present SCL method with an conventional CL method using hydrogen peroxide as an oxidizing agent, the flow system as shown in Fig. 2 was also assembled. Recommended conditions are given in the figure.

Absorption spectra of luminol were measured by a Shimadzu UV-240 spectrophotometer.

Reagents. Chemicals of analytical grade were used as received. The water used was prepared by distillation of Millipore (milli-R) water in an all-Pyrex glass apparatus, with a Teflon membrane inserted to block mist evolved. Stock solutions (10^{-2} M, 1 M=1 mol dm^{-3}) of various species were prepared by dissolving chlorides or nitrates, or sodium or potassium salts in water otherwise stated elsewhere. Luminol solution were prepared daily.

Analysis of Real Samples. Pepperbush or Pond Sediment (0.5 g) was boiled with 10—20 ml of concentrated nitric acid on a hot plate until the appearance of white fumes, and with concentrated sulfuric acid until the solution became colorless. After cooling, the solution was diluted to 100 ml. A 1 ml portion was added to each of several 100 ml volumetric flasks for standard addition of cobalt before dilution to volume, and cobalt was determined as described above.

Results and Discussion

Reagent Concentrations. The concentrations of luminol and sodium hydroxide were optimized at $F_1=1.8$, $F_2=2.7$, and $F_3=4.1$ ml min^{-1}, where F_1,F_2, and F_3 were the flow rates of R_1, R_2, and R_3, respectively. There is a reagent concentration giving the highest signal as shown in Figs. 3 and 4. The concentrations of 5×10^{-5} M for luminol and 0.16 M for sodium hydroxide were chosen for further experiments. These concentrations are several times higher than those in the previous system[18] because of the dilution of reagent solution with water of R_2, but the luminol concentration is one-fiftieth of that in the conventional CL system. From the absorption spectra, it was confirmed that there was no appreciable decrease in the luminol concentration due to the sonication.

Flow Rates of the Reagent Solutions. The effect of the flow rates F_1, F_2, and F_3 on the signal is represented in Fig. 5. In the experiment, F_1 is set at the lowest flow rate, 1.3 ml min^{-1} which can be achieved readily because the longer the resident time of luminol solution in the sonication cell, the higher the signal. As can be seen from the figure, the higher signal is obtained at each F_2 when F_3 is nearly equal to F_1+F_2, the highest signal being obtained at 1.6 for F_2 and 2.8 ml min^{-1} for F_3. With F_2 over 1.6 ml min^{-1}, further increased signal was not observed because of excess dilution of the sonicated luminol solution with water.

Effect of Surfactants. Surfactants (amphiphilic molecules) which have distinct hydrophobic and hydrophilic regions spontaneously form molecular aggregates in solution called micelles when they reach a certain concentration (critical micelle concentration, cmc). Organized molecular assemblies like micelles have currently been utilized in many types of analytical method,[20,21] because solutes accommodated in molecular assemblies often achieve a great degree of organization compared to homogeneous solution. In CL measurements, for instance, the use of micellar solution as reaction medium is very attractive because of the acceleration of CL reaction and the solubilization of CL reagents insoluble in water. So far there have been several reports on the analytical application of CL in micellar solution.[22–26]

In order to investigate whether micellar media func-

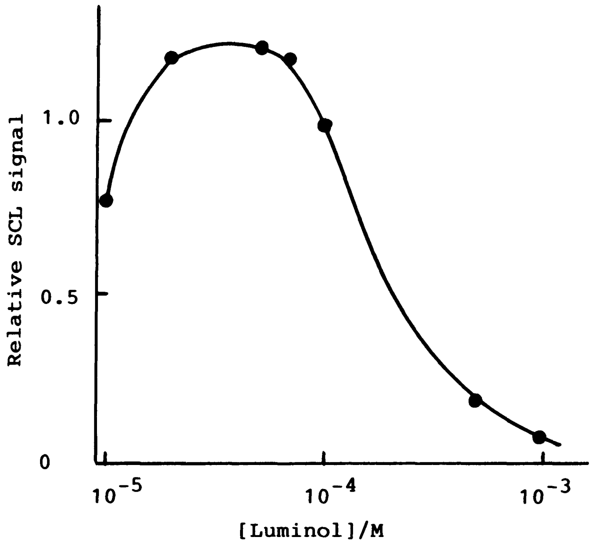


Fig. 3. Effect of luminol concentration on the SCL signal for Co(II).
0.16 M NaOH, 10^{-8} M Co(II), Flow rate (ml min^{-1}): $F_1=1.3$, $F_2=2.7$, $F_3=4.1$.

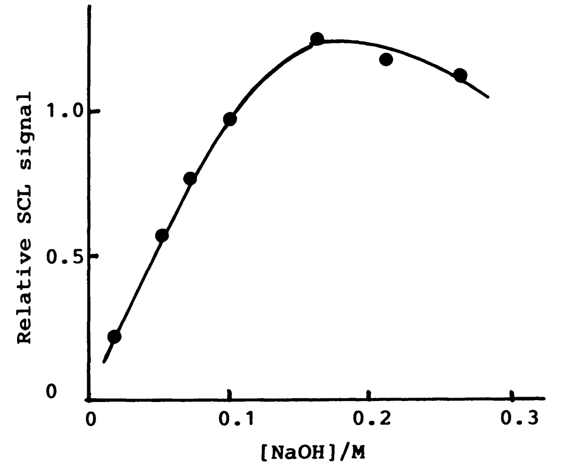


Fig. 4. Effect of sodium hydroxide concentration on the SCL signal for Co(II).
10^{-4} M luminol, 10^{-8} M Co(II), Flow rate (ml min^{-1}): $F_1=1.3$, $F_2=2.7$, $F_3=4.1$.

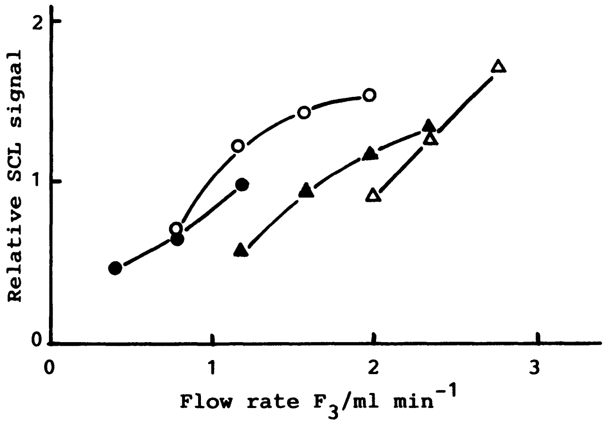


Fig. 5. Effect of flow rates on the SCL signal for Co(II).
0.16 M NaOH, 5×10^{-5} M luminol, 10^{-8} M Co(II), $F_1=1.3$ ml min^{-1}, F_2(ml min^{-1}): ●: 0, ○: 0.8, ▲: 1.2, △: 1.6.

Table 1. Effect of Surfactant Micelles on the Signal for Co(II)[a)]

Surfactant[b)]	Concentration[c)] /10^{-3} M	Relative signal[d)] SCL method	Relative signal[d)] CL method
CTAB	1.8	5	360
MDBAC	0.7	5	145
SDS	16	530	320
SDBS	16	120	250
Triton X-100	0.8	100	190
Brij 35	0.2	75	370

a) 10-μl injection of 10^{-8} M solution. b) CTAB: hexadecyltrimethylammonium bromide, MDBAC: tetradecylbenzylammonium chloride (zephiramine), SDS: sodium dodecyl sulfate, SDBS: sodium dodecylbenzenesulfonate. c) [CMC]×2. d) Normalized with respect to the value (=100) in the absence of surfactant.

tion effectively for the present SCL system, various surfactants were examined by adding to the carrier stream R_2. The results are shown in Table 1. Anionic surfactants increased the signal (max. 6 times increase for 0.03 M sodium dodecyl sulfate, SDS), whereas for cationic surfactants significant decreases in the signal were observed. This might be rationalized in terms of the following micellar effect. Owing to its charge, luminol monoanion (the most abundant species of luminol in the present alkaline solution) migrates easily on the cationic micellar surface. From the absorption spectra of luminol showing that λ_{max} at 300 and 349 nm in water are red-shifted by ca. 5 nm in the hexadecyltrimethylammonium bromide (CTAB) micellar solution, it is reasonable to consider that luminol monoanion is solubilized in the Stern layer where is less polar than in bulk water. This is supporte by the fact that the degree of the red shift is equivalent to that in 50% ethanol solution, namely, the hydrophobicity in the solubilization site is corresponding to that in 50% ethanol solution. For SDS, Triton X-100, and Brij 35 micellar solutions, no spectral changes were observed. This means that luminol monoanion is mainly solubilized in bulk water. Superoxide anion radical (a reactive species in the present SCL system) also migrates easily on the cationic micellar surface and hence reacts with luminol monoanion noncatalytically through a pathway in which cobalt(II) does not participate as stated later. On the other hand, cobalt ion is repelled electrostatically from the cationic micellar surface, but attracted to and concentrated on the anionic micellar surface. Consequently, the positively charged micellar surface causes the decrease in superoxide anion radical participating in Co(II)-catalyzed SCL reaction and/or the decreased cobalt ion-luminol monoanion interaction due to the charge separation, resulting in the suppression of Co(II)-catalyzed SCL reaction. In contrast, the concentration of cobalt ion on the negatively charged micellar surface favors the Co(II)-catalyzed

Table 2. Analytical Characteristics

Characteristic	SCL method[a)]	CL method[b)]
Background current, pA	48	250
Noise current, pA	1.2	5.0
Lower detection limit (S/N=3)		
10-μl injection, pg	0.06	0.04
continuous flow, pg ml^{-1}	0.06[b)]	0.06
Linear dynamic range		
10-μl injection	1000	250
continuous flow	100	100
Sampling rate, h^{-1}	120	180
R.s.d. for 6 pg (n=10), %	3.9	5.7

a) With SDS. b) Without SDS.

SCL reaction.

The results for the conventional CL system are also shown in the table, indicating that any surfactants tested slightly increased the signal. This suggests that a cobalt(II)-hydrogen peroxide complex which is considered to work as a catalyst in the conventional CL system[27)] may be noncharged species. And also this strongly suggests that the mechanism of SCL is different from that of the conventional CL.

Analytical Characteristics of the SCL System. Under the recommended conditions (as specified in Fig. 2), the analytical characteristics of the system were investigated. The results are summarized in Table 2. The SCL method has extremely high sensitivity and good reproducibility; the analytical characteristics are comparable to those for the conventional CL system. The detection limit is 10 times lower than that by the gallic acid CL method developed previously by the authors[28)] which is more sensitive than any other method. For the measurement by continuous sample flow, the presence of SDS did not serve to improve sensitivity because it caused high background and severe noise; this was also the case for both types of the measurement in the conventional CL system. The logarithmic calibration graph for 10-μl sample injection exhibited a straight line with a slope of unity and linear dynamic range of 10^3. For continuous sample flow it gave a slightly larger slope and narrow linear dynamic range as well as in the conventional CL system.

Effect of Other Substances. Most of classical solution CL methods suffer from poor selectivity. Especially, the luminol CL method permits 30 species to enhance the luminescence reaction.[29)] The present SCL system is very selective as shown in Table 3, despite of the use of luminol. Only strong oxidizing agents like hexacyanoferrate(III) and permanganate provided CL signals 0.1% of that for cobalt(II); other species enhanced the emission very weakly or gave rise to no emission. The selectivity for the conventional CL system is also represented in the table, the selectivity being equivalent to that for the SCL system. This means that the SCL technique itself does not yield such high selectivity. The high selectivity presumably derives from the measurement in flow. In general, a flow injection system often provides better selectivity than the corresponding batch system.

Table 3. Selectivity

Species[a)]	Relative molar signal	
	SCL method	CL method
Co(II)	1000	1000
[Fe(CN)$_6$]$^{3-}$	2	0.2
MnO$_4^-$	1	0.02
Fe(II)	0.2	0.06
Ag(I)	0.04	
Fe(III)	0.03	0.03
Mo(VI)	0.02	
Cr(VI)	0.02	0.01
Mn(II)	0.007	0.02
Cr(III)	−0.04	0.3
Cu(II)	−0.08	0.1

a) 10-μl injection of 10^{-5} M solution of chloride or nitrate, or potassium salt except ammonium sulfate for Fe(II, III) and ammonium molybdate for Mo(VI), and of 10^{-8} M Co(II) solution.

Table 4. Effect of Other Substances on the CL Signal for Co(II)[a)]

Species	SCL signal[b)]		Species	SCL signal[b)]	
	10^{-4} M	10^{-5} M		10^{-4} M	10^{-5} M
Fe(II)	130	120	MnO$_4^-$	7600	1700
Ag(I)	100		[Fe(CN)$_6$]$_3^-$	1900	400
Cr(VI)	100		NH$_4^+$	90	100
Cd(II)	100		CO$_3^{2-}$	60	110
Zn(II)	90	100	S^{2-}	35	120
Al(III)	55	60	CN$^-$	−5	65
Pb(II)	50	70	EDTA	−20	−5
Mn(II)	35	90			
Cu(II)	25	20			
Mg(II)	25	40			
Fe(III)	15	50			
Cr(III)	15	45			
Ca(II)	10	25			
Ni(II)	−10	20			

a) 10-μl injection of 10^{-8} M solution. b) The value 100 means no interference.

To check the effect of concomitant species on the signal for cobalt(II), 10-μl of a 10^{-8} M Co(II) solution containing each common species(10^{-4} and 10^{-5} M) was injected. The results are shown in Table 4. Many

Table 5. Effect of the Addition of Trappers on the Signal for Co(II)[a]

Reactive species	Trapper	Concentration/M	Relative signal[b] SCL method	Relative signal[b] CL method
$\cdot$OH	HCOONa	10^{-5}	110	110
		10^{-4}	140	130
		10^{-3}	140	130
	2-C_3H_7OH	10^{-5}	120	95
		10^{-4}	130	95
		10^{-3}	130	90
$O_2^{\overline{\cdot}}$	NBT[c]	10^{-5}	45	100
		10^{-4}	10	110
		10^{-3}	NS[e]	110
$^1O_2$	NaN_3	10^{-5}	110	95
		10^{-4}	120	95
		10^{-3}	130	95
	DABCO[d]	10^{-5}	110	100
		10^{-4}	140	100
		10^{-3}	130	90

a) 10-µl injection of 10^{-8} M solution. b) The value 100 means no effect. c) Nitro Blue Tetrazolium (Registry No. 38184-50-8). d) 1,4-Diazabicyclo[2.2.2]octane. e) No signal.

species eliciting no emission or very weak emission per se suppressed the Co(II)-catalyzed emission, except permanganate and hexacyanoferrate(III). The suppressions due to anionic species are based on the complexation or precipitation reaction with cobalt(II). Although the suppressions due to cationic species can not be fully explainable, such cationic species at high concentration levels may compete the site on the anionic micellar surface with cobalt, resulting in inhibition of the interaction between cobalt and luminol monoanion (and/or superoxide anion radical) and/or may catalyze effectively the disproportionation reaction of superoxide anion radical[30,31] on the anionic micellar surface, resulting in decrease in the superoxide anion radical concentration. Accordingly, the presence of SDS seems to cause or amplify the suppression . In fact, for instance, the suppressive interferences due to lead and calcium were no longer observable in the absence of SDS; these species at 10^{-4} M increased the Co(II)-catalyzed signals by 10 and 20%, respectively and 10^{-5} M they did not interfere. Therefore, no addition of SDS to the system may be recommended in order to reduce or eliminate interferences, although the sensitivity decreased slightly. Needless to say, the interferences can be reduced by dilution.

Mechanistic Study of the SCL. As stated above, the effect of surfactants on the Co(II)-catalyzed signal strongly suggests the difference in luminescent reaction mechanism between the SCL and the conventional CL. In order to confirm this suggestion, various trappers for reactive species which were considered to react luminously with luminol were added to the carrier stream R_3. The results are summarized in Table 5. Remarkable decrease in the Co(II)-catalyzed SCL signal was led to by the addition of Nitro Blue Tetrazolium (NBT), indicating that superoxide anion radical ($O_2^{\overline{\cdot}}$) contributed to the Co(II)-catalyzed SCL reaction. It is well known that luminol react with $O_2^{\overline{\cdot}}$ to emit light.[32] On the contrary, any trapper tested did not cause appreciable change in the Co(II)-catalyzed CL signal. Therefore, it can be said that these reactive species do not take part in the conventional CL reaction. This is consistent with the idea that a Co(II)–hydrogen peroxide complex plays an important role in the Co(II)-catalyzed CL reaction.[27]

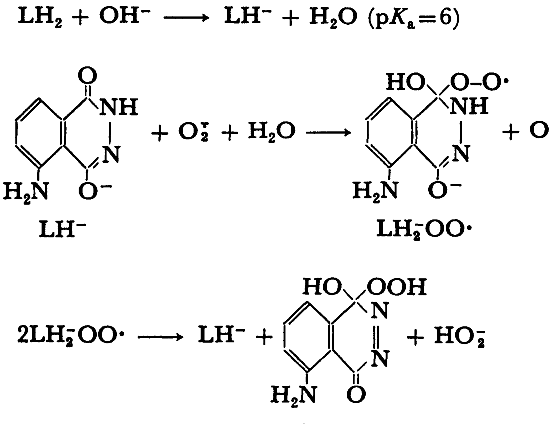
Superoxide anion radical is generated ultrasonically in alkaline solution. The irradiation of strong ultrasound first leads to the dissociation of water molecule to hydrogen atom ($\cdot$H) and hydroxyl radical ($\cdot$OH). The $\cdot$H produced reacts with dissolved oxygen molecule to form hydroperoxide radical,[33,34] which immediately deprotonates to form $O_2^{\overline{\cdot}}$ in alkaline solution.

$$\cdot H + O_2 \longrightarrow HO_2^{\cdot}$$

$$HO_2^{\cdot} \rightleftharpoons O_2^{\overline{\cdot}} + H^+ \quad (pK_a=4.8)$$

Superoxide anion radical is unstable in water, but its stability is greatly increased in alkaline solution;[35] the half-life of its decay is 10 s at pH 11.3.[32] In fact, the sonication of alkaline solution without luminol (in this case, luminol is added to the stream R_3) also provided Co(II)-catalyzed signal, about half the signal in the sonication of alkaline luminol solution. Although how much $O_2^{\overline{\cdot}}$ is produced by the sonication is unknown, its concentration will not exceed 10^{-5} M, the concentration produced upon electron irradiation of alkaline solution without luminol but with methanol or formate as a trapper for $\cdot$OH which consumes $O_2^{\overline{\cdot}}$.[32] In the present SCL system, the presence of luminol and furthermore the absence of such trapper will enable the $O_2^{\overline{\cdot}}$ concentration at the mixing joint J (see Fig. 1) to be far below 10^{-5} M. This low concentration of $O_2^{\overline{\cdot}}$ might cause in part severe interferences due to other substances as stated above.

According to the pulse radiolysis experiments by Merényi et al.,[32] there are two routes where luminol (LH_2) may react with $O_2^{\cdot-}$ to chemiluminesce, that is,

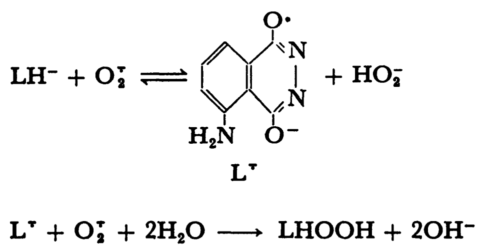


$LH_2 + OH^- \longrightarrow LH^- + H_2O$ ($pK_a = 6$)

$2LH_2^-OO\cdot \longrightarrow LH^- + LHOOH + HO_2^-$

Scheme 1.

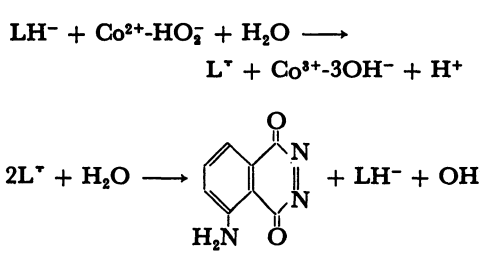
The hydroperoxide LHOOH formed, a short-lived CL intermediate, affords the excited aminophthalate through a rearrangement to the endoperoxide and a two-step decomposition.[36]



$L^{\cdot-} + O_2^{\cdot-} + 2H_2O \longrightarrow LHOOH + 2OH^-$

Scheme 2.

The SCL signal in the absence of Co(II), i.e., the background signal is conceivably based on reaction Scheme 1 with very small luminescence quantum efficiency (10^{-6}).[32] In contrast, the quantum efficiency for the luminescence arising from reaction Scheme 2 is 10^{-2}—10^{-3},[32] the same order of that for the conventional CL reaction whose reaction mechanism is proposed by Burdo and Seitz as shown in Scheme 3.[27]



$LH^- + Co^{2+}\text{-}HO_2^- + H_2O \longrightarrow L^{\cdot-} + Co^{3+}\text{-}3OH^- + H^+$

$L + HO_2^- + H_2O \longrightarrow LHOOH + OH^-$

Scheme 3.

The diazaquinone L produced gives LHOOH through nucleophilic attack by hydroperoxide ion HO_2^-.[34,37] That the SCL method has the analytical sensitivity comparable to that for the conventional CL method, implies that both methods have the same order of luminescence quantum efficiency. Therefore, it is reasonable to consider that reaction Scheme 2 operates in the presence of cobalt(II). Furthermore, considering the similarity that the formation of luminol radical ($L^{\cdot-}$) appears in reaction Schemes 2 and 3, it seems likely that cobalt(II) works catalytically on the direct electron-transfer reaction to form $L^{\cdot-}$. At present stage, however, we can not say how cobalt(II) contributes to the electron transfer reaction.

Application to Real Samples. The applicability of the proposed method was evaluated by assaying NIES (National Institute for Environmental Studies) standard reference materials (Pepperbush[38] and Pond Sediment[39]). Standard additions of cobalt to acid-digested samples indicated that the results obtained for Pepperbush (23, 24 μg g^{-1}) by the 10-μl sample injection method with SDS and Pond Sediment (30, 29 μg g^{-1}) by the continuous sample flow method without SDS were within the certified values (23±3 and 27±3 μg g^{-1}, respectively).

Conclusion

In this paper, we have indicated the analytical utility of ultrasound-induced luminescence in solution through the determination of ultratraces of Co(II) using luminol SCL phenomenon. This novel SCL method is unique in being capable of detecting Co(II) selectively at sub-pg or sub-pg ml^{-1} levels with no use of oxidizing agents intentionally added, in contrast with the conventional luminol CL method. No other method can surpass the SCL method with regard to the sensitivity, the detection limit (0.00006 ng ml^{-1}) being much lower than those for flameless atomic absorption (0.2 ng ml^{-1}) and fluorescence methods (1 ng ml^{-1}), neutron activation analysis (0.5 ng ml^{-1}), and inductively coupled plasma emission method (0.1 ng ml^{-1}). We have also made it clear that the mechanism of SCL reaction is different from that of conventional CL reaction and ultrasonically generated $O_2^{\cdot-}$ plays a key role in the Co(II)-catalyzed SCL emission.

Although the SCL method could not be superior to the conventional CL method with respect to the analytical characteristics, the present work revealed that strong ultrasound was of great value as an energy source for eliciting luminescence. Accordingly, there is much possibility of finding out new luminescence systems usable in analysis because the reactive species ultrasonically generated react luminously with various organic compounds in solution and because the direct excitation of chemical species in solution by ultrasound leads to sonoluminescence (SL). These investigations are now in progress.

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