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SONIC CHEMILUMINESCENCE OF LUMINOL FOR THE DETERMINATION OF ULTRATRACES OF COBALT(II)

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Ultrasonically induced chemiluminescence of luminol in an aqueous alkaline solution is described for the determination of cobalt(II). This novel method is capable of detecting cobalt(II) more sensitively than any other method with a detection limit of 0.07 pg and more selectively than any other chemiluminescence method.

Sonic chemiluminescence(SCL) is observed when ultrasonic waves is propagated through an aqueous alkaline luminol solution containing dissolved oxygen.[1-3] The SCL is usually produced accompanied by an emission arising from water, i.e., sonoluminescence(SL).[4] Both luminescences are caused by acoustic cavitation responsible for many of the chemical reactions which occur in an ultrasonic field. Therefore, dissolved gases are necessary for an occurrence of SCL or SL; in contrast to SL, luminol chemiluminesces acoustically only in the presence of dissolved oxygen. We have already applied the SL phenomenon to the estimation of water content in methanol.[5] This paper demonstrates preliminary investigations on highly sensitive and selective determination of cobalt(II) by the SCL method. It is based on the measurement of SCL enhanced by the catalytic effect of cobalt(II) in an aqueous alkaline luminol solution.

A schematic diagram of the experimental setup is given in Fig. 1. An oscillator with an exponential horn used for insonation at 28 kHz,[5] a 10-µl sample injector,[6] and a light-detecting device including a flow cell D[7] have been described previously. Teflon tubing of 1 mm i.d. is used for flow lines except pump tubes and the flow cell. In order for adequate and stable cavitation to occur continuously, an alkaline luminol solution is cooled with ice water before insonation. Unlike the SL experiment,[5] the Co(II)-catalyzed SCL is monitored at D ca. 30 cm apart from an insonation cell to avoid high background signals due to SL and SCL produced in the insonation cell. The diameters of pump tubes are chosen so that the luminol solution within the insonation cell is kept to be a constant volume(ca.1.3 ml) during insonation.

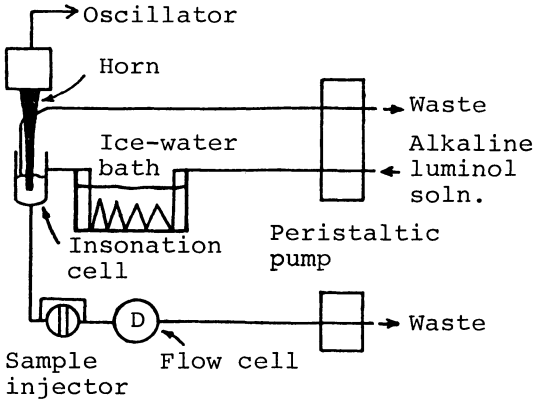

Fig. 1. Experimental setup.

Experiments under conditions of 8×10^{-6}M luminol and 5×10^{-2}M sodium hydroxide, the reagent concentrations roughly optimized for the cobalt determination, indicated that the Co(II)-catalyzed SCL signal increased with decreasing the flow rate of reagent stream into the insonation cell(F_R) and with increasing the flow rate of insonated reagent stream into the flow cell(F_S) at a given F_S and F_R, respectively. They also indicated that the higher the F_S, the higher the background signal, resulting in the higher the noise level, while the F_R was independent of the background signal. For sensitive detection of cobalt, the background signal must be as low as possible because high background causes high noise. Under the prerequisite that the F_S should be less than the F_R, the combination of F_R and F_S giving the highest signal-to-noise ratio was found to be 1.4 for F_R and 1.2 ml min^{-1} for F_S. The conditions stated above provided a detection limit of 0.07 pg(S/N=3); to our knowledge, this is the lowest one for cobalt(II) which can not be achieved by any other method.

A practical difficulty in using normal luminol chemiluminescence, produced chemically through the oxidation of luminol by hydrogen peroxide in alkaline solutions, is that many species enhance light emission[8] and therefore the luminol chemiluminescent system suffers most from lack of selectivity. The present SCL method, on the contrary, is very selective for the cobalt determination as shown in Table 1; oxidizing agents which give rise to emissions without insonation are only major enhancers. This selectivity is comparable to that of the gallic acid chemiluminescent system which is the most selective for the cobalt(II) determination.[7]

These preliminary results imply that ultratrace amounts of cobalt(II) can be determined feasibly by the SCL method with fewer interferences than any other chemiluminescent system. Further work is required for more detailed characteristics of the SCL method.

Table 1. Selectivity of the luminol SCL method

Species[a]	SCL signal, 10^{-11}A	Relative molar signal for SCL
Co^{2+}	18 (0.2)[b]	1000
MnO_4^-	67 (45)[b]	36
$Fe(CN)_6^{3-}$	43 (10)[b]	2
Cu^{2+}	22 (N)[c]	0.1
Cr^{3+}	1.7 (N)	0.009
Mn^{2+}	1.0	0.005
Fe^{2+}	1.0 (N)	0.005
Fe^{3+}	0.2 (N)	0.001
Mo^{6+}	0.2	0.001
$Cr_2O_7^{2-}$	0.2 (N)	0.001

[a] 10-μl injection of 10^{-4}M soln. of chloride or nitrate, or sodium or potassium salt except ammonium sulfate for Fe^{2+}, potassium sulfate for Fe^{3+} and ammonium molybdate for Mo^{6+}, and 10^{-8}M for Co^{2+}, 10^{-6}M for MnO_4^- and 10^{-5}M soln. for $Fe(CN)_6^{3-}$. [b] Emission signal observed without insonation. [c] No emission observed without insonation. Each of 10^{-4}M soln. of Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Ni^{2+} and Mg^{2+} gave rise to no emissions.

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