

# Radioluminescent Light Source for Optical Oxygen Sensors

Han Chuang and Mark A. Arnold\*

Department of Chemistry, University of Iowa, Iowa City, Iowa 52242

**A self-powered radioluminescent (RL) light source is evaluated as a means of supplying incident radiation for optical chemical sensors. The light source consists of  $^{147}\text{Pm}$  (a  $\beta$ -emitting radionuclide) and ZnS:Ag phosphor. Blue light (450 nm) is produced following the excitation of ZnS:Ag from  $\beta$  particles released by the  $^{147}\text{Pm}$ . The utility of this source is judged by evaluating the analytical performance of optical oxygen sensors, where the blue light from the RL source excites a ruthenium complex immobilized in a plasticized PVC or silicon membrane. Analytical information is acquired by measuring the magnitude of oxygen-induced fluorescence quenching of the ruthenium complex. The resulting RL oxygen sensors show good stability and reversibility, with detection limits of 0.25 Torr in gaseous samples and 0.028 ppm in aqueous samples. Although the RL light source is not as bright as conventional electrical-powered sources, RL sources offer the advantages of compact size, simple configuration, low power consumption, and essentially no photobleaching of the oxygen-sensitive indicator dye. In addition, different phosphors are available to provide a variety of emission wavelengths and band-passes over a wide spectral range.**

The concept of using radioluminescence (RL) as a source of incident radiation for optical chemical sensors is evaluated. RL is a well-known process where ionizing radiation excites a phosphor, from which light is subsequently produced via a radiative relaxation process. RL has been studied extensively as a means of illumination. As a result, a wide variety of nuclides and phosphors have been combined to produce different colors and brightnesses of light.<sup>1–3</sup>

The use of RL sources for analytical measurements has been limited. Hobbs and Hieftje recently evaluated the utility of RL sources for time-resolved fluorescence lifetime measurements based on the pulsatile nature of radionuclide scintillation.<sup>4</sup> Low cost, compactness, reliability, and low power are identified as principal advantages of RL sources for such measurements. RL sources have also been proposed for optical sensing applications, but their utility has not been demonstrated.<sup>5</sup> Radiant power of these sources is the critical issue for most sensing applications. From a practical standpoint, optical sensors require that the resulting light be measured by an inexpensive photodiode detector

system. Given this restriction, the key question becomes, can relatively dim RL sources provide sufficient incident power for analytical measurements? Limit of detection will be the primary indicator of utility, based on its dependence on signal-to-noise ratio (SNR). SNRs should be enhanced by the extreme low noise associated with RL sources.<sup>6</sup> This advantage may be overshadowed, however, by small signals created by limited radiant power.

The RL source used in this investigation is based on promethium-147 coupled with a solid-state silver-doped zinc sulfide phosphor (ZnS:Ag). Promethium-147 is a  $\beta$ -emitting nuclide with a half-life of 2.5 years and a maximum  $\beta$  particle energy of 225 keV.<sup>7</sup> The decay of promethium-147 produces samarium-147, which is a relatively harmless  $\alpha$  emitter with a half-life of  $1.05 \times 10^{11}$  years. ZnS:Ag is a stable, inexpensive, and commercially available inorganic phosphor. The mechanism of light production involves formation of donor/acceptor pairs within the solid-state matrix upon excitation by  $\beta$  electrons. Visible photons are produced with the recombination of these donor/acceptor pairs.<sup>8,9</sup> Mixing promethium-147 and the ZnS:Ag phosphor produces a self-powered source of blue electromagnetic (em) radiation.

The feasibility of using RL sources for optical chemical sensing technology is demonstrated by coupling the above-mentioned  $^{147}\text{Pm}/\text{ZnS:Ag}$  RL source with an oxygen-sensitive, ruthenium-containing membrane. Oxygen is measured by fluorescence quenching of tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) chloride ( $\text{Ru}(\text{dpp})_3\text{Cl}_2$ , herein referred to simply as  $\text{Ru}(\text{dpp})_3$ ).  $\text{Ru}(\text{dpp})_3$  has been well characterized and is generally accepted as an excellent indicator for the optical sensing of oxygen.<sup>10–17</sup> Figure 1 presents the various phases and processes involved in the operation of this unique oxygen sensor.  $\beta$  particles emitted from promethium-147 excite the nearby ZnS:Ag phosphor, which emits photons with sufficient energy to excite the immobilized

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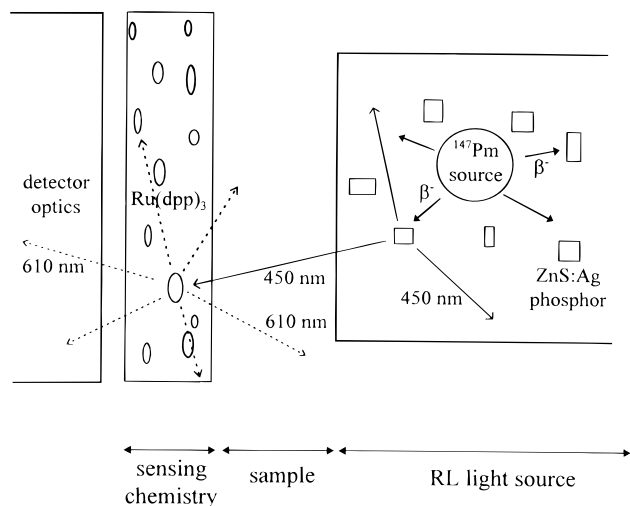


Figure 1. Phases and operation processes of the oxygen sensor, where bold arrows correspond to  $\beta^-$  emission, solid arrows correspond to 450 nm em radiation, broken arrows correspond to ruthenium luminescence, squares represent the ZnS:Ag phosphor, and ellipses represent membrane-bound Ru(dpp)<sub>3</sub>.

**Ru(dpp)<sub>3</sub> fluorophore.** Ru(dpp)<sub>3</sub> luminescence is dynamically quenched in the presence of oxygen. The intensity of the Ru(dpp)<sub>3</sub> luminescence is measured and related to the level of oxygen in the sample by a standard Stern–Volmer-type calibration curve.<sup>10–17</sup>

The analytical performance of our proposed RL oxygen sensor is reported for measurements in both gaseous streams and aqueous solutions. In addition, the potential merits of using RL devices as sources for optical chemical sensors are discussed.

## EXPERIMENTAL SECTION

**Reagents and Chemicals.** *N,N*-Dimethylformamide (DMF, reagent grade), tetrahydrofuran (THF, 99.5+% purity), and hypophosphorous acid (50%) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Toluene (HPLC grade) and hydrochloric acid (PLUS grade) were obtained from Fisher Scientific (Pittsburgh, PA). Methanol (GR grade) and silica gel (No. 7747-3) were products from EM Science (Gibbstown, NJ). Ethanol (dehydrated, 200 proof) was obtained from Pharmco (Brookfield, CT). Poly(vinyl chloride) (PVC, high molecular weight, purum grade) and 2-nitrophenyl octyl ether (NPOE, puriss grade) were purchased from Fluka (Ronkonkoma, NY). 4,7-Diphenyl-1,10-phenanthroline (dpp, 98+%) was used as received from Lancaster (Windham, NH). Acetic acid-releasing, one-component silicone prepolymer was a product from Dow Corning, sold as a common household clear silicone sealant. Potassium pentachlororuthenate monohydrate (K<sub>2</sub>(RuCl<sub>5</sub>·H<sub>2</sub>O)) was purchased from Alfa (Ward Hill, MA).

<sup>147</sup>Pm was purchased from ICN (Costa Mesa, CA) as a chloride salt dissolved in 1.17 M HCl. In this form, the radionuclide is nonvolatile and can be manipulated by standard handling techniques for  $\beta^-$  emitters. *Exposure and contamination were minimized by performing all operations with the <sup>147</sup>Pm solution inside a fume hood. Appropriate safety equipment, including lab coat, eye goggles, shield plate, and double gloves, was used at all time. Outer gloves were changed frequently and disposed in an appropriate manner. Dry wipes followed by liquid scintillation counting were used periodically to confirm the absence of radioactive contamination. A Beckman LS 5801 liquid scintillation counter was used for all*

radioactivity measurements, with a 1  $\mu$ Ci sample of carbon-14 as a reference standard.

All commercially obtained chemicals and reagents were used as received without further purification. Distilled, deionized water was obtained by passing house-distilled water through a Milli-Q three-house purification unit. Oxygen and nitrogen gases were obtained 99.8% and 99.99% pure, respectively, from Air Products and Chemicals (Allentown, PA).

Ru(dpp)<sub>3</sub> was synthesized according to the procedures reported by Lin et al.<sup>18</sup> The crude product was recrystallized from 30 mL of 50% (v/v) ethanol–water.

**Construction of the RL Source.** The RL source was constructed at the bottom of a common glass vial (3.4 cm  $\times$  0.7 cm o.d.). Initially, 15.2 mg of the ZnS:Ag phosphor, 110.3  $\mu$ L of 1 M sodium hydroxide, and 0.5 mCi of <sup>147</sup>PmCl<sub>3</sub> were mixed and placed in the vial. The solvent was allowed to evaporate at room temperature in a fume hood for 4 days. The dried residue was covered with  $\sim$ 0.8 mL of epoxy (Epotek 301, Epoxy Technology, Inc., Billerica, MA), and the epoxy was oven-cured for 1 h at 65  $^{\circ}$ C. Once constructed, the vial was capped with a screw lid. Light from the radioactive ZnS:Ag layer is visible when viewed in darkness.  $\beta^-$  particles are blocked within the 1 mm thick glass vial because the maximum penetrating depth of 225 keV  $\beta^-$  particles in glass is 0.25 mm.<sup>19</sup>

**Preparation of Oxygen-Sensitive Membranes.** The Ru(dpp)<sub>3</sub> indicator was immobilized in two different membranes. For measurements in gaseous streams, the indicator was placed in a layer of plasticized PVC. Aqueous solution measurements were made with a silicone membrane. Details are provided below for each.

PVC membranes were prepared by first dissolving 1 g of PVC powder in 10 mL of tetrahydrofuran. Ru(dpp)<sub>3</sub> (0.012 g), 0.36 mL of methanol, and 1 mL of NPOE were mixed with 3 mL of this PVC solution, and this viscous mixture was vortexed until all components were dissolved. Membranes were formed by dip-coating clean microscope glass slides and allowing the solvent to evaporate slowly. The resulting membranes were transparent, with an estimated density of 1.09 g/cm<sup>3</sup> and a calculated Ru(dpp)<sub>3</sub> concentration of 4.7 mM. The membrane thickness was estimated to be 110  $\mu$ m.

Silicone membranes were prepared according to the method described by Lippitsch and co-workers, except that the initial Ru(dpp)<sub>3</sub> solution was prepared in ethanol instead of water.<sup>13</sup> Approximately 200  $\mu$ m thick membranes were coated on clean microscope glass slides.

**Construction and Characterization of Oxygen Sensors.** Sensors designed for both gaseous and aqueous samples were characterized by monitoring the luminescence intensity from immobilized Ru(dpp)<sub>3</sub> while flowing samples past the sensing unit. The measurement configuration is shown schematically in Figure 2. The sensing unit was constructed within a common disposable polystyrene fluorescence cell. The RL source and ruthenium-containing sensing membrane were mounted on opposite sides of the cell. Sample entered the bottom of the cell through a thin stainless steel tube and exited through an opening at the top. In this configuration, excitation light from the RL source passes through the sample before striking the sensing membrane.

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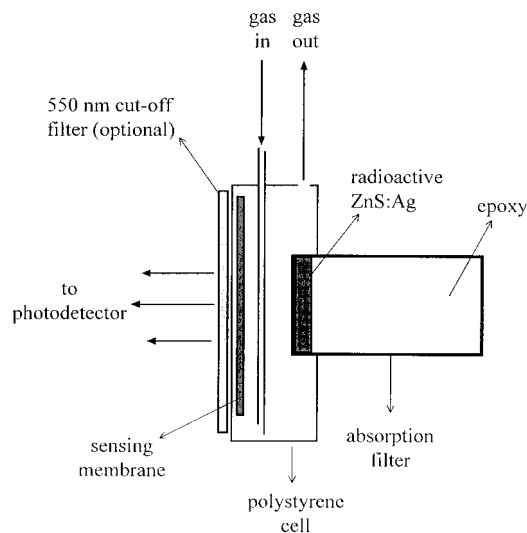


Figure 2. Flow-through cell for the optical oxygen sensor with a self-powered RL light source.

Ruthenium luminescence was measured with a detector located outside the cell. Two detector configurations were used. Initially, the flow cell was mounted at the entrance slit of the emission monochromator of an SLM Aminco SPF-500C spectrofluorometer. The monochromator was set to transmit  $610 \pm 20$  nm light, and the corresponding ruthenium luminescence was measured with a standard photomultiplier tube (PMT) detector. Intensity was monitored and recorded as a function of time with the software resident on the spectrofluorometer (version 2.4). Subsequently, the monochromator/PMT detection optics were replaced with a simple silicon photodiode detector (Hamamatsu HC 210-3314, Bridgewater, NJ) coupled with a 550 nm cut-off long-pass absorbance filter. Power for the diode detector electronics was supplied by a Heathkit Model IP-28 power supply. The resulting signal was measured with a common digital multimeter and recorded on a strip chart recorder.

Sensor response characteristics were established by exposing the sensing unit to samples with different levels of oxygen. Oxygen standards were prepared by mixing appropriate levels of nitrogen and oxygen gases. For gaseous samples, Gilmont GF-5521-1606 flowmeters (Barrington, IL) were used to generate the required nitrogen/oxygen mixtures. Manostat 36-541-055 flowmeters (New York, NY) were used to prepare aqueous solutions with known oxygen levels. Calibration functions supplied by the flowmeter manufacturers were used to calculate standard oxygen concentrations in both cases.

Limits of detection were computed by using 3 times the standard deviation of 20 blank measurements taken from either pure nitrogen gas or nitrogen-saturated water. Sensor sensitivities, and their corresponding uncertainties, were taken as slopes of the first three points in Stern–Volmer plots. For measurements in aqueous solutions, Henry's law was used to correlate oxygen solubility in water to the partial pressure of gaseous oxygen. A value of  $3.3 \times 10^7$  Torr/mole fraction of oxygen was used as the Henry's law constant at 25 °C.<sup>20</sup>

## RESULTS AND DISCUSSION

The bare promethium-147-powered RL light source based on the ZnS:Ag phosphor generates a broad band of em radiation with

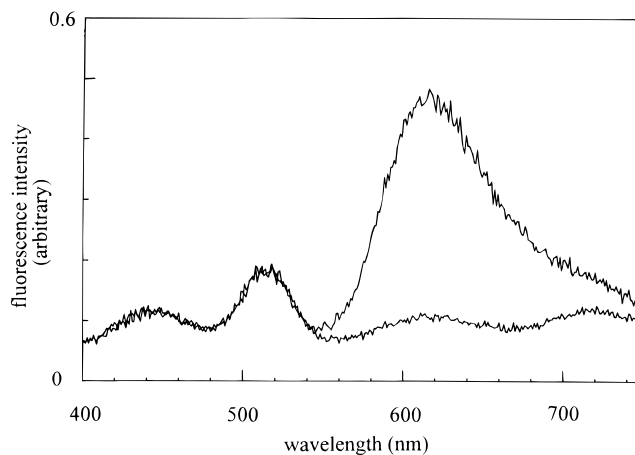


Figure 3. Emission spectra of the proposed RL source in combination with Ru(dpp)<sub>3</sub> immobilized in a plasticized PVC membrane when exposed to pure nitrogen (upper trace) and pure oxygen (lower trace).

a peak emission at 443 nm and a fwhm of 60 nm. This emission maximum corresponds to a 7 nm blue shift relative to that observed when the ZnS:Ag phosphor is excited by  $450 \pm 1$  nm radiation from a 250 W xenon arc lamp. This slight blue shift is related to the specific activity of the radioactive source. The 7 nm blue shift observed with RL sources prepared with 0.5 mCi drops to 5 nm when 0.1 mCi is used. These observations are consistent with the well-characterized relationship between electron excitation density and emission wavelength of inorganic phosphors.<sup>8,9</sup> From a practical standpoint, magnitude of the blue shift is relatively small and has a negligible impact on performance as an excitation source for the ruthenium fluorophore.

Emission spectra in the presence and absence of oxygen are presented in Figure 3 for plasticized PVC membranes with Ru(dpp)<sub>3</sub>. In these spectra, the excitation radiation is provided by the proposed RL light source. The drastic change in emission intensity at 610 nm corresponds to oxygen quenching of Ru(dpp)<sub>3</sub> luminescence. The emission bands centered at 443 and 518 nm correspond to em radiation generated by the RL source and not completely absorbed by the ruthenium complex. This undesirable radiation is eliminated by either a monochromator or an optical filter before detection. A third emission band from the RL source is evident at 720 nm in the spectrum with oxygen. This light is removed in the monochromator/PMT configuration but not in the filter/photodiode configuration.

Feasibility of the proposed RL source must be judged on the basis of sensor performance. In this regard, limit of detection is critical, given the fact that such devices are based on fluorescence measurements with a dim excitation source. In our first sensor configuration, the monochromator/PMT detection optics were used. Excellent reversibility and a 95% response time of  $12.5 \pm 0.6$  s are observed when the sensor is exposed to alternating gaseous streams of pure oxygen and nitrogen. Limit of detection was estimated by extrapolating from a Stern–Volmer calibration line produced for oxygen levels from 0 to 760 Torr. The resulting Stern–Volmer plot was nearly linear with a slope of  $0.011 \pm 0.004$ . The computed limit of detection ( $S/N = 3$ ) is  $5.0 \pm 1.9$  Torr, or  $0.66 \pm 0.25\%$  oxygen.

This first sensor configuration demonstrates the feasibility of using a self-powered RL source for chemical sensing technology. Sufficient SNR is possible for detection limits in the low Torr range. A second prototype RL oxygen sensor was design to

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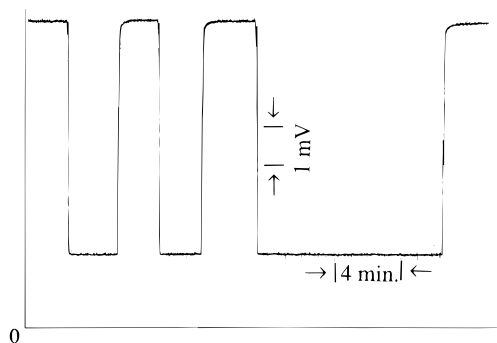


Figure 4. Voltage (mV)–time profile of the RL oxygen sensor when alternatively exposed to pure nitrogen and oxygen. A silicon photodiode is used as the photodetector.

improve SNR by enhancing optical throughput. The second prototype was constructed by replacing the monochromator/PMT detection optics with a simpler detection scheme composed of a single long-pass filter and a photodiode detector. Optical throughput is enhanced by mounting the detector in close proximity to the sensing membrane and widening the detection band-pass.

In addition, this second prototype sensor was designed to permit measurements in aqueous solutions. Although ruthenium-containing plasticized PVC membranes function well for gaseous samples, these membranes are not well suited for aqueous samples. The ruthenium complex rapidly leaches from such membranes when exposed to aqueous solutions. Although the rate of leaching can be reduced, but not eliminated, by lowering the amount of plasticizer, sensitivity to oxygen is reduced dramatically in the absence of plasticizer. This reduction in sensitivity is consistent with reports of enhanced oxygen permeability in plasticized polymeric membranes.<sup>21</sup> Incorporation of the ruthenium complex in a silicon membrane eliminates leaching into aqueous solutions.

Response characteristics for the RL oxygen sensor are improved by enhancing optical throughput and by using a silicon membrane. Figure 4 shows a typical intensity–time trace for altering nitrogen and oxygen gaseous streams across a silicon-based sensing membrane. SNR values for responses to 100% oxygen and 100% nitrogen are 101 and 415, respectively. SNR values were only 36.0 and 42.4, respectively, from an analogous intensity–time trace for the initial sensor design. Under these conditions, SNRs are improved by 181% and 879%, respectively, for the second sensor configuration. The resulting limit of detection in gaseous samples is  $0.25 \pm 0.03$  Torr ( $0.033 \pm 0.004\%$ ), which corresponds to a 20-fold improvement. This detection limit is superior to those reported by others where a halogen–tungsten lamp,<sup>22</sup> a xenon lamp,<sup>10</sup> or a frequency-modulated LED<sup>13</sup> is used as the excitation source. These reported detection limits are 0.5, 0.7, and 2 Torr, respectively. The proposed RL sources provide lower detection limits with a simpler design.

The magnitude of fluorescence quenching is related to oxygen levels in a nonlinear manner. Figure 5 shows a typical Stern–Volmer plot for gaseous samples. Such nonlinearity is generally reported for optical oxygen sensors based on ruthenium complexes incorporated within silicon membranes.<sup>10–17</sup> Presumably,

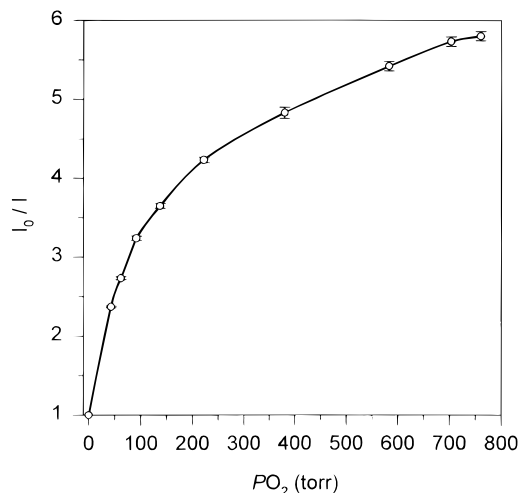


Figure 5. Stern–Volmer plot of the RL oxygen sensor with aqueous samples. Error bars correspond to the standard deviation from at least 10 measurements.

heterogeneity in the microenvironment around the ruthenium fluorophore is responsible for this effect. In our case, however, stray light also contributes because the RL source also emits em radiation between 550 and 750 nm (see Figure 3). To minimize this stray radiation effect, a blue absorption filter (see Figure 2) was coated on the outer surface of the RL source housing. This filter absorbs 99.8% of the em radiation between 560 and 660 nm but transmits at least 50% of the em radiation with wavelengths longer than 720 nm. Hence, 720 nm light generated from the RL source is not completely eliminated and, therefore, serves as a source of stray radiation. In addition, responsivity of the photodiode detector is large at 720 nm. These factors combine to diminish sensor response at elevated oxygen concentrations when quenching is high and luminescence intensities are low. More effective optical filtering should eliminate this stray light effect in future sensor designs.

The detection limit for oxygen in aqueous solution is  $0.028 \pm 0.003$  ppm, as estimated from response curves generated for oxygen levels from 0 to 16.5 ppm. Radiant power can be estimated given the output voltage, area, and responsivity of the specific detector. Such an analysis indicates a radiant power of only 0.5 pW for the ruthenium luminescence in the presence of 8 ppm oxygen. Only the low noise level of the RL source permits low detection limits, given such extremely low radiant power levels.

Stability of the sensor response will be strongly affected by stability of the excitation source and photostability of the ruthenium complex. Although photodecomposition (darkening) of ZnS:Ag is observed when exposed for 1 h to  $450 \pm 5$  nm radiation supplied from a 250 W xenon lamp, no  $\beta$ -induced decomposition of the phosphor was observed after 30 days of operating the RL light source. Changes in the RL source excitation intensity due to the natural decay of the radionuclide can be easily computed on the basis of a 2.5 year half-life for promethium-147. Assuming source stability is dictated by this single-exponential radioactive decay, only a 6% change in signal is expected over a 3 month operating period.

Photostability of the ruthenium complex is also a significant issue for optical oxygen sensors when the ruthenium complex is exposed to strong light sources.<sup>11,17</sup> Photodecomposition rates are typically too high for the development of practical, long-term sensors. For this reason, fluorescence lifetime measurements,

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which are insensitive to the absolute amount of fluorophore present, are generally preferred for optical oxygen measurements.<sup>13</sup> Although not completely characterized yet, negligible photodecomposition is expected for the RL source-based oxygen sensors because of the low excitation intensities involved. In our work to date, photodecomposition of Ru(dpp)<sub>3</sub> has not been observed for oxygen-sensing membranes exposed for as long as 42 days to ambient room light, which is several orders of magnitude brighter than that for our RL source.

#### CONCLUSIONS

The proposed RL source offers an attractive alternative to conventional light sources for the design of optical sensors. Such sources provide stable incident intensities with minimal noise.<sup>6</sup> The zero power requirement for RL sources significantly reduces the overall power requirements and simplifies sensor configuration, which makes them attractive for remote sensor applications, such as aboard spacecraft missions and extended environmental field experiments. Furthermore, the total solid-state design is attractive from the standpoint of manufacturing and operation reliability and flexibility. Finally, the concept of using RL sources for optical sensing technology is general. Different phosphors

are available to provide em radiation spanning the ultraviolet and near-infrared spectral regions.<sup>1-3</sup> Different radionuclides are available to provide stronger and longer lasting signals.<sup>4</sup> Operating in the ultraviolet region is especially important, given the fact that no inexpensive electrical light source will serve this purpose, and LEDs are not available for this spectral region. Hence, RL sources can be designed for a variety of optical chemical sensing strategies based on fluorescence quenching, direct luminescence, absorption spectroscopy, and Kromoscopy.<sup>23</sup>

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