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Measuring Atomic Emission from Beacons for Long-Distance Chemical Signaling

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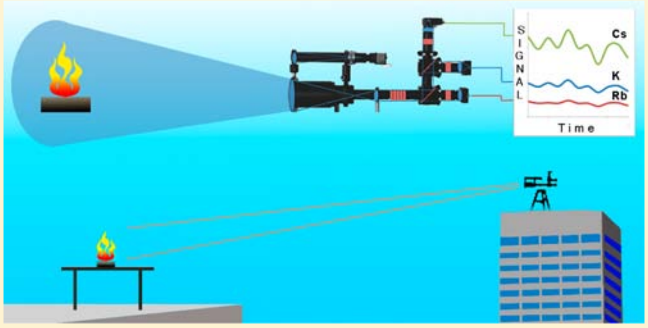
Ⓢ *Supporting Information*

ABSTRACT: In an effort to exploit chemistry for information science, we have constructed a system to send a message powered by a combustion reaction. Our system uses the thermal excitation of alkali metals to transmit an encoded signal over long distances. A message is transmitted by burning a methanol-soaked cotton string embedded with combinations of high, low, or zero levels of potassium, rubidium, and/or cesium ions. By measuring the intensities at the characteristic emission wavelengths of each metal in the near-infrared, 19 unique signals can be distinguished. We have built a custom telescope to detect these signals from 1 km away for nearly 10 min. The signal is isotropic, is self-powered, and has a low background. A potential application of this platform is for search and rescue signaling where another layer of information can be transmitted, in addition to the location of the beacon. This work, which seeks to encode and transmit information using chemistry instead of electronics, is part of the new field of "infochemistry".



In this paper, we describe a chemically powered light source that acts as a simple signaling beacon over long distances. The beacon is fueled by the combustion of methanol. Our atomic emission beacon is prepared by doping a cotton wick with metal salts; these salts are atomized during combustion and release thermally excited atomic emission. We detect the emission from metal atoms using a custom telescope equipped with bandpass filters and photodiodes (Figure 1). This work builds on our previous work using an "infofuse" to transmit messages encoded in flashes of atomic emission.[1−3] These efforts, along with previous work done using microfluidics[4] and bacteria-based encoded messages[5] aim to explore the nascent field of infochemistry.

Figure 1. Atomic emission beacon composed of a cotton wick doped with one or more metal salts. Upon combustion of methanol, the metal ions become atomized and release characteristic emission that can be detected 1 km away using collection optics, bandpass filters, and photodiodes.

Infochemistry seeks to use chemical reactions to encode bits of information that can be used for communication or computation. This approach is a different way of thinking about information technology, which is now dominated by binary signals. By removing the assumption that communication must be electronic, one is free to imagine new chemical-based platforms for information transmission.[6] These new systems can draw from all chemical and physical phenomena and need not rely solely on solid-state physics. We envision that these new platforms, such as the atomic emission beacon, will provide simple solutions for transmitting information in resource-limited environments, such as the scene of a disaster.

The previously developed infofuse is capable of sending data at rates of several bits per second but suffers from one major drawback, the message is short-lived, usually only lasting a few seconds.[1,3] This brevity could make detection difficult if the detector is not aimed at the right place at exactly the right time. The atomic emission beacon seeks to remedy this issue and can transmit its message steadily for several minutes at the expense of lower information density. The atomic emission beacon

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should serve a role akin to a lighthouse, isotropically signaling a piece of critical information to all those within sight.

Our system takes advantage of several unique characteristics of atomic emission: (1) it is simple to create and transmit the thermally excited signal using a combustion reaction, (2) the emission is isotropic, which means the receiver(s) can scan a region and find the sender without knowing the precise location in advance, (3) the line width is very narrow (typically <100 pm), which eases the separation of the signal from the background, and (4) the signal ratios are stable for several minutes.

We use different amounts of K, Rb, and Cs ions to encode a signal. These metal ions were chosen because they emit strongly between 700 and 900 nm. Using these three metal ions in a ternary encoding scheme, 19 different combinations are distinguishable. If each metal ion is present at high, low, or zero concentration, then there are 26 ($3^3 - 1$) different concentrations not counting (0, 0, 0), 19 of which are distinguishable over a wide distance range. The seven combinations that do not contain any "highs" were eliminated because they could be confused if measured at different distances. For example, K_{high}, Rb_{high}, and Cs_{high} at a long distance could be mistaken for K_{low}, Rb_{low}, and Cs_{low} at a short distance. The composition for the 19 remaining combinations is shown in Table S1 of the Supporting Information. We have detected atomic emission from these beacons from a distance of 1 km and can reliably identify each signal as one of the 19 combinations.

The detection telescope was custom built to simultaneously detect the emission of the beacon at three wavelengths (Figure 2). When light enters the telescope, it is first filtered with both long and short pass filters to isolate wavelengths between 700 and 900 nm. A long pass dichroic mirror then transmits the Cs emission at 852 nm and reflects the K and Rb emission at 766 and 780 nm, respectively. These two signals are then separated by another long pass dichroic mirror before being detected by highly amplified Si photodiodes. A CCD camera coupled to a scope is used to align the system.

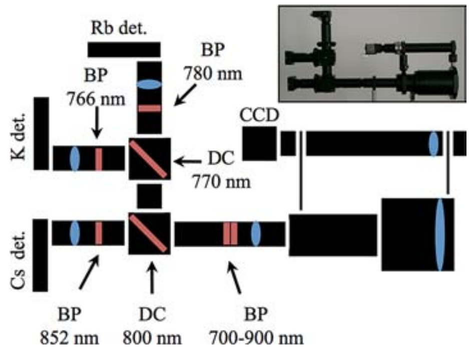

Figure 2. Telescope schematic showing lenses in blue; bandpass filters (BP) and long-pass dichroic mirrors (DC) in red. The inset shows a photograph of the telescope.

A beacon composed of K_{high}, Rb_{high}, and Cs_{high} was burned indoors for 10 min to monitor how the signal of each metal decreases with time. Burning at a rate of 1.5 mL/min, only 15 mL of methanol is required to transmit a message for 10 min. Figure 3 shows that the signal increases as the wick thermally equilibrates in the first 2 min and then is stable for nearly 10 min. The signal is still detectable beyond the 10 min shown in Figure 3, but the Cs signal decreases more rapidly than K and Rb over longer times. This difference with Cs changes the ratios of the three signals over time and can lead to misidentification. Therefore, it is important to terminate the burning when the signal changes or else it may be misinterpreted.

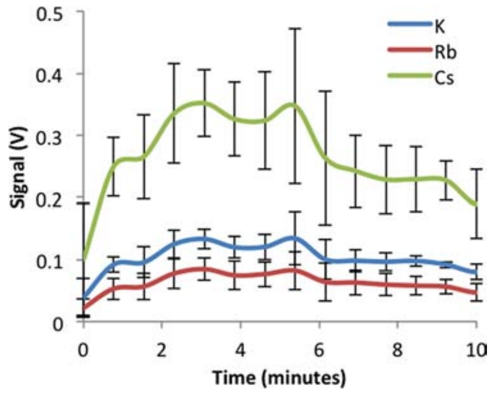

Figure 3. Long duration burn of a beacon composed of K_{high}, Rb_{high}, and Cs_{high}. Data were collected at 1 point/s and then 60-point boxcar averaged to smooth the data. The error bars indicate the standard deviation from three different beacons.

Outdoor measurements were made at night to determine over what distances the beacon would remain detectable. The K and Rb signals are generally similar in magnitude and both are lower than Cs due to the filters used within the telescope. The limit of detection is therefore dictated by the K and Rb signals. Figure 4 shows data from a beacon composed of K_{low}, Rb_{low}, and Cs_{high} as a function of distance. Several beacons were burned at different distances for between 3 and 10 min. The time varied because data collection was sometimes interrupted due to automobile traffic in the line of sight between the detector and the beacon. The signal was averaged over 1 min, and then three such data sets were averaged to give each point in the figure. The best-fit curve for the K signal shows the expected inverse-square dependence of the signal with distance. The standard deviation of the background with no flame present was 9 mV (not shown). While the farthest distance tested was 1 km, using the best-fit equation for the K signal and a detectable signal definition of three times the background standard deviation, the distance limit of detection for our system was calculated to be 1.7 km.

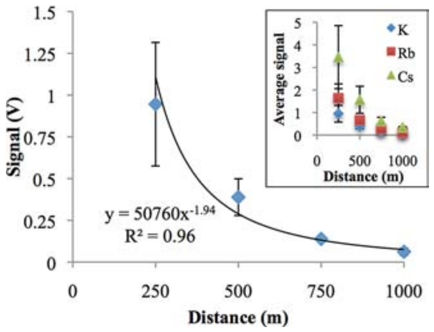

Figure 4. Average signals for three trials of a beacon composed of K_{low}, Rb_{low}, and Cs_{high} are shown as a function of distance. The best-fit line for the K signal was used to estimate a theoretical distance limit for a signal that is three times the background standard deviation. This calculated distance limit is 1.7 km. The inset shows the average signals of all three metals.

To decode a signal and identify it as 1 of the 19 combinations, the raw signals for K, Rb, and Cs are averaged over a short time (e.g., 20 s), then put through a three step algorithm: (i) the three values, which we call a signal vector, *s*, are multiplied by an experimentally determined instrument response matrix, **R**, (ii) the corrected vector, *c*, is scaled so the highest value equals 2, and then (iii) these three values are compared to threshold values to determine if the concentrations are zero (~0), low (~1), or high (~2). Figure 5 shows an example of the decoding algorithm.

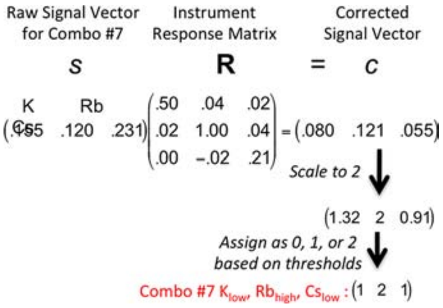

Figure 5. Data processing algorithm to identify the raw signal vector as originating from zero, low, or high concentrations of metal ions. The raw signal vector is multiplied by the instrument response matrix, which is experimentally determined, the result is scaled, and the values 0, 1, or 2 are assigned based on threshold values. In this example, combination no. 7 is correctly identified.

The 3 × 3 instrument response matrix, **R**, corrects for differences between the three channels of the detector and any crosstalk. To determine **R**, we used experimental data for *s* and knowing *c*, we solved for **R** using a linear least-squares regression analysis. Multicomponent spectroscopic analysis of this sort has been used to analyze UV−vis absorbance data to quantify components of a mixture.[7,8] We recorded data for the overdetermined system having 76 signal vectors from measurements taken at 1 km and 500 m, and we knew the corresponding combinations for each. These data and combinations formed 3 × 76 matrices for the signal, **S**, and for the combinations, **C**. The matrix representation of the least-squares analysis is as follows:

$$\begin{pmatrix} \mathrm{K}_1 & \mathrm{Rb}_1 & \mathrm{Cs}_1 \\ \mathrm{K}_2 & \mathrm{Rb}_2 & \mathrm{Cs}_2 \\ \mathrm{K}_3 & \mathrm{Rb}_3 & \mathrm{Cs}_3 \\ \vdots & \vdots & \vdots \\ \mathrm{K}_{76} & \mathrm{Rb}_{76} & \mathrm{Cs}_{76} \end{pmatrix} \begin{pmatrix} \mathrm{K}_{\mathrm{K}} & \mathrm{Rb}_{\mathrm{K}} & \mathrm{Cs}_{\mathrm{K}} \\ \mathrm{K}_{\mathrm{Rb}} & \mathrm{Rb}_{\mathrm{Rb}} & \mathrm{Cs}_{\mathrm{Rb}} \\ \mathrm{K}_{\mathrm{Cs}} & \mathrm{Rb}_{\mathrm{Cs}} & \mathrm{Cs}_{\mathrm{Cs}} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 2 \\ 0 & 2 & 2 \\ 0 & 2 & 1 \\ \vdots & \vdots & \vdots \\ 2 & 0 & 0 \end{pmatrix} \tag{1}$$

or

$$\mathbf{SR} = \mathbf{C} \tag{2}$$

Multiplying both sides of eq 2 by the transpose of the signal matrix gives eq 3.

$$\mathbf{S}^{t}\mathbf{SR} = \mathbf{S}^{t}\mathbf{C} \tag{3}$$

Equation 3 can be solved for **R** by multiplying by the inverse of $\mathrm{S^tS}$, as shown in eq 4.

$$\mathbf{R} = (\mathbf{S}^{t}\mathbf{S})^{-1}\mathbf{S}^{t}\mathbf{C} \tag{4}$$

This equation represents the least-squares fit of **R** and minimizes the sum of the squares of the differences between the observed signal and the expected combinations. From our data **R** was determined to be

$$\mathbf{R} = \begin{pmatrix} 4.50 & 0.35 & 0.14 \\ 0.21 & 8.98 & 0.40 \\ -0.04 & -0.19 & 1.86 \end{pmatrix} \tag{5}$$

which was scaled to

$$\mathbf{R} = \begin{pmatrix} 0.50 & 0.04 & 0.02 \\ 0.02 & 1.00 & 0.04 \\ 0.00 & -0.02 & 0.21 \end{pmatrix} \tag{6}$$

After multiplying the signal vector from one sample by the instrument response matrix, the resulting corrected-signal vector is then scaled so that the highest of the three values becomes 2. This scaling corrects for variations in the signal due to distance and is analogous to the use of an internal standard, which is commonly used in atomic emission spectroscopy. Figure 6 shows raw data and data that have been processed using the algorithm for three different beacons measured at a distance of 1 km. The thresholds, >1.6 for high and <0.7 for zero, are shown as dashed lines and indicate the ranges for zero, low, and high. These thresholds were determined by systematically varying both threshold values until the number of incorrect combinations from the known data set was minimized.

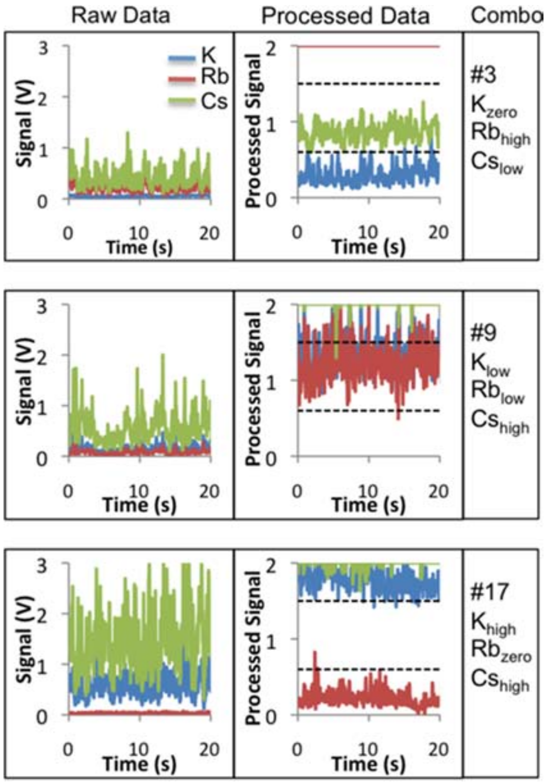

Figure 6. Examples of decoded beacons. The left column shows raw data of a single beacon recorded from a distance of 1 km. These data are then processed and shown in the central column. The dashed lines indicate the threshold values to distinguish between zero, low, and high levels of metal. The right column correctly identifies the concentration of metal ion based on the 20 s averages of each of the processed spectra.

Despite the significant noise in the signal due to flame flickering, the ratios of the three signals are fairly constant and allow the processed data to be readily identified as being zero, low, or high. All 19 possible combinations can be identified. In the trials where 76 different beacons were burned, we correctly identified 75 of them.

The atomic emission beacon has several characteristics that make it well suited for sending low-density information over long distances: (i) the combinations could be quickly prepared on site by dispensing drops from premade solutions, (ii) approximately 15 mL of methanol will transmit a signal for 10 min, (iii) isotropic emission means the receiver need not know exactly where to look for the beacon but should be able to find it within a scan window, (iv) currently 19 combinations have been demonstrated, but by including Na, Li, and Ca, 665 unique spectral fingerprints should be possible with ternary encoding, and (v) the optical efficiency of the system is quite high at 0.02%, which is about 5% as efficient as a laser diode.[9]

One major issue with the atomic emission beacon is its sensitivity to environmental factors such as wind, rain, and sunlight. The beacon will continue burning under windy conditions, but the flicker greatly reduces the signal. Rain will extinguish the flame. A simple housing could protect the flame from wind and rain. Also, despite the sharp bandpass filters used, direct sunlight near the beacon is too intense to completely remove and so the beacon is more easily detected at night or under low light conditions.

We have created a simple system to transmit a message through free space that is powered by a combustion reaction and generates light for several minutes by thermally excited atomic emission. This work combines chemical encoding with truly long distance communication. The atomic emission beacon adds to previous efforts in the field of infochemistry, such as the infofuse,[1] which can send short-lived messages over long distances, and fluorescently encoded bacteria,[5] which can encode long-lived messages that are read with the message in hand. The atomic emission beacon uniquely transmits a low information density signal over a long distance for a long duration. The simplicity of the signal generation and detection makes it potentially applicable to resource-poor environments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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