Document Title: Transition Metal Cluster Compounds for the Fluorescent Identification and Trace Detection of Substances of Abuse

Author(s): Richard G. Blair, Ph.D.

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2012-R2-CX-K005 Final Summary Overview

Purpose of the project

Sensitive, rapid, high-sensitivity and low cost methods for detecting substances of abuse were developed. This work focused on the investigation of fluorescent indicators for substances of abuse with enhanced specificities. These new fluorescent indicators are be based on d^{10} metal complexes and allow greater detection sensitivity and flexibility. These indicators are shelf stable and low cost. The complexes formed can be stored for long periods of time without loss of fluorescence. The fluorescence observed in these complexes is due to the nature of the metal and metal-analyte bonds present in the complex. This is a well understood phenomena and will stand up to Daubert challenges.

By coupling new sources, fluorescent indicators, and digitizing systems we will be produce a system capable of positively identifying compounds rapidly in the field and in the lab. Ultimately, this approach will be implemented in a small handheld system that will allow assessment of multiple indicators in the field.

Subject Protection

Not Applicable

Project Design

Task 0 - Initial Selections

Initial selections focused on three types of compounds. Cyclic amines such as PCP and cocaine have produced detectable fluorescence with a CuI indicator. Aromatic and aliphatic amines such as MDMA should form complexes with d^{10} metal cluster. An important aspect of this research was the selection of salts that have produce complexes with fluorescent emission in the visible region. For example, CuCN salts also exhibit fluorescence. These salts are relatively inexpensive and have a negligible water solubility. Since the ^{3}XLCT band is due to energy transfer from the metal cluster through the salt anion to the ligand, changing the anion will result in different accessible energies and produce different fluorescence colors.

At the University of Central Florida we utilized a Tecan Infinite® M200 PRO microplate reader to gather fluorescence data.

Task 1 - Indicator Assessment

We found that CuI can be very useful in the identification of many, but not all, amines of interest. No unique fluorescence was observed with aliphatic amines or non-amine compounds. In order to expand the utility of these compounds we screened an array of metal salts. Work focused on d^{10} metals. It has been found that a d^{10} electronic configuration is one common motif in fluorescent organometallic complexes. Cations with d^{10} configuration include Cu(I), Ag(I), Au(I), Zn(II) and Cd(II). Fluorescent molecules can be formed from ligand-metal clusters or as metal containing molecules. Exposing solid metal salts to the analyte can easily form fluorescent cluster complexes. By using a solvent with a high vapor pressure (such as ethanol) the solid complex was left behind and its fluorescence was

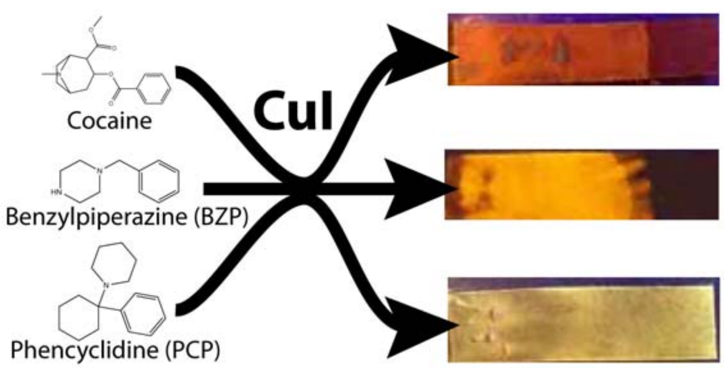


Figure 1. Copper iodide can be used to identify and differentiate scheduled substances.

observed and recorded. Halides of Cu and Ag both exhibit solubility in acetonitrile allowing the preparation of indicator strips. Other counter ions such as SCN^-, CN^-, and OH^- offer the potential for interaction with different molecular functionalities. These were investigated through combinatorial screening.

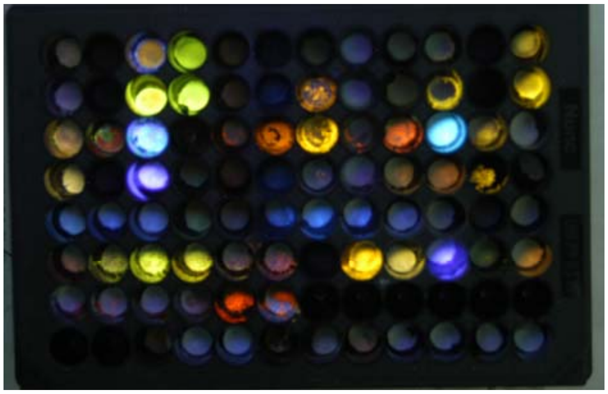


Figure 2. An example well plate under 254 nm illumination.

Task 2 - Spectroscopy

We utilized high throughput fluorescence measurements to rapidly screen new indicators. The chemistry department at the University of Central Florida houses a Tecan Infinite® M200 PRO microplate reader. This allowed us to examine up to 96 samples at a time. We also began development of a low-cost portable spectrometer. This spectrometer utilizes smart phone technology to gather the data.

Task 3 - Protocol Development and Library Management

Standard protocols have been developed for laboratory and field implementation of the instruments and tests developed. The focus was on reproducibility, accuracy, and safety. Reproducibility and accuracy were assessed through the testing of multiple samples. Libraries of the fluorescence spectra recorder will be stored on cloud-based servers. The raw data will be freely available to the community. Additionally, the data will be searchable through a combination of dedicated hardware (spectrometer) and a smart phone app.

Task 4 - Detection limits.

Maximum detection limits were assessed using the Tecan system. Detection limits were determined through multiple dilution experiments. Fluorescent intensity was recorded as a function of analyte concentration. We found that visible fluorescence can be detected from the Cu_4I_4-analyte complexes with as little as 5 ppt.

Task 5 - Protocol for Use in Gathering Trace Evidence

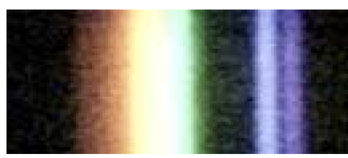
Standard protocols were developed for applying the tests developed to the gathering of trace evidence. This focused on simplicity, safety, specificity, and minimization of impact on the crime scene. Indicator solutions, ethanol swabbing techniques, and test strips were developed.

Task 6 - Calibration Standards

The fluorescence source chosen for the portable spectrometer was a cold cathode lamp. This lamp utilizes mercury to produce strong narrow emission at 253.6517, 398.3931, 435.8328 and 546.0735 nm. Two approaches to calibration have been taken. A cut-off filter filters the source itself so that it only produces 253 nm light. Removal of this filter by a technician allows calibration using the mercury lines. For field calibration, a standard emitter with P39 phosphor embedded in a UC transparent polymer was developed. The emission spectrum of the P39 phosphor is well characterized. It is readily available and stable (samples retain their fluorescence after decades). Calibration data will be stored in the app.

Methods

Fundamental studies of indicators and analyte indicator fluorescence were performed using 6 mm paper chads coated in indicator and a Tecan Infinite F500 plate reader. Paper chads (6 mm disks) and paper strips were produced by soaking filter paper in a saturated acetonitrile solution of the d10 metal halide. The solvent was allowed to evaporate to produce a shelf stable indicator. A series of chemical compounds was screened for fluorescence signal when in contact with the indicator (Figures 1 and 2). These compounds included common adulterants (such as caffeine), OTC agents (such as diphenhydramine HCl), model compounds with subtle functional group changes (such as the position of a substituent on a benzene ring), and substances of abuse (cocaine, PCP, etc.). The fluorescence spectra were obtained using 255 nm excitation. Sampling methodology was tested to develop the best procedure for getting reproducible results. Indicator strips were subjected to accelerated aging to simulate long term storage. Indicator strips that had been used were also subjected to accelerated aging to determine the proper protocol for storage of evidence once gathered.



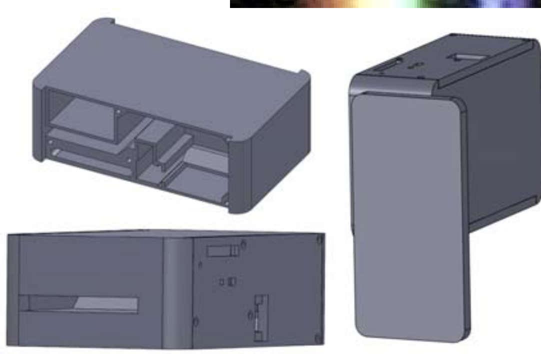


Figure 3. The final design of the spectrometer features a longer path length and improved orientation for easier sample testing.

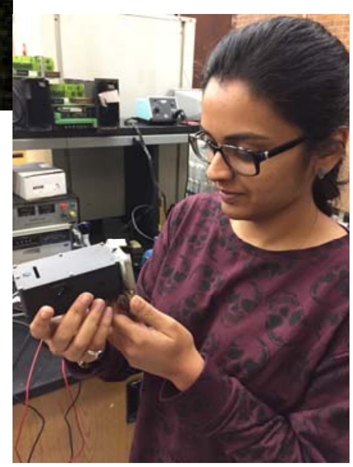


Figure 4. A low-cost spectrometer will be coupled with a smart phone for field use. A sample spectral image is shown in the upper right.

Analytes were also extracted from used indicator strips and analyzed by GCMS to allow a confirmatory test to be performed on the actual evidence gathered. In conjunction with the laboratory

validations fluorescence spectrometer utilizing the camera from a smart phone for its detector was developed. A low-cost cold cathode lamp supplies the excitation light and a prototype was produced via 3d printing. The entire spectrometer is powered by a rechargeable lithium ion battery and is compact. As part of this project components were selected with cost and supply in mind. The final design utilizes readily available parts that are expected to have long production runs.

Data Analysis

Data gathered from the plate reader was collected and analyzed for peak position and shape. These spectra are currently stored for implementation in a searchable database to be linked with the smart phone spectrometer.

Scholarly Products Produced

1. Nash, D.J., D.A. Siddhanti, R.A. Penabade, K. Bertrand, A. Andinoa, K. Smith, S. Hick, K. Kawamoto, W.K. Moorehead, and R.G. Blair, “Copper Cluster Compounds for the Identification of Substances of Abuse,” *in preparation*.
2. Nash, David; Blair, Richard, “Fluorescent d^{10} metal complexes for the presumptive identification of substances of abuse and the implementation of a cell phone fluorimeter for field identification,” *249th ACS National Meeting & Exposition*, Boulder, CO, United States, **March 25, 2015**, INOR-915
3. Nash, David; Blair, Richard, “Luminescent d^{10} Metal Cluster Compounds for the Trace Detection and Presumptive Identification of Substances of Abuse,”

American Academy of Forensic Science Live Seminar Series, Online, **May 14, 2014**

4. Nash, David; Blair, Richard, “Luminescent d^{10} Metal Cluster Compounds for the Trace Detection and Presumptive Identification of Substances of Abuse,” *American Academy of Forensic Science Live Seminar Series,* Online, **May 6, 2014**
5. Nash, David; Blair, Richard, “Luminescent d^{10} Metal Cluster Compounds for the Trace Detection and Presumptive Identification of Substances of Abuse,” *American Academy of Forensic Science Live Seminar Series,* Online, **May 14, 2014**
6. Nash, David; Blair, Richard, “Luminescent d^{10} Metal Cluster Compounds for the Trace Detection and Presumptive Identification of Substances of Abuse,” *2014 Forensic Science R&D Grantees Meeting at the 66th Annual AAFS Meeting,* Seattle, WA, United States, **February 18, 2014**
7. Siddhanti, D., “Transition Metal Cluster Compounds for the Luminescent Identification and Trace Detection of Substance of Abuse,” *Thesis for Master’s Degree in Forensic Science*. 2013, University of Amsterdam: Amsterdam, Netherlands. p. 28.
8. Siddhanti, Deepti; Nash, David; Bertrand, Kevin ; Penabade, Rachel; Blair, Richard; “A Smart Phone Spectrometer for the Analysis of Fluorescent d^{10} metal-ligand cluster compounds (ligand = alkaloid or opiate) for the presumptive identification of illicit drugs and other common substances of abuse,” *89th ACS Annual Florida Meeting and Exposition*, Tampa, FL, United States, **May 10, 2013**

9. Blair,R.G, "*A Portable Spectrometer for the Presumptive Identification of Illicit Drugs and Substances of Abuse,*" US Patent Appl. *Provisional Application* filed **05/09/2013**, US 61/821,472.

Implications to Criminal Justice Policy and Practice in the United States

This work identifies a relatively inexpensive and non-toxic indicator for detecting the presence and identity of substances of abuse. By utilizing smart phone hardware developed to implement spectroscopic techniques (fluorimetry) in conjunction with this indicator a chain of evidence can be established for just prosecution.

False positives have plagued law enforcement and led to detainment of innocent individuals. For example:

"Student mistakenly held on drug charge settles with Phila.," http://articles.philly.com/2007-01-04/news/25220490_1_opium-and-cocaine-drug-settlement

Where a student spent three weeks incarcerated before the error was admitted.

"Drug Suspects had Soap, not Cocaine Bricks," http://articles.mcall.com/2013-12-13/news/mc-state-police-arrest-cocaine-was-hand-soap-20131213_1_trooper-drug-suspects-soap

Where a pair spent a month incarcerated before the error was admitted. Soaps have been shown to give false positives as well.

"Germs Drummer's Soap Tests Positive For GHB," http://www.billboard.com/articles/news/1052909/germs-drummers-soap-tests-positive-for-ghb

Current field tests are destructive and transient. They depend upon proper implementation of the test and do not produce a sample that can be re-examined. This disrupts the chain of evidence and can be abused by the unscrupulous. Additionally, crime labs are often pressed for time. The temptation to partially screen samples is high and was responsible for a high profile case that caused over 1000 cases to be dismissed.

> "Massachusetts chemist who faked drug test results sentenced to 3 to 5 years," http://www.nydailynews.com/news/national/massachusetts-chemist-faked-drug-test-results-sentenced-5-years-behind-bars-article-1.1526005#ixzz2t8FJIDwu

This newly developed approach has several advantages:

1. The original sample is preserved. A breakable complex is formed, not reaction products.
2. Color interpretation is minimized though the use of spectroscopic techniques
3. Existing cell phone technology can be used to record and analyze tests.
4. The test is robust and low cost. Areas with limited financial resources can implement this test with little outlay. Copper iodide indicators have long shelf lives and represents less of a danger than the concentrated sulfuric acid used in many NarcoPouches. Many LE officers have cut themselves using NarcoPouches or similar technology.
5. The test is the only non-destructive presumptive test that can:
    a. Distinguish between PCP and cocaine using the naked eye
    b. Identify benzylpiperazine.
6. The observed fluorescence is based on well-understood phenomena. In fact, fluorescence spectra can be predicted using *ab initio* methods :

a. T.B. Rawal, V. Turkowski and T.S. Rahman, "Complementary roles of benzylpiperazine and iodine "vapor" in strong enhancement of orange photoluminescence from CuI(111) thin film", Journ. of Phys.: Cond. Mat. 26, 185005 (2014).

7. With a firm scientific basis to the observed phenomenon this test represents one of the few forensic tools that can stand up to scientific scrutiny. Such tests are much needed in the field of forensic science as it has come under fire for use of unscientific tests.

New specific presumptive tests for substances of abuse will provide an immediate benefit to forensic analysts, law enforcement officials, and the general public with fewer false positives as well as faster and more specific identifications.