I&EC research
Industrial & Engineering Chemistry Research

Research Note

pubs.acs.org/IECR

A High-Throughput Method To Detect Palladium in Ores

Jessica M. Williams and Kazunori Koide*

Department of Chemistry, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260, United States

Supporting Information

ABSTRACT: Platinum-group metals are in increasing demand for industrial use. Herein, we present a fluorometric method for palladium detection that can be used to prioritize ore samples on site. The analyses of solid ore samples were sufficiently correlated with that of aqua regia extracts of the same ore samples. Twenty samples could be analyzed in parallel and more samples can be if so desired due to the high throughput nature of the assay method. Although the correlational study was performed after 90 min incubation, 30 min incubation was sufficient to obtain strong fluorescence signals (i.e., 1.5 min per sample). Given the visible nature of the green fluorescence and the procedural simplicity, palladium and coexisting platinum ores are identifiable in the field with the naked eye.

Palladium and platinum are valued for their use in sustainable clean energy (e.g., fuel cells) and environmental protection (e.g., catalytic converters) among other applications. Although these precious metals are in great demand, deposits are scarce, and their supply is unstable.[1,2] Therefore, new sources need to be discovered and mined at low cost. In the current discovery process, precious metals in ore samples are extracted by aqua regia or heat and quantified in off-site analytical laboratories equipped with large instruments such as inductively coupled plasma mass spectrometers. This whole operation is expensive and time-consuming. A more economical method requiring only portable instruments would be preferred, particularly in the remote areas that are major sources of the platinum-group metals.[3] Furthermore, such efficiency is imperative when exploring space for these metals, a pursuit already being undertaken.[4]

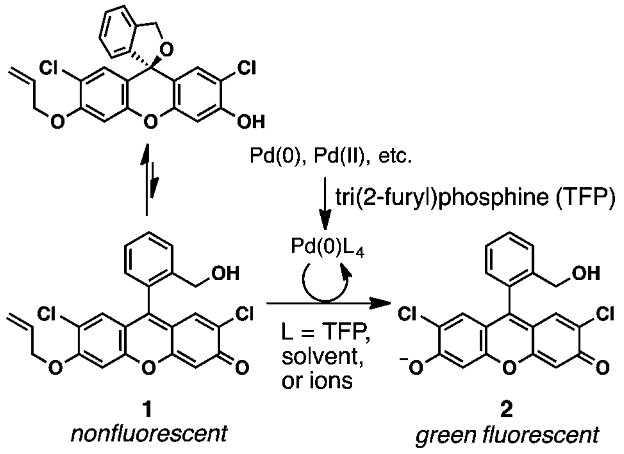

Figure 1. Chemical reaction for palladium detection.

Palladium in solution can be inexpensively detected by a high throughput method shown in Figure 1.[5] In this method, palladium catalytically converts the nearly nonfluorescent allyl ether **1** to the green fluorescent phenoxide **2** in the presence of tri(2-furyl)phosphine (TFP). The resulting green fluorescence can be readily visualized with a blue laser pen. Excess TFP unifies heterogeneous palladium(0/II) species to a TFP-bound palladium(0) species, thus total palladium can be quantified regardless of the structures of palladium species in complex samples.[6,7] Previously, we digested samples with strong acids as part of the quantification process.[8] The fluorescence signals are amplified by the analyte through catalysis, rendering the method highly sensitive.[5] This fluorometric method is selective for palladium and does not suffer from false positive signals with other metals even when $NaBH_4$, an additive we previously used, was omitted.[7] Trace palladium could be detected in synthetic compounds and commercial reagents and in the presence of other metals, indicating the robustness of our fluorometric method in complex solutions.[9,10]

In this study, our method was applied for the analysis of 20 ore samples A−T. The premise was that if an ore sample contains twice as much palladium as another, aqua regia treatment will provide palladium solutions of these two samples proportionally (Figure 2a, diagram). As such, the samples were treated with aqua regia, and the resulting metal extracts subjected to our fluorometric method (Figure 2a; for raw data, see Table S1 in the Supporting Information). These data showed that the palladium contents ranged from 0 to 68 ppm in the original solid samples based on the standard curve (Supporting Information).

Despite numerous other fluorometric methods to detect palladium, none have been applied to the detection of palladium in solid ore samples.[11−32] For the quantitative analysis of ores, an assay solution must dissolute a fraction of the palladium such that the resulting solutions reflect the relative concentrations of palladium in the original ore samples (Figure 2b, diagram). It was not obvious whether our method could meet this criterion because it has never been applied under such heterogeneous conditions. Nonetheless, using the data set described above as a reference, we asked whether our fluorometric

Received: April 1, 2013
Revised: May 25, 2013
Accepted: June 12, 2013
Published: June 18, 2013

dx.doi.org/10.1021/ie400959z | *Ind. Eng. Chem. Res.* 2013, 52, 8612−8615

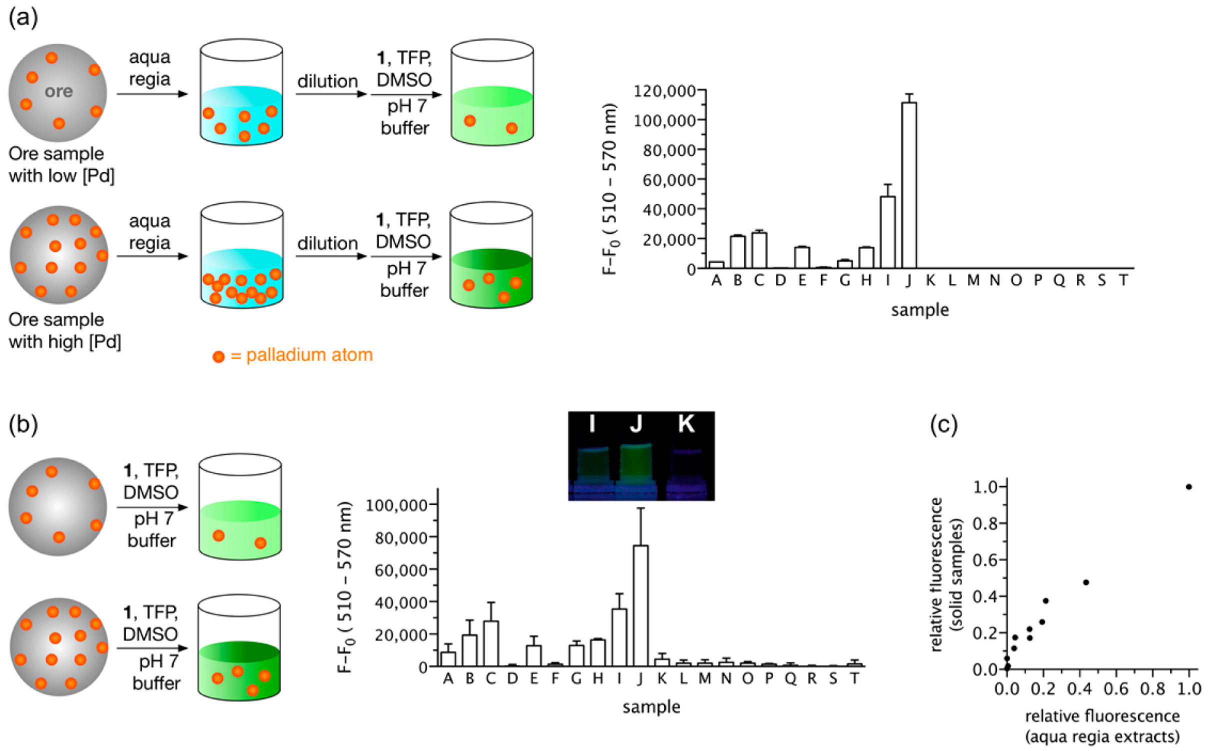

Figure 2. (a) Aqua regia extracts of ore samples were subjected to the method in Figure 1; $n = 3$. (b) Solid ore samples were subjected to the method in Figure 1; $n = 3$. The photo of the supernatants was taken by placing the centrifuged samples above a blue light source in a dark room. (c) Correlation between the analyses in parts a and b after normalization. Samples A−K are shown for clarity. For parts a and b, $F - F_0$ (510−570 nm) = fluorescence signal of sample − fluorescence signal of blank in the 510−570 nm range in arbitrary unit (average ± standard deviation).

method could visualize the presence of palladium in undigested solid ore samples. The solid samples were treated with the premixed solution of **1** and TFP in a pH 7 buffer. The presence of palladium in some samples could be visualized by green fluorescence as representative samples I−K are shown in the photograph of Figure 2b. For a quantitative assessment, the fluorescence signals of the 20 samples A−T are shown in the bar graph of Figure 2b (for raw data, see Table S2 in the Supporting Information). Figure 2c compares Figure 2a and Figure 2b; the results were highly correlated and supported the potential use of this method with a hand-held fluorometer to determine relative palladium concentration between solid ore samples on site.[33] For qualitative analyses, one only needs pipettes, vials, disposable filtering columns, a solution of **1** and TFP in DMSO/buffer, and a blue laser pen. Although the deallylation of **1** at ambient temperature requires a longer time,[7] all of these materials are portable, indicating the capability of on-site analysis of multiple samples in parallel.

To further expedite the analysis, the deallylation reaction with sample J was performed for 30 min at 45 °C using the same premixed solution in duplicate. The fluorescence intensities were 3.4×10^4, which was sufficiently high to visibly distinguish this sample from ore samples that lack palladium.

These somewhat surprisingly positive results prompted us to ask whether the method detected palladium species in solution or in solid, and if in solution, how rapidly palladium species in ore samples dissolved into the fluorogenic solution. Both questions could be answered in one experiment; sample J (250 mg) was incubated in a solution of TFP (120 μM) in 1:19 DMSO/1.23 M phosphate pH 7 buffer at 24 °C for either 15, 30, 45, or 60 min (Figure 3, diagram). Subsequently, these

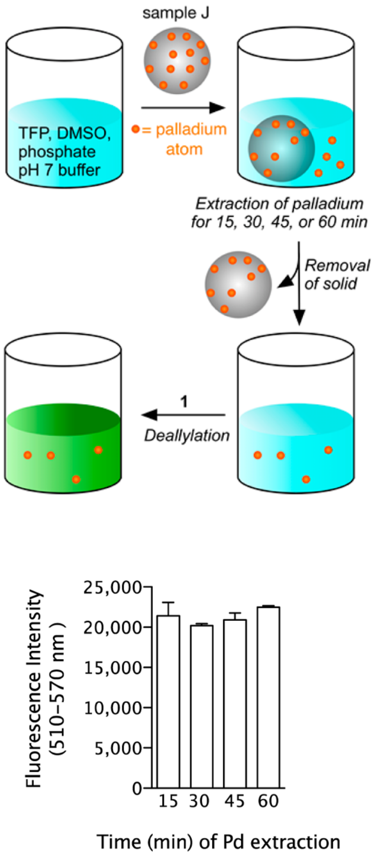

Figure 3. The concentrations of palladium in solution after ore sample J was treated with a solution of TFP in DMSO/pH 7 buffer for 15, 30, 45, and 60 min as determined by fluorescence. $n = 3$.

mixtures were centrifuged to remove the solid. The resulting supernatant was transferred to a solution of **1** and TFP in DMSO/pH 7 buffer, and the resulting solutions were incubated at 45 °C for 30 min before fluorescence measurement. The signals were 21 252 ± 1144 for these samples and independent of the time during which palladium was extracted (Figure 3, graph). This indicates that all soluble palladium species in the solid dissolved into the solution within the first 15 min.

In summary, with only portable equipment and without acid treatment of ore samples, we demonstrated that the presence of palladium in powdered ore samples could be visualized by means of fluorescence. Although we only used 20 samples, more ore samples can be analyzed in 30 min (i.e., <1.5 min per sample). The procedure was simple enough to be carried out by a first-year undergraduate student with minimal training (2−4 h) and no research experience prior to this study. Given the commercial availability of hand-held fluorometers, it is possible to quantify palladium in the field. Palladium and platinum coexist in nature; therefore, detection of palladium in ores is sufficient for discovering both metals.[34,35] This approach may change the way platinum-group metals are discovered from a multiple-day process to an in-the-field process employing a simple laser pen to narrow down multiple samples.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: koide@pitt.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was in part supported by the US National Science Foundation (CHE-0911092) and the Brackenridge Research Fellowship from the University of Pittsburgh (for J.M.W.). We thank Stanford Foy (Stillwater Mining Company, MT, USA) for the ore samples.

■ REFERENCES

(1) Tollerfson, J. Worth its weight in platinum. *Nature* **2007**, *450*, 334−335.

(2) Tollerfson, J. Energy crisis upsets platinum market. *Nature* **2008**, *451*, 877.

(3) Lindholt, L. Arctic natural resources in a global perspective. *Econ. North* **2006**, 27.

(4) Schrunk, D.; Sharpe, B.; Cooper, B. L.; Thangavelu, M. *The moon: Resources, future development and settlement*; Praxis: St. Paul, MN, 2007.

(5) Song, F.; Garner, A. L.; Koide, K. A highly sensitive fluorescent sensor for palladium based on the allylic oxidative insertion mechanism. *J. Am. Chem. Soc.* **2007**, *129*, 12354−12355.

(6) Garner, A. L.; Song, F. L.; Koide, K. Enhancement of a catalysis-based fluorometric detection method for palladium through rational fine-tuning of the palladium species. *J. Am. Chem. Soc.* **2009**, *131*, 5163−5171.

(7) Song, F. L.; Carder, E. J.; Kohler, C. C.; Koide, K. Studies toward an ideal fluorescence method to measure palladium in functionalized organic molecules: Effects of sodium borohydride, temperature, phosphine ligand, and phosphate ions on kinetics. *Chem.—Eur. J.* **2010**, *16*, 13500−13508.

(8) Bu, X.; Koide, K.; Carder, E. J.; Welch, C. J. Rapid analysis of residual palladium in pharmaceutical development using a catalysis-based fluorometric method. *Org. Process Res. Dev.* **2013**, *17*, 108−113.

(9) Li, D.; Campbell, L. D.; Austin, B. A.; Koide, K. Detection of trace palladium in flasks and metal reagents using a fluorogenic Tsuji−Trost reaction. *ChemPlusChem* **2012**, *77*, 281−283.

(10) Inamoto, K.; Campbell, L. D.; Doi, T.; Koide, K. A highly sensitive fluorescence method reveals the presence of palladium in a cross-coupling reaction mixture not treated with transition metals. *Tetrahedron Lett.* **2012**, *53*, 3147−3148.

(11) Tang, B.; Zhang, H.; Wang, Y. Determination of trace palladium with salicyladehyde furfuralhydrazone (SAFH) by catalytic kinetic spectrofluorimetry. *Anal. Lett.* **2004**, *37*, 1219−1231.

(12) Nielsen, K. T.; Bechgaard, K.; Krebs, F. C. Effective removal and quantitative analysis of Pd, Cu, Ni, and Pt catalysts from small-molecule products. *Synthesis* **2006**, 1639−1644.

(13) Duan, L. P.; Xu, Y. F.; Qian, X. H. Highly sensitive and selective Pd^{2+} sensor of naphthalimide derivative based on complexation with alkynes and thio-heterocycle. *Chem. Commun.* **2008**, 6339−6341.

(14) Houk, R. J. T.; Wallace, K. J.; Hewage, H. S.; Anslyn, E. V. A colorimetric chemodosimeter for Pd(II): a method for detecting residual palladium in cross-couping reactions. *Tetrahedron* **2008**, *64*, 8271−8278.

(15) Jun, M. E.; Ahn, K. H. Fluorogenic and chromogenic detection of palladium species through a catalytic conversion of a rhodamine B derivative. *Org. Lett.* **2010**, *12*, 2790−2793.

(16) Li, H. L.; Fan, J. L.; Du, J. J.; Guo, K. X.; Sun, S. G.; Liu, X. J.; Peng, X. J. A fluorescent and colorimetric probe specific for palladium detection. *Chem. Commun.* **2010**, *46*, 1079−1081.

(17) Li, H. L.; Fan, J. L.; Liu, X. J.; Sun, S. G.; Peng, X. J. Rhodamine-based fluorescence probe for Pd^{2+} detection. *Chem. J. Chin. Univ.-Chin.* **2010**, *31*, 1725−1728.

(18) Li, H. L.; Fan, J. L.; Song, F. L.; Zhu, H.; Du, J. J.; Sun, S. G.; Peng, X. J. Fluorescent probes for Pd^{2+} detection by allylidene-hydrazone ligands with excellent selectivity and large fluorescence enhancement. *Chem.—Eur. J.* **2010**, *16*, 12349−12356.

(19) Santra, M.; Ko, S. K.; Shin, I.; Ahn, K. H. Fluorescent detection of palladium species with an *O*-propargylated fluorescein. *Chem. Commun.* **2010**, *46*, 3964−3966.

(20) Baker, M. S.; Phillips, S. T. A two-component small molecule system for activity-based detection and signal amplification: Application to the visual detection of threshold levels of Pd(II). *J. Am. Chem. Soc.* **2011**, *133*, 5170−5173.

(21) Jiang, J.; Jiang, H. E.; Liu, W.; Tang, X. L.; Zhou, X.; Liu, R. T.; Liu, W. S. A colorimetric and ratiometric fluorescent probe for palladium. *Org. Lett.* **2011**, *13*, 4922−4925.

(22) Kim, H.; Moon, K. S.; Shim, S.; Tae, J. Cyclen-conjugated rhodamine hydroxamate as Pd^{2+}-specific fluorescent chemosensor. *Chem.-Asian J.* **2011**, *6*, 1987−1991.

(23) Liu, B.; Bao, Y.; Du, F.; Wang, H.; Tian, J.; Bai, R. Synthesis and characterization of a fluorescent polymer containing 2,6-bis(2-thienyl)pyridine moieties as a highly efficient sensor for Pd^{2+} detection. *Chem. Commun.* **2011**, *47*, 1731−1733.

(24) Liu, B.; Dai, H. G.; Bao, Y. Y.; Du, F. F.; Tian, J.; Bai, R. K. 2,6-Substituted pyridine derivative-containing conjugated polymers: Synthesis, photoluminescence and ion-sensing properties. *Polym. Chem.* **2011**, *2*, 1699−1705.

(25) Mukherjee, S.; Chowdhury, S.; Paul, A. K.; Banerjee, R. Selective extraction of palladium(II) using hydrazone ligand: A novel fluorescent sensor. *J. Lumin.* **2011**, *131*, 2342−2346.

(26) Yu, S. y.; Rhee, H.-W.; Hong, J.-I. Fluorescent sensing system for palladium(II) based on the Heck reaction. *Tetrahedron Lett.* **2011**, *52*, 1512−1514.

(27) Zhu, B.; Gao, C.; Zhao, Y.; Liu, C.; Li, Y.; Wei, Q.; Ma, Z.; Du, B.; Zhang, X. A 4-hydroxynaphthalimide-derived ratiometric fluorescent chemodosimeter for imaging palladium in living cells. *Chem. Commun.* **2011**, *47*, 8656−8658.

(28) Liu, B.; Bao, Y. Y.; Wang, H.; Du, F. F.; Tian, J.; Li, Q. B.; Wang, T. S.; Bai, R. K. An efficient conjugated polymer sensor based on the

aggregation-induced fluorescence quenching mechanism for the specific detection of palladium and platinum ions. *J. Mater. Chem.* **2012**, *22*, 3555−3561.

(29) Liu, B.; Wang, H.; Wang, T. S.; Bao, Y. Y.; Du, F. F.; Tian, J.; Li, Q. B. A.; Bai, R. K. A new ratiometric ESIPT sensor for detection of palladium species in aqueous solution. *Chem. Commun.* **2012**, *48*, 2867−2869.

(30) Mohapatra, H.; Schmid, K. M.; Phillips, S. T. Design of small molecule reagents that enable signal amplification via an autocatalytic, base-mediated cascade elimination reaction. *Chem. Commun.* **2012**, *48*, 3018−3020.

(31) Pershagen, E.; Nordholm, J.; Borbas, K. E. Luminescent lanthanide complexes with analyte-triggered antenna formation. *J. Am. Chem. Soc.* **2012**, *134*, 9832−9835.

(32) Wang, Z.; Liao, F. Fluorescent probes for Pd^{2+} detection by poly(*o*-phenylenediamine) nanospheres with fluorescence enhancement. *Synth. Met.* **2012**, *162*, 444−447.

(33) We note that sample G produced a false positive signal.

(34) Cawthorn, R. G. The platinum and palladium resources of the Bushveld complex. *S. Afr. J. Sci.* **1999**, *95*, 481−489.

(35) Cawthorn, R. G. The platinum group element deposits of the Bushveld complex in South Africa. *Platinum Met. Rev.* **2010**, *54*, 205−215.