# Conductometric Sensors for Detection of Elemental Mercury Vapor

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Several organic and inorganic materials have been tested for possible incorporation into a sensing array in order to add elemental mercury vapor to the suite of chemical species detected. Materials have included gold films, treated gold films, polymer-carbon composite films, gold-polymer-carbon composite films and palladium chloride sintered films.

## Introduction

The toxicity of mercury and its adverse effect on human and animal health has made environmental monitoring of mercury in gas and liquid phases important (1,2). As consumer products which contain elemental mercury, such as fluorescent lighting, become more widespread, the need to monitor environments for the presence of vapor phase elemental mercury will increase. Sensors in use today to detect mercury in gaseous streams are generally based on amalgam formation with gold or other metals, including noble metals and aluminum. Recently, NASA has recognized a need to detect elemental mercury vapor in the breathing atmosphere of the crew cabin in spacecraft and has requested that such a capability be incorporated into the JPL Electronic Nose (3). The detection concentration target for this application is 10 parts-per-billion (ppb), or 0.08 $mg/m^3$.

In order to respond to the request to incorporate mercury sensing into the JPL Electronic Nose (ENose) platform, it was necessary to consider only conductometric methods of sensing, as any other transduction method would have required redesign of the platform. Any mercury detection technique which could not be incorporated into the existing platform, such as an electrochemical technique, could not be considered.

## Background

The JPL Electronic Nose (ENose) is an array-based chemical sensing device which uses an array of conductometric sensors to detect, identify and quantify leaks and spills of selected chemical species (4). It is designed to run continuously in order to detect sudden changes in the air composition against a background. In earlier versions of the JPL Electronic Nose, polymer-carbon composite sensing materials have been used in the 32-element array (5-8). The device in its current design has a 32-element array, of which four are not polymer-carbon black composite films.

The ENose monitors the environment by pumping air from the surroundings into the sensor chamber, where the response of a sensing array is read. As air enters the sensing chamber, resistance of each element in a 32-sensor array is measured. A baseline of clean

air background is established and deviations from that baseline are recorded as changes in resistance of the sensors. The pattern of distributed response of the sensors is deconvoluted, and chemical species to which the device has been trained are identified and quantified by using a set of software analysis routines developed for this purpose. The device is meant to monitor the air for sudden appearance of targeted species, such as from a leak or a spill.

In order to incorporate sensors capable of detecting elemental mercury ($Hg^o$) vapor, we have tested several different materials which might be used conductometrically to augment the set of polymer-carbon black composite sensors now in use (4-5). Previous work in development of materials which might be used in conductometric sensors for Hg detection by other researchers has focused primarily on using thin films of gold and other noble metals to form a metal-mercury amalgam, and reading the change in resistance with amalgam formation (9, 10-18). In addition, palladium chloride with tetrahydroxyethyl-ethylenediamine (THEED) has been used in a study of Hg sensing (19). Palladium chloride has also been used as a colorimetric indicator of Hg vapor (20, 21).

We have previously reported use of quantum mechanical modeling to predict the binding energies of Hg with organic compounds in an effort to screen polymers for inclusion in the ENose array (3, 7, 22). The results of those modeling studies showed that mercury might be detected using polymers containing a primary or secondary amine as the matrix for sensors.

Four candidate sensing surfaces which could be incorporated onto existing sensor substrates were selected, discussed below. The materials selected for testing for Hg sensing include gold films, polymer-carbon black composite films with amines in the polymer structure, gold islands on polymer-carbon composite films, and sintered palladium chloride films. These materials were selected based on literature reports, molecular modeling, and laboratory trials. Gold islands on polymers selected for response to organic materials were tested in the laboratory in an effort to make a sensor for both mercury and organic compounds. Performance of these materials as sensors for elemental mercury vapor was tested in the concentration range 3 to 30 ppb Hg, at room temperature in humidified air.

Two types of electrode substrates were considered for use with sensors to detect mercury, the standard ENose substrate and microhotplates. The standard ENose substrate is an alumina substrate 25 mm by 10 mm on which eight electrode sets of Pd-Au have been screen printed. Each ENose standard electrode set is 2mm x 1 mm and electrode spacing is approximately 250 μm. These substrates include thermistors and screen-printed heaters on the back side; substrates can be heated to temperatures of $40^oC$ using the standard ENose circuitry. Microhotplate sensor substrates are arrays of 4 electrode sets on a 6x6 $mm^2$ silicon die. Each array element consists of a 1 μm thick silicon nitride diaphragm with an electrode set that is 400 μm on a side. The electrodes are interdigitated platinum with 10 μm widths and gaps. Each die (set of four sensor elements) can be heated to temperatures as high as $600^oC$, although ENose circuitry will allow temperatures up to $200^oC$. Microhotplate sensors were included in the set of 32 ENose sensors because it was considered that regenerating sensors after exposure to Hg could require temperatures as high as $200^oC$.

## Experimental

Sensing Films

Gold films were deposited on standard ENose substrates and on microhotplate substrates by evaporation in vacuum. Films ~15 nm thick were used in these studies. In some cases, the surface area of gold films were treated by abrading them using a grit blaster with SiC grit propelled by compressed air.

Polymer-carbon composite sensors were made by solution casting dispersions of polymer in solution and carbon black. Deposition of polymer-based sensing films and standard ENose electrode substrates have previously been discussed in detail (6, 7, 9). Polymer-carbon composite sensors were tested on microhotplate sensor substrates as well as on standard substrates. These sensing materials were deposited onto the substrates using techniques similar to those developed for the standard substrates. Instead of 1 μL deposits of solution, deposits of 5 -50 nL were made on the microhotplate sensor elements.

Gold islands on polymer films were made by evaporating gold in vacuum to a thickness of ~5 nm; gold islands were evaporated onto polymer-carbon composite films deposited on standard ENose substrates.

Palladium chloride sensing films were formulated by preparing a saturated solution of $PdCl_2$ solution in water, then solution casting on microhotplate sensor substrates. The films were sintered in air for one hour at 425$^{o}$C by heating the microhotplate.

Sensors were tested by exposing them repeatedly to Hg vapor in humidified air for periods of 30 minutes. Air temperature was 22-27$^{o}$C, with humidity held at 10,000 ppm water (28-38 % relative humidity). Sensor temperatures were held at 28$^{o}$C for ENose substrates and at air temperature for microhotplate substrates.

Mercury Vapor Delivery System

Hg vapor was delivered at concentrations ranging from 3 ppb to 3 ppm using a home-built, computer controlled, vapor delivery system. In this system, mercury is held in a chamber heated to 100$^{o}$C and the vapor above the mercury is mixed with air by flowing dry air through the headspace then mixing it with humidified air. The mixture is flowed across the sensors at 250 mL/minute; clean air is provided by turning off flow through the mercury headspace. Flow is controlled using mass flow controllers. Humidity is compensated when mercury is provided in dry air; there is no change in humidity when mercury is turned on or off. The system is calibrated using a Jerome 431-X mercury vapor analyzer.

## Results and Discussion

Gold Film and Treated Gold Film Sensors

Initial studies of Hg sensing focused on repeating the well-known ability of thin gold films to amalgamate Hg, resulting in a decrease in conductivity in the film (10). Thin gold films are the standard approach to detection of mercury vapor; they may be used several times before regeneration, then are regenerated by heating in air at temperatures up to 200°C. Studies have shown that these films change conductivity sufficiently at a thickness of ~15 nm and would be suitable for integration the JPL ENose sensing platform. With a NASA goal of keeping power utilization at a minimum and the need to regenerate gold films at temperatures well in excess of 40°C, these sensors can be used in the ENose only on microhotplate sensors.

The response of gold sensing films deposited on JPL ENose substrates and treated after deposition was also evaluated. The gold films were vacuum deposited, then treated by physical abrasion by grit blasting with SiC particles. The high speed abrasive particles thin and roughen films; the films then exhibit greater surface area as compared to as-deposited evaporated gold film. As seen in Figure 1, abraded gold films show good sensitivity to mercury in the ppb range, but do not regenerate in air at room temperature.

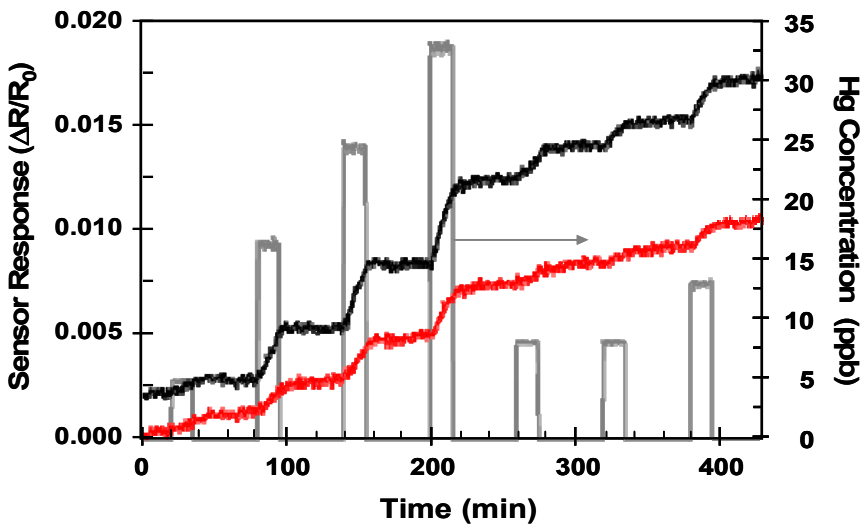


**Figure 1:** Response of two abraded gold films on ENose substrates to Hg vapor. Light, rectangular traces are Hg delivery concentrations.

Such films may be used as a dosimeter, but must be regenerated at high temperature or replaced after they no longer respond to Hg. It can also be seen that the sensing response of abraded gold films is repeatable for a single film, and that the magnitude of response may be used to determine mercury concentration, but the films are not reproducible from one to the other. This lack of reproducibility from sensor to sensor may be attributed to the challenges involved in obtaining similar films through the abrasion technique. This lack of reproducibility in films makes these films suitable for detecting the presence of mercury vapor, but not for quantifying the vapor. Further work in treating the surface repeatably may make these films viable as quantifying sensors.

Polymer-Carbon Composite Film Sensors

Based on results of modeled quantum mechanical binding energy between mercury and organic ligands (22), two polymers were selected and made into polymer-carbon black composite sensors. These two polymers, designated EYN1 and EYN2 (7) are both poly-4-vinyl pyridine derivatives with a quaternary and a primary amine, and have also been used for detection of $SO_2$ (7). It was expected from the small magnitude of the binding energy that any response of sensors made from these polymers would be weak, as the binding energy is on the order of -0.3 kcal/mole (22). Generally polymer-carbon composite sensors which show significant response to the presence of target species have binding energies in excess of -2 kcal/mole; for example, the binding energy for these same polymers with $SO_2$ is on the order of -10 kcal/mole.

As shown in Figure 2, polymer EYN1, with a primary and quaternary amine in its structure, has a weak response to mercury vapor at concentrations of 30 ppb and higher. The three traces in the figure are sensors made with different loads of carbon black for conduction; 15% (w/w) carbon black (red) has the largest response, while 10% (green)

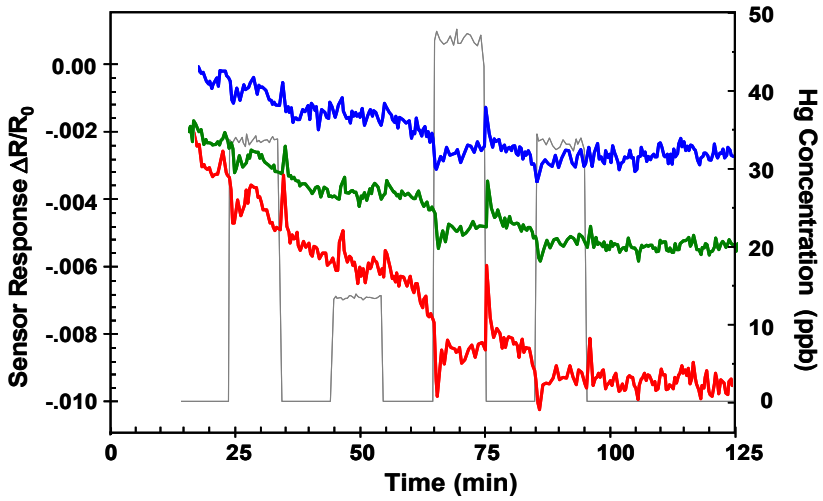


**Figure 2:** Response of three sensors made from polymer EYN1 to Hg in air. Light, rectangular traces are Hg delivery concentrations.

and 12% (blue) loads have smaller responses. Previous work has shown that carbon load will influence the strength of response in polymer-carbon composite sensors. In some cases, analyte sorbs to the carbon, causing changes in conductivity in the sensing film by changing the conductive pathways in the films. In the case of mercury, it is clear that carbon load has a significant effect on the magnitude of response, and that larger response is correlated with higher carbon load. In sensing other materials, larger response is correlated with smaller carbon load. The role of carbon load in sensing has not been fully explored for the sensing materials used in the ENose.

The level of response to mercury for this polymer-carbon composite sensor is not suitable for a mercury sensor at concentrations required for this application. It may be possible to optimize sensors made from these polymers for use as mercury sensors at a higher range than 3-30 ppb.

Gold Films on Polymer-Carbon Composite Films

In an effort to develop a sensor which would combine the sensing functionalities of polymer-carbon composite films with those of gold films, islands of gold were deposited on polymer-carbon composite films. In this study, we investigated sensing capabilities of several polymer-carbon composites with a 10 nm gold film vacuum deposited on the composite film. Films based on some of the polymers used in the ENose showed

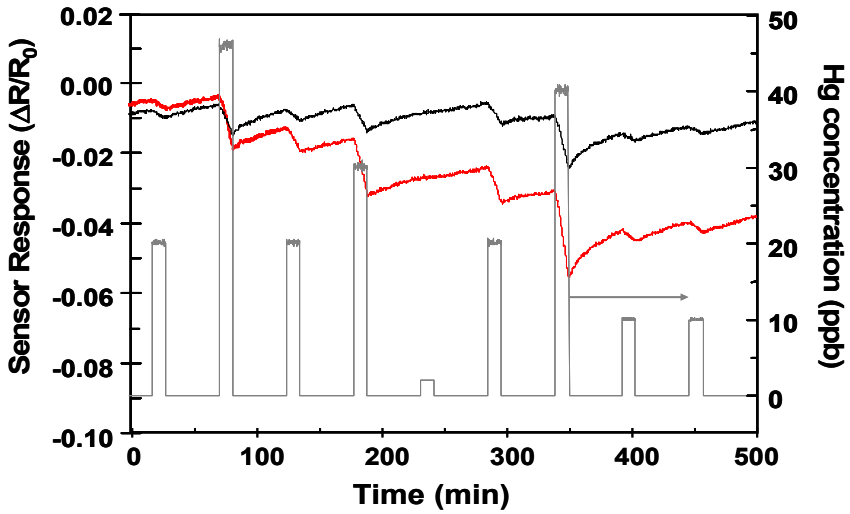


**Figure 3:** Response of two sensors made of gold film deposited on poly(caprolactone) polymer-carbon composite films to mercury in air at room temperature. Light rectangular traces are Hg delivery concentrations.

repeatable response to Hg at concentrations higher than 10 ppb, while maintaining their sensitivity to organic vapors. As seen in Figure 3, there is strong, reproducible response to mercury in the ppb concentration range. These sensors recover after mercury is removed from the air stream.

Electron microscopy studies of the sensors shows that the gold is distributed as partially interconnected islands across the polymer-carbon composite film. This distribution of gold as islands allows the polymer to respond to organic vapors in the usual manner, by sorption into the polymer and swelling, to reduce conductivity, but also allows Hg to amalgamate with gold and influence the overall conductivity of the film. Some gold will penetrate beyond the surface of the polymer film, and Hg atoms or vapors of other targeted species may enter the polymer matrix and cause a change in the resistance of the film, either because of swelling in the matrix (23) or because of changes caused to the conductive medium, such as through amalgamation or sorption. These films do not need to be used on microhotplate sensors, as they regenerate sufficiently at moderate temperatures for use.

The sensing mechanisms in this type of film have not been well studied, and while sensors can be made reproducibly with some polymers, sensing response is not reproducible on all polymers tested. Further work will be necessary to understand the use of these polymers as combination organic and mercury vapor sensors.

Palladium Chloride Sintered Films

Palladium chloride has been used as a component in polymer-metal composite films used for Hg detection (19) as well as a dosimeter to monitor Hg vapor exposure in dental offices (20, 21). In a study of films to be used for mercury sensing with piezoelectric detectors, it was found that a coating which was 50% $PdCl_2$ was the optimum preparation for detection of Hg in the single ppm range. Reasoning that the polymer acted primarily as a carrier for $PdCl_2$, we chose to study sintered thick films of $PdCl_2$ for mercury vapor sensing.

As seen in Figure 4, $PdCl_2$ sensing films show good sensitivity and reproducibility of response to Hg concentrations of 2 - 10 ppb at 23°C in humidified air. $PdCl_2$ sensor response magnitude does not increase above 10 ppb Hg. These sensing films also show partial regeneration under mild conditions, temperatures <40°C, and good repeatability of response for concentrations 10 ppb and under.

Upon initial exposure of $PdCl_2$ films to Hg vapor of any concentration, the sensor response is about one order of magnitude greater than subsequent exposures (initial exposures not shown in Figure 4.) $PdCl_2$ films cannot be regenerated completely, but they can be regenerated to some extent by heating at elevated temperatures in flowing clean air for several minutes. $PdCl_2$ sensors have been used up to 30 exposures of 3-30 ppb Hg in air with no significant change in magnitude of response.

At concentrations above 10 ppb, the magnitude of sensor response to Hg does not increase. Initial response magnitudes are also linear with concentration up to 10 ppb. In operation, $PdCl_2$ sensors will be exposed to Hg vapor before they are used in a monitoring situation, so it will not be necessary to make a distinction between initial and subsequent responses during operation.

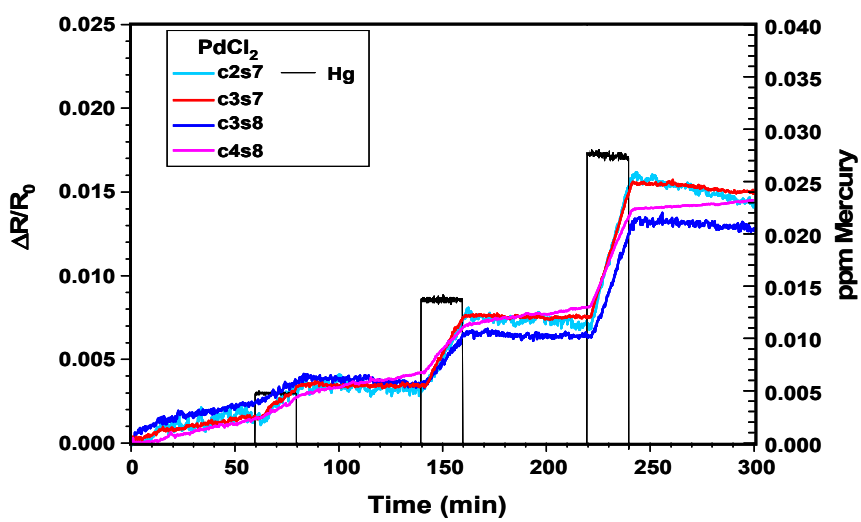


**Figure 4:** Response of four sintered $PdCl_2$ sensors to mercury in air at room temperature. Rectangular traces are Hg delivery concentrations.

## Conclusions

Several organic and inorganic sensing materials have been tested for their ability to detect vapor phase, elemental mercury at ppb concentration levels at room temperature. Sensing materials tested include thin gold films, treated gold films, polymer-carbon composites, and gold on polymer-carbon composite and sintered $PdCl_2$,. These materials have been tested for response to mercury vapor and regeneration, and selections for inclusion into the Electronic Nose Technology Demonstration have been made.

Polymer-carbon composite films made from amine containing polymers, previously selected for $SO_2$ detection (7), show a small response to Hg. The response is not evident until ppm level concentrations of Hg; thus these materials cannot be used for primary Hg sensing, but may be used to follow clean up processes if a high concentration of mercury is released into the air by a containment failure.

Materials which showed good response to mercury vapor but which will not be used in the current version of the ENose include abraded gold films and gold-on-polymer-carbon composite films. Both abraded gold films and gold-on-polymer-carbon composite films show promise as conductometric sensing surface for mercury detection. However, because there is poor sample-to-sample reproducibility of response magnitude, these materials require further work. In addition, the mechanism of response in gold-on-polymer-carbon composite films, both for response to organic vapors and to mercury vapor, is not well understood and will require further work.

The two materials selected for inclusion into the current version of the ENose, to be used as a Technology Demonstration on board the International Space Station in late 2008, are thin gold films, the standard material for vapor phase Hg detection, and sintered $PdCl_2$ thick films. With these two materials, the ENose includes dissimilar redundancy for Hg detection. Gold films do not respond to any of the other targeted analytes for the ENose in this phase. However, $PdCl_2$ is not specific to Hg. It will respond to the presence of some other species targeted for monitoring by the ENose. In particular, $PdCl_2$ responds strongly to the presence of ammonia above a few tens of ppm. However, as the ENose is an array based sensor, this sensitivity will not impact the ability of the device to distinguish between targeted species. In the case of ammonia, several other sensors which do not respond to Hg will respond to ammonia, resulting in a significantly different pattern of response.

## Acknowledgments

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## References

1. A. Carpi, Water Air and Soil Pollution, **98**, 241 (1997)
2. T. F. Baumann, J. G. Reynolds, and G. A. Fox, *Reactive & Functional Polymers*, **44**, 111 (2000**).**

3. M.A. Ryan, M.L. Homer, H. Zhou, K. Manatt, A. Manfreda, A. Kisor, A. Shevade and S.P.S. Yen; *Journal of Aerospace, SAE Transactions*, 2005-01-2880 (2005).
4. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, F. Zee, and J. Graf, *Proc. 27th International Conference on Environmental Systems,* SAE, 97ES-84 (1997).
5. M.A. Ryan, M.L. Homer, M.G. Buehler, K.S. Manatt, B. Lau, D. Karmon, and S. Jackson, *Proc. 28th International Conference on Environmental Systems,* SAE, 981564 (1998).
6. M.A. Ryan, H. Zhou, M.G. Buehler, K.S. Manatt, V.S. Mowrey, S.P. Jackson, A.K. Kisor, A.V. Shevade, and M.L. Homer, *IEEE Sensors Journal*, **4**, 337 (2004).
7. M.A. Ryan, M.L. Homer, H. Zhou, K. Manatt, A. Manfreda, A. Kisor, A. Shevade and S.P.S. Yen; *Proc. 36th International Conference on Environmental Systems,* SAE, 2179 (2006).
8. M.A. Ryan, A.V. Shevade, H. Zhou and M.L. Homer, *MRS Bulletin*, **29**, 714 (2004).
9. J.J. McNerney, P.R. Busek and R.C. Hanson, *Science*, **178**, 611 (1972).
10. Q. Bristow, *J. Geochem. Expt.,* **1,** 55 (1972).
11. B. Mazzolai, V. Mattoli, V. Raffa, G. Tripoli, D. Accoto, A. Menciassi and P. Dario, *Sens. & Act. A*, **113**, 282 (2004).
12. T. Thundat, E.A. Wachter, S.L. Sharp and R.J. Warmack, *App. Phys. Lett.*, **66**, 1695 (1995).
13. J.J. Caron, R.B. Haskell, P. Benoit, J.F. Vetelino, *IEEE Trans. Ultrasonics Ferroelectrics and Freq. Control*, **45**, 1393 (1998).
14. C.L. Britton, R.L. Jones, P.I. Oden, Z. Hu, R.J. Warmack, S.F. Smith, W.L. Bryan, and J.M. Rochelle, *Ultramicroscopy*, 82, 17 (2000).
15. B. Rogers, L. Manning, M. Jones, T. Sulchek, K. Murray, B. Beneschott, J.D. Adams, Z. Hu, T. Thundat, H. Cavazos, and S.C. Minne, *Rev. Sci. Inst.*, **74**, 4899 (2003).
16. F.L. Fertonani, E. Milare, A.V. Benedetti and M. Ionashiro, *J. Thermal Anal. and Cal*, **67**, 403 (2002).
17. E. Milare, F.L. Fertonani, A.V. Benedetti and M. Ionashiro, *J. Thermal Anal. and Cal.*, **59**, 617 (2000).
18. F.L. Fertonani, A.V. Benedetti and M. Ionashiro, *Thermochim. Acta,* **265**, 151 (1995).
19. D. P. Ruys, J. F. Andrade and O.M. Guimaraes, *Anal. Chim. Acta*, **404**, 95 (2000).
20. D. Brown, Journal of Dental Research, **60**, 189 (1981).
21. D. Brown and M. Sherriff, *British Dental Journal* **192**, 437 **(**2002).
22. A.V. Shevade, M. L. Homer, H. Zhou, A.D. Jewell, A. K. Kisor, K.S. Manatt, J. Torres, J. Soler, S.-P.S. Yen, M. Blanco, W. A. Goddard, III and M. A. Ryan; *Journal of Aerospace*, SAE Transactions, 2007-01-3149, 225 (2007).
23. E.J. Severin and N.S. Lewis, *Anal. Chem.* **72**, 2008 (2000).