Trace Analysis of Elements in a Palladium Matrix

David A. Kidwell
Chemistry Division
Naval Research Laboratory
Washington, DC 20375

Abstract

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique for trace elemental analysis and isotopic distribution determination at trace levels, but ICP-MS cannot handle directly high concentrations of ions. Dimethylglyoxime will selectively precipitate palladium from acid solutions leaving most of the impurities in solution and allowing their quantitation by ICP-MS without dilution. By avoiding dilution, the sensitivity and precision of the analysis can be increased to sub-PPM levels. A convenient method for controlled etching of palladium is also described.

Introduction

The exact requirement(s) for the Fleischmann-Pons Effect (FPE) [1] is not clear, but it may be dominated by surface effects. Trace contaminants on the surface influence the uptake and recombination of deuterium (or hydrogen) by blocking or enhancing certain catalytic centers or causing certain crystalline phases to form during processing that may influence the FPE. A classic example in organic synthesis is Lindlar's catalyst.[1] Normally, palladium in the presence of hydrogen will completely hydrogenate triple and double bonds to the saturated alkanes. However, in the case of Lindar's catalyst the palladium is poisoned with lead and further deactivated with either quinoline (an amine) or a thiol. This deactivated catalyst has a sufficiently slow hydrogenation rate to allow stopping the hydrogenation at the double-bond stage. Lindar's catalyst allows the preparation of many cis-alkenes from acetylenes. For example, several steps in the multi-step preparation of Vitamin E are accomplished on an industrial scale with this catalyst.[2]

To fully understand the FPE requires analysis of the palladium before and after various processes to determine if either:

(1) An impurity is present that inhibits or enhances some chemical or other process. The impurity may come from the surface, bulk of the palladium, or from the reagents or equipment used in the reaction; or,

---

[1] Although the mechanisms may be completely different, I use the term Fleischmann-Pons Effect in this a paper to refer to a palladium matrix exposed to deuterium and production of excess heat, elements, or isotopes. The method of introduction of deuterium need not be only through electrolysis, as in the original Fleischmann-Pons experiments.

(2) Transmutation had occurred where a new element or isotope was formed that was not initially present in either the bulk starting palladium, solutions, or equipment used for the reaction.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique for trace elemental analysis. The Thermo-Finnigan Element 2 instrument used in this work will detect most elements that form positively charged ions.[3] For use in ICP-MS, a sample is dissolved in high-purity acid (generally a strong oxidant such as nitric acid), diluted to 2-5% acid with high-purity water and sprayed through a nebulizer into a desolvation chamber that removes most of the water. The semi-dry droplets are carried into an Argon plasma torch that dissociates and ionizes all molecules such that only the elements are left.[4] The ions are then extracted from the plasma though a series of differently-pumped chambers, which reduces the pressure, into a magnetic mass-separator that allows mass analysis of the extracted ions. Once mass separated, the positive ions are detected with an electron multiplier that can be automatically switched from ion counting to analog modes. Because of the analysis process – dissolution, dissociation, and ionization - it is highly unlikely that any molecule could survive intact. Furthermore, the acid and water used to prepare the samples are not isotopically enriched, so any initial deuterium compounds (for example PdD) that may be present are diluted to normal isotopic abundance.

ICP-MS has three limitations: adduct formation, isotopic ratios, and overloading. They are discussed below.

Adduct Formation

During the extraction of the ions from the Argon plasma, ion-atom recombination can occur. I will refer to this as adduct formation.[5] The primary adducts that form are those with the main constituents of the plasma: Argon and Oxygen[6] (from the water solution). Other adducts may be present if the sensitivity is increased – *i.e.* into the PPT[1] and PPQ range. As the ion-atom recombination occurs in the region after the plasma, the proportions of adducts formed varies with the plasma conditions, the exact placement of the plasma torch relative to the extraction lens (as this affects the residence time of the ions in the plasma), the extraction voltages, and the ion concentrations in the test solution. The Ar+matrix ions may interfere with other desired analytes, especially if the host matrix is sufficiently high in concentration (>1 PPM). With analysis of palladium solutions, one often observes Pd+Ar adducts as shown in Figure 1. Scanning over a narrow window without considering adducts may lead to the false conclusion that some element is present that a wider scan would correctly identify as an adduct (Figure 1a *vs.* 1b). Palladium has the advantage that its adducts will reflect the isotopic ratio of palladium plus Argon making them easy to identify. Other elements are not so easy to identify, so caution is called for when interpreting the presence of unexpected elements.

ICP-MS uses two techniques to reduce interferents from adduct formation: collision cells and high resolution. For a collision cell instrument, after extracting the ions from the plasma but

---

[1] Units used: PPM = parts per million ($1:10^{-6}$), PPB = parts per billion ($1:10^{-9}$), PPT = parts per trillion ($1:10^{-12}$) and PPQ = parts per quadrillion ($1:10^{-15}$).

before mass analysis, the ions are collided with an inert gas where the energy of collision is sufficient to break apart weakly held complexes. A collision cell is often used on ICP-MS instruments that use a quadrupole as the mass resolving element. The Element 2, used in this work, is a high-resolution ICP-MS. The resolution can be greater than 10,000, which can resolve many, but not all, adduct ions. In addition to reducing interferences directly, interferences from adducts may be mathematically removed with reduced precision (described below).
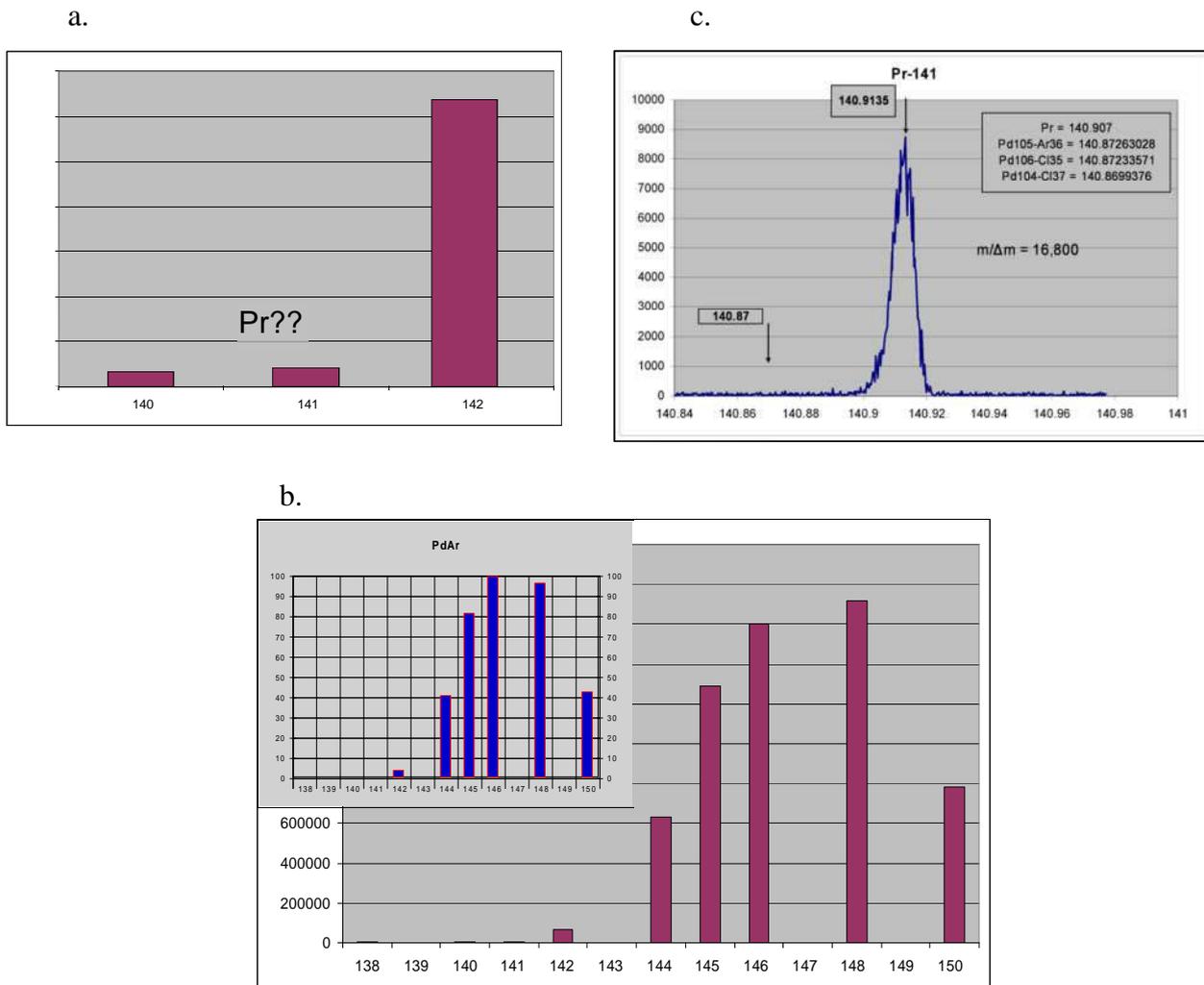
a.

c.

b.

Figure 1. Examples of an Argon-Palladium adduct. Figure 1a: A minor peak in the Ar-Pd adduct occurs at *m/z* **141 (Pd-105 + Ar-36) and interferes with the detection of Pr (which is mono isotopic). Scanning a narrow mass window may miss the characteristic isotopic envelope of Palladium, which would indicate an adduct ion. Figure 1b: A larger scan range of the top spectra indicating the Pd-Ar adduct, with the inset showing the expected isotopic distribution. Argon is mostly mono-isotopic (Ar-40 99.6%) but palladium has six stable isotopes. For the analysis of Pr, if other adducts are absent, one can use the expected distribution of the ions for the Ar-Pd adduct to calculate what the intensity should be at** *m/z* **141 and subtract that intensity form what is observed with the remaining intensity attributed to Pr. Such a correction can correct up to a 20 fold interferent. The use of multiple isotopes increases the confidence in the correction. Higher corrections are suspect because the isotopic ratios vary due to plasma conditions. Note that the calculated ion distribution, shown in the insert, and the measured distribution do not agree exactly (** *m/z* **148 should be smaller than m/z 146). This is due to rapid scanning of the ICP-MS, and the discrepancy can be decreased by scanning a narrow range of ions. Figure 1c: This spectrum shows the unambiguous identification of Pr by high resolution. The Pd-Ar adduct interferent (not observed here) can be separable from Pr with higher resolution (>4000) as they have slightly different mass (140.8726303 vs. 140.907648). The preferred method to confirm the presence of some unique element is to both reduce the palladium concentration (to reduce the interference) and use higher resolution rather than a mathematical correction.**

Although adducts form in ICP-MS, they form in greater abundance in Secondary Ion Mass Spectrometry (SIMS). Adduct ions in the SIMS analysis may complicate the identification of an unexpected element.[7] SIMS readily analyzes surface impurities but can have several orders of magnitude discrimination among the materials on the surface. Furthermore, the ionization efficiency and discrimination can change depending on what is present on the surface, making accurate quantitation difficult. Species that form cations readily are enhanced in SIMS, and this has been used to advantage for selectively detecting one species in the presence of others.[8,9] Not having a surface present to influence the ionization process makes ICP-MS more quantitative than SIMS. Not having large amounts of adduct ions make isotopic ratios easier to determine.

Isotopic Ratios

When the ions are extracted from the plasma, they are not all extracted with the same efficiency. ICP-MS shows about a 1% per AMU discrimination in the intensities.[10] The raw intensities should not be directly compared to published values but may be corrected by analysis of known standards. A scanning instrument may not measure isotopic ratios with great precision because the plasma can fluctuate slightly even over a scan. This is partially mitigated with the Thermo-Finnigan Element 2 by rapid scanning using an electric sector over a narrow mass range. Nevertheless, for more precise work, instruments used for isotopic ratios often have multiple collectors that simultaneously detect all ions. Even with multiple collectors, the isotopic ratios may be affected by other elements present in the matrix slightly altering the plasma conditions and the ion extraction efficiency.[11] For the most precise work, all matrix conditions should be as identical as possible to known standards or other techniques be employed, such as thermal ionization mass spectrometry.

Overloading

ICP-MS is a trace analytical procedure that can analyze PPB levels routinely and PPQ levels in carefully prepared samples. Because ICP-MS is a trace technique, high amounts (PPM) of analyte can interfere. Worse than interference, high amounts can irreversibly contaminate the instrument – especially the sample introduction nebulizer that is frequently made of glass and can absorb materials. The contamination from a sample with high concentrations of species provides a constant background for subsequent analysis that can be a substantial problem if one wished to analyze the same element at trace levels.

One may ask: If ICP-MS can detect routinely PPB levels of elements, why do we need to reduce the matrix? Can it be analyzed directly? To answer these questions, one needs to consider how the whole procedure is performed using an example analysis. One mg of palladium dissolved in 1 mL of acid would correspond to 1000 PPM of palladium. To reach 1 PPM of palladium so as to avoid instrumental contamination, this solution must be diluted 1:1000. This also dilutes any impurity that was being sought in the original palladium sample the same 1:1000. If your sensitivity were 1 PPT for that impurity, the concentration in the original palladium would correspond to 1 PPM.[12] Quantitation at lower levels would either require a smaller dilution and potential contamination of the instrument, or use of another technique. Besides sensitivity, the precision that can be claimed for the absence of some

element is also affected by the dilution, mainly due to the blanks. For example, assume the blanks had signal levels for the impurity Praseodymium, maybe due to adduct ions, which corresponded to 1 PPT level with some precision. Because of the 1:1000 dilution and precision in the blank measurement, one could not say with confidence that the original palladium sample had less than 1 PPM of Pr present, or 1 µg of Pr/g Pd. If the palladium matrix could be reduced 100-10,000 fold, without reducing the analyte, then the dilution could be reduced and the sensitivity proportionally increased.

This report describes a procedure to reduce the main matrix element – palladium – to PPM levels so that one can observe trace levels (PPB-PPQ) of other elements in the palladium matrix without grossly contaminating the ICP-MS or requiring excessive dilution of the matrix. Precautions in interpreting ICP-MS data are also emphasized.

Experimental

Reagents and Supplies

JT Baker Ultrex® II nitric acid (cat #6901-05) and hydrochloric acid (cat #6900-05) were used in preparing solutions. Fischer Optima nitric acid (cat #A467-500) has also been used with success. Only pasticware was used for preparing samples and reagents, as glass quickly leaches trace elements. All samples were prepared in 15 mL Falcon® Blue Max® (cat #352097) polypropylene test tubes. These tubes have unlined plastic caps that are not completely resistant to concentrated nitric acid – they discolor after a few days, but they appear to be resistant to 5% nitric acid for long periods of time. Other brands may have linings in some caps with traces of impurities that are extracted and cause high blanks. Blanks of the starting solutions are always done, often before samples are prepared, to insure that contamination is minimized. Some analysts soak their plasticware in 5% nitric acid before use. For the elements of interest, this was not necessary but may be necessary for some of the more common, first-row transition metals. Dimethylglyoxime (DMG) was purchased from Sigma-Aldrich (cat #162574-500g). Distilled water was triply distilled directly into PFTE bottles in-house using a quartz still. Transfer of solutions was made by either direct pouring, where possible, or using disposable plastic transfer pipettes (PGC Scientifics Cat #304-001)). ICP-MS standards were purchased from Alfa Aesar. A hood was dedicated to sample preparation and was scrubbed, sampled for blanks, lined with bench paper, and several layers of disposable paper towels (Techwipes) placed on top of the bench paper. A layer was renewed between each sample. A Teflon hood is recommended for elements in the first row of the transition metals. Pall VM-1 5.0 µm (cat #60693) filters were used for environmental surveys, extracted with 5% nitric acid, and analyzed without dilution. The white disks are the filters and the blue disks are spacers. The ICP-MS analysis was performed on a Thermo-Finnigan Element 2 running in both low resolution (300 AMU) and medium resolution (4000 AMU) modes. Selected ions were collected in both modes. For confirmation of an element, high resolution (nominally 10,000 AMU) was used.

Surface Analysis

The goal of surface analysis is to look for impurities that may have migrated to the surface during processing. To preserve sensitively, use of minimal amounts of solutions and prevention

of dissolution of the palladium is desirable. For surface analysis, approximately 120 mg of palladium foil or a few mg of palladium powder was placed in a polypropylene tube and 5 mL of 5% nitric acid was added. The acid was allowed to react at least 30 min. at room temperature, decanted into another tube or analyzed directly by ICP-MS (the fewer the steps, the less likely the contamination). The solution should be colorless or only light yellow in color – yellow being the color of the palladium ion in water. For some samples, after this initial surface analysis, the 5% nitric acid was decanted and 500 µL - 1 mL of concentrated nitric acid was added to the palladium. This was allowed to stand for 30 min., diluted with distilled water to 5-10% nitric acid, and analyzed. If chloride is present, then the nitric acid will slowly dissolve the palladium. If the solution becomes yellow, due to dissolution of the palladium, then too much palladium is present and the sample must be diluted.[13] Generally, the 5% nitric acid initial exposure removes most of the halides and prevents nitric acid from attacking the palladium but allows a stronger etch for other impurities. A survey scan by ICP-MS of most of the elements was made on these surface extracts.

Bulk Analysis

After the surface analysis, bulk analysis is performed on the same sample. The palladium foil is dissolved in minimal amounts of *aqua regia* (3:1 $HCl:HNO_3$). For recovery experiments, the solution is spiked with 5 ng of Sm and varying amounts of rare earths. For most analysis, no internal standard is added because the composition is unknown and the elements used as an internal standard may be present as an impurity. Alternatively, the palladium may be dissolved more slowly in concentrated nitric acid with 1% or less HCl. This procedure avoids excess chloride in the final solution that may interfere with certain elements by forming cluster ions. The excess acid may be removed by evaporation under nitrogen and 7 mL of 0.1M HCl added (2 % nitric acid may be used if the chloride needs to be minimized). After dissolving the palladium, 300 mg of DMG was introduced (for 120 mg of palladium – this was a 14% excess over a 2:1 DMG-Pd complex), the tubes capped, shaken, and rocked overnight at room temperature. Occasional shaking is helpful to disperse the DMG as its water solubility is low. The amount of DMG was varied depending on the amount of palladium analyzed and the amount added must be known for correction of the blank, as DMG contains traces of certain elements. Large excess of DMG should be avoided as uncomplexed DMG will float on the acid and make decantation in the next step more difficult. The samples were centrifuged to separate the DMG-Pd complex and the supernatant decanted into another tube (3-5 mL generally recovered). This solution was analyzed by ICP-MS directly. The supernatant will be yellow due to a decomposition products and the color is not reflective of the palladium concentration. The removal of the acid under nitrogen can be eliminated if the acid is kept to a minimum as evaporation takes time and the nitrogen stream may introduce contaminants. Some samples of supernatant were filtered through Whatman® Autovial® 0.45 um PTFE membranes (cat # AV125UORG). This filtration appears to introduce barium, likely from the glass prefilter present in the assembly. To avoid filtration, the solutions may just be decanted from the precipitate. If care is taken in decanting the supernatant from the DMG-Pd complex, no particles (which can plug the ICP-MS nebulizer) will be transferred to the second tube. DMG was not fully characterized for its ability to precipitate Pd selectively in the presence of traces of other elements as the focus of this work was on analysis of rare earths and silver.

Results and Discussion

Dimethylglyoxime (DMG) is known to precipitate only nickel and palladium by forming a 2:1 (DMG:metal) complex. This precipitation has been used to separate palladium from other platinum group metals for analysis of the palladium.[14] The focus of this work was on analysis of rare earths and silver in a palladium matrix rather than the palladium itself. Figure 2 shows a typical tube containing the DMG complex with palladium. Although some of the DMG floats, the solution can be carefully poured into another tube without any precipitate being transferred. Direct transfer eliminates filtering, which can introduce contamination. The nebulizer on the ICP-MS has not been plugged by particles of DMG or the complex even though many samples have been analyzed. The DMG-Pd complex solubility varies with the acid strength (Figure 3), but the solubility does not appear to be affected by the type of acid used. Acid concentrations below 0.6M provide palladium levels sufficiently low (<1 PPM) to allow the solutions to be analyzed directly by ICP-MS without dilution.

For reproducibility of the precipitation, ten separate palladium foils were cut and analyzed. The amount of palladium remaining had a relative standard deviation of 2% and as the acid concentration was high, the palladium concentration averaged 6.5 PPM. Ayres and Berg used 1M HCl and found about 100 PPB of palladium in solution compared to 2.5 PPM in this work.[14] Their solution, being cold, may account for the lower palladium levels, so further improvement in the present method could be envisioned.

Figure 2. A typical reaction of DMG with palladium. (a) shows the tube before centrifugation and (b) shows the tube after centrifugation. The solution turns yellow, which is due to the palladium complex or impurities. In this case, only 6 mL of 0.1M HCl was used for reconstituting the dissolved palladium.
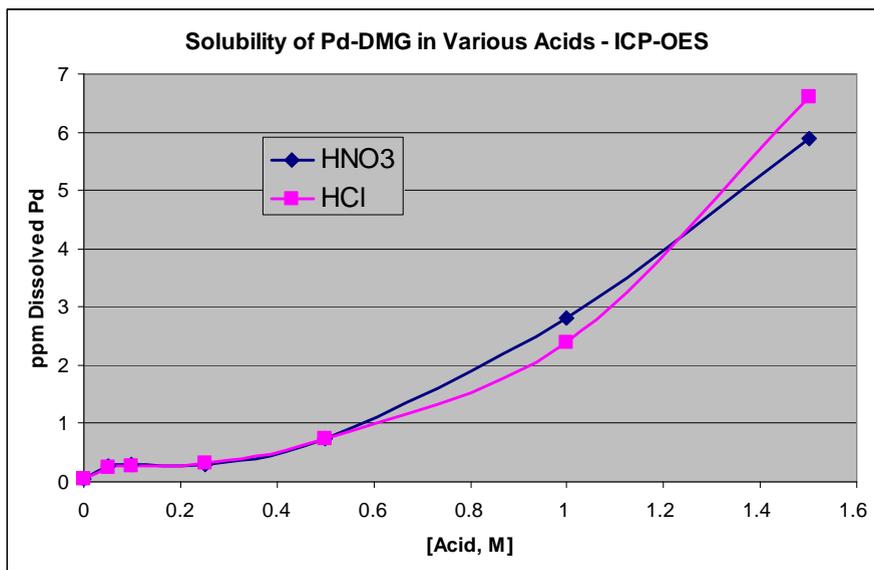
Figure 3. Amount of dissolved Pd vs. acid concentration. Recovered DMG-Pd complex was recrystalized from ethanol and air dried. This was shaken in the various media overnight before analysis. The quantitation was done by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

Example of Surface Analysis

One common occurrence when investigating the FPE is variation in heat production for different lots of palladium. Anecdotally, some electrolysis process will be working well, producing heat in excess of input power repeatedly for many runs. However, the palladium stock material is eventually exhausted and the replacement material no longer produces heat. The FPE may be dominated by surface impurities which may affect surface morphology and loading or unloading of deuterium. Selected data from the surface analysis on two lots of palladium are shown in Figure 4. L-25 was working in a process for many years, whereas L-40 was a newer lot that no-longer produced heat even though the production process was unchanged.[15] Figure 4 shows a limited mass range of the typical broad scan run during bulk analysis. L-40 has substantial amounts of Zirconium relative to L-25, which cannot even be seen on this scale. Discussions with the manufacturer indicated that they had melted L-40 in a Yttrium stabilized Zirconium crucible. Likely the Zirconium arose from this source as traces of Yttrium were also observed. Although not demonstrated in this work, it is possible that there will be within lot variations on impurities that are not reflected in any certificate of analysis issued by the manufacturer. If palladium is poured in large amounts – say 25 kg at a time – then liquid near the center of the crucible should have a different composition than that near the walls. The effects of these impurities on the reproducibility of the FPE remain to be delineated.
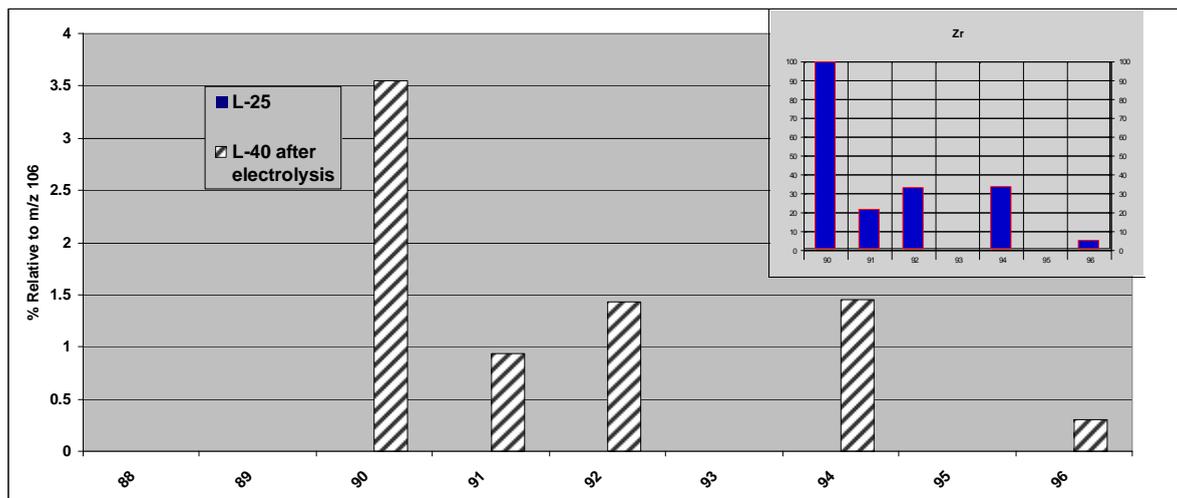
Figure 4. Examples of surface analysis. A limited mass range is shown. L-25 was working for heat production for many years, whereas L-40 was newly purchased material and showed no heat production. The Zirconium signal from L-25 is so low (at least 100 × less) as not to be visible. The signal levels are reported relative to raw ion intensities of Palladium, but this is NOT an accurate measure of concentration as the relative dissolution rate of Zirconium vs. Palladium is unknown. The insert shows the expected isotopic distribution for Zirconium.

Example of Bulk Analysis

Bulk and surface analysis can help confirm if other measurements have correctly identified a change in impurity level of some element. In one Arata-type experiment,[16] carried out in another laboratory independently of Arata, palladium black was pressurized inside a palladium cathode electrochemically. Analysis of the palladium black before and after use by Neutron Activation Analysis (NAA) suggested that there was an increase in silver level. A hypothesis was that the reaction $^{105}Pd + D \rightarrow {}^{107}Ag$ could be occurring. If this reaction were to take place and produce all the silver increase observed, then the ^{107}Ag to ^{109}Ag isotopic ratio would be greatly changed from the natural 52:48 ratio. NAA is not ideally suited to this type of analysis because of background radiation from activated palladium takes years to decay to levels that can reveal trace amounts of silver. Surface analysis by ICP-MS indicated similar levels in silver between the two samples with the natural isotopic ratio for silver. Bulk analysis showed a 13x increase in silver (to 140 PPM) but with a natural isotopic ratio. Unfortunately, the palladium tube used for the cathode during electrolysis was unavailable so the source of the silver increase in the palladium undergoing pressurization is still unknown. However, the hypothesis that the silver was a transmutation product from palladium is unlikely since the isotopic ratio is what would be expected from natural abundance silver.

Reporting Limits of Detection

A typical calibration curve for DMG separations is constructed by spiking standards into a palladium solution (Figure 5). For accurate work, the amounts of palladium should be standardized. The blanks with DMG were always higher than that for DMG alone or for stock solutions likely reflecting impurities in the palladium used for preparing the standard curves. This makes answering the question – Is element X in the bulk palladium? – difficult because

the answer depends on what element is being sought, what are the blank levels, and how low a number is needed. To provide a better answer to that question, limits of the concentration of an element should be calculated in three ways:

(1) With no blank subtraction. In this case the raw ion intensity is converted to concentration using only the slope of the calibration curve. This is the most conservative method and likely overestimates the presence of element X.

(2) With the intercept of the DMG-Pd calibration curve subtracted from the ion counts. This is equivalent to subtracting a blank and accounts for both the purity of the DMG and the purity of the palladium making the standards. This procedure could underestimate the amount of element X in the bulk as element X may also be present in the palladium used to make the standard curve.

(3) With blank subtraction of the DMG blanks without added palladium. This method does not take into account an untested hypothesis that the DMG may complex elements as impurities during manufacture and only have them released if they are displaced by palladium. If this hypothesis is correct, then this subtraction method will overestimate the amount of some target element.

The reporting of the absence of some element is only relevant if the absence of element X (*i.e.* the lower amount that some element was present) in the bulk starting material was a concern. If this case, blank subtraction using method 3 is preferred. For example, if some process was claimed to be producing element X, one might want to know if element X were in the bulk and just migrating to the surface during a chemical process rather than a true transmutation event. Obviously, if all three reporting methods produce limits on the amount of element X substantially below that found during the process being tested, then elements X cannot come from the bulk palladium. Of course, other sources of element X, such as contamination during handling, are not eliminated.

Figure 5 shows a calibration curve for Silver and Indium in a palladium matrix after DMG precipitation. Normally 8 point calibration curves are employed for quantitation and have correlation coefficients >0.999. The concentration on the X-Axis refers to the concentration in the liquid sample. For example, 1 PPB would be prepared by adding 5 ng to a 5 mL solution of palladium in 2.5% nitric acid. In parallel experiments without DMG or palladium, the slopes are about 12% higher, indicating that some silver and indium are lost in the DMG precipitation. The intercept corresponds to a Limit of Detection (LOD) of 3 PPT. If 10 mg of Pd powder were analyzed without dilution, a 3 PPT LOD would correspond to 3.3 PPB in the Pd powder. Where possible, quantiation (and calibration) is done with multiple isotopes (^{107}Ag and ^{109}Ag in this example) and at multiple mass resolutions (LR = low resolution of 300 AMU). If no interferents are present, then the various calculations should agree. The calibration plots for both isotopes of silver overlay each other.
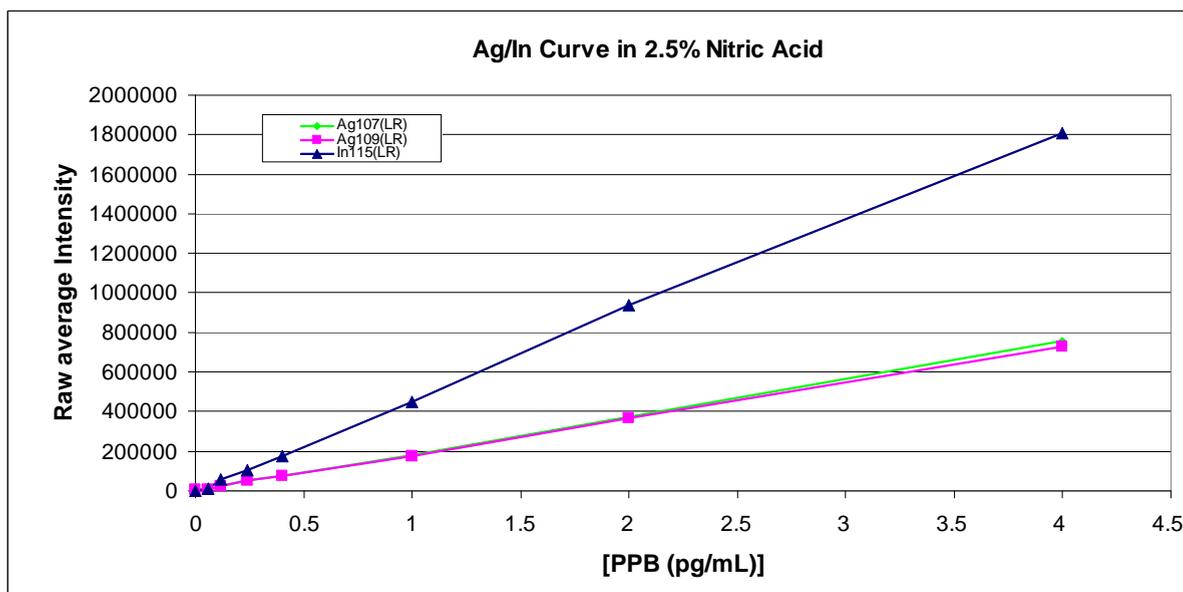
Figure 5. Calibration curve for Silver and Indium in a palladium matrix after DMG precipitation

Controlled Etching of Palladium

Palladium is often dissolved in *aqua regia*, a 3:1 mixture of HCl and HNO_3. For the nobel metals, *aqua regia* is thought to oxidize a small amount of metal on the surface and then complex the ion with the excess chloride. The complex shifts the reaction to the dissolved metals otherwise nitric acid alone should not completely dissolve gold, platinum, or palladium. Palladium is often cleaned with concentrated nitric acid. In this process substantial palladium is sometimes removed as the acid turns yellow. Yet, no chloride is intentionally added. We have used that observation to both control the etching rate and measure the amounts of chloride (or likely other halides) present on the surface as impurities. The chemistry in *aqua regia* is complex and other oxidants, such as chlorine and nitrosyl chloride may be present, being produced from nitric acid reacting with the chloride from the HCl. These other oxidants could oxidize the palladium directly and in the process be reduced back to chloride that can be reoxidized by the nitric acid in a catalytic cycle. Figure 6 shows how the rate of oxidation can be translated into the amount of chloride present on the surface. Sample 1 was a multilayered sample and appeared to have buried chloride as its slope was substantially different than the controls after adding the HCl. Through control of the nitric acid concentration and chloride content, one can slow down the etching to remove impurities without greatly etching the palladium. For surface analysis, 5% nitric acid without chloride appears satisfactory as an initial cleaning.

Figure 6 shows the effects of controlled etching of palladium and measuring chloride content. The control samples had been previously etched with high-purity nitric acid and rinsed before use with 5% nitric acid. Etching was done with 25% nitric acid (to slow the etching rate) under constant sonication. Aliquots (200 µL) were removed at each time point and diluted to 4 mL for analysis by ICP-MS. UV spectroscopy could have also been employed with reduced sensitivity.[17] After 30 min., 5 µL of concentrated HCl was added. Comparing the slopes with

the known addition of chloride to the initial slopes estimates the original chloride surface contamination as shown in the insert.
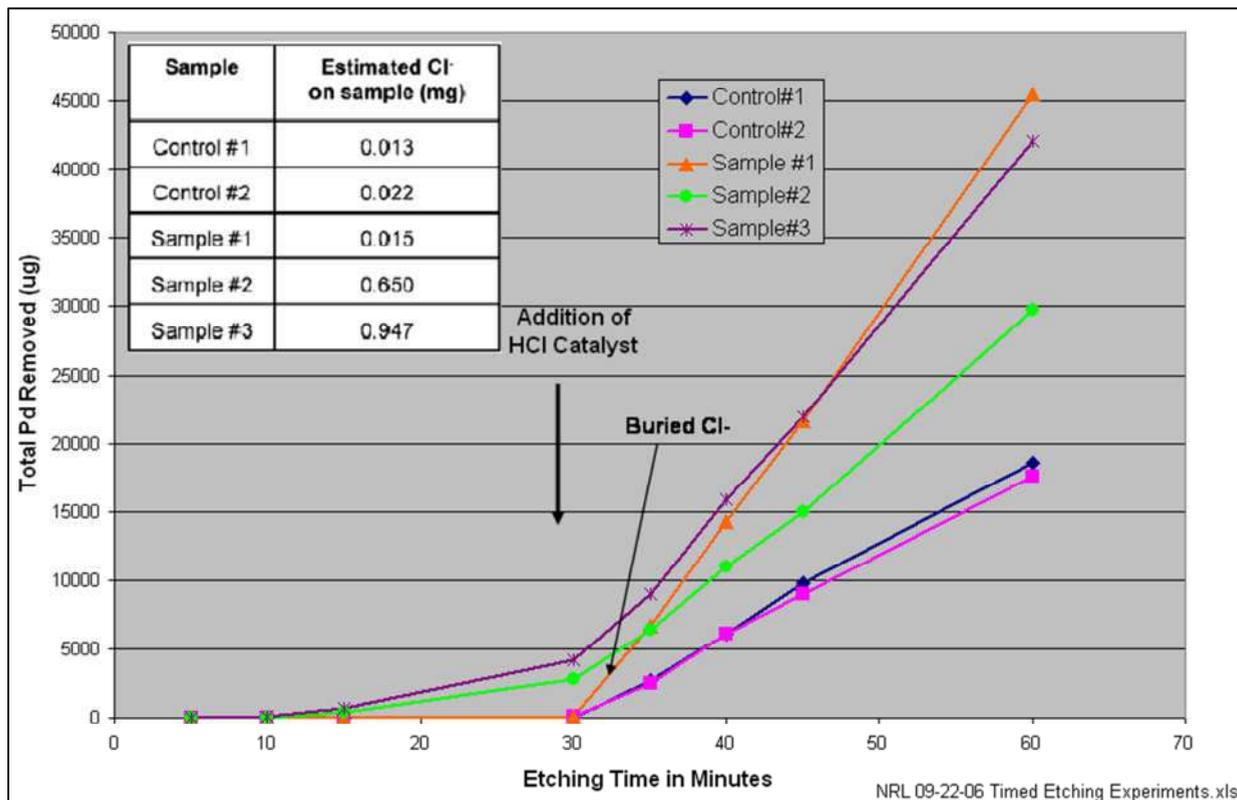

Figure 6. Controlled etching of palladium and measuring chloride content

Conclusions

If the Fleischmann-Pons Effect is dominated by impurities, then surface and bulk analysis can help identify those impurities. Dimethylglyoxime will precipitate selectively palladium from acid solutions leaving most of the impurities and allow analysis by ICP-MS without dilution. By avoiding dilution, the sensitivity and precision of the analysis can be increased. By controlling the amount of chloride in the nitric acid used to etch palladium, a controlled etch is possible, which may be useful to prepare certain structures on the palladium surface.

Acknowledgements

References and Notes

1. H. Lindlar and R. Dubuis, "Palladium Catalyst for Partial Reduction of Acetylenes", *Organic Syntheses, Collected Volume 5*, p.880.
2. W. Bonrath, M. Eggersdorfer, and T. Netscher, "Catalysis in the industrial preparation of vitamins and nutraceuticals", Catalysis Today, **121** (2007) 45-57.
3. Nitrogen, Carbon, Oxygen, and all the Inert Gases cannot be measured due to their presence in the matrix or ionization gas. Also, other elements are difficult if they have masses that overlap adducts or dimers of the main matrix or ionization gas. For example, Sulfur-32 has an interference from an O2 adduct ion.
4. The Argon plasma is at approximately 10,000°K.
5. I use the term adduct formation to refer to any ion not elemental in nature irrespective of the mechanism of formation. The process of formation of adducts is different in ICP-MS than in SIMS. In SIMS the molecules may come from the surface as an intact molecular ion or a neutral and subsequently have attached a cation, such as sodium, in the gas phase. In ICP-MS the adducts may arise though recombination between the plasma torch and the ion extraction optics.
6. M.A. Vaughan and G. Horlick, "Oxide, Hydroxide, and Doubly Charged Analyte Species in Inductively Coupled Plasma/Mass Spectrometry", *Applied Spectroscopy*, **40** (1986) 434-445.
7. For a discussion of some adduct ions in SIMS see: T. Hioki, J. Gao, N. Takahashi, S.Hibi, A. Murase, T. Motohiro, and J. Kasagi, "Influence of Deuterium Gas Permeation on Surface Elemental Change of Ion-Implanted Pd", Abstract #29, 14th International Conference on Condensed Matter Nuclear Science, Hyatt Regency, Washington, DC, August 10-15, 2008.
8. D.A. Kidwell, M.M. Ross, and R.J. Colton, "The Mechanism of Ion Production in Secondary Ion Mass Spectrometry", *Int. J. Mass Spectrom. Ion Proc.*, **78** (1987) 315-328.
9. D.A. Kidwell, "Selective detection of species in complex matrices by chemical derivatization and secondary ion mass spectrometry", U.S. Patent #4,902,627 issued February 20, 1990.
10. These authors observed a 4.7% mass bias/AMU using a quadrupole instrument. Generally it is in the 1%/AMU range. See: A.R. Warren, L.A. Allen, H.M. Pang, R.S. Houk, and M. Janghorbani, "Simultaneous Measurement of Ion Ratios by Inductively-Coupled Plasma-Mass Spectrometry with A Twin-Quadrupole Instrument", *Applied Spectroscopy*, **48** (1994) 1360-1366.
11. J. Barling and D. Weis, "Influence of non-spectral matrix effects on the accuracy of Pb isotope ratio measurement by MC-ICP-MS: implications for the external normalization method of instrumental mass bias correction", *Journal of Analytical Atomic Spectrometry*, **23** (2008) 1017-1025.
12. Generally, ICP-MS can detect 1 PPT of an element, which would correspond to 1 PPM in the original sample if a 1:1000 dilution were made. Other techniques, such as glow discharge mass spectrometry, can also detect 1 PPM impurity levels directly.
13. Diluted *aqua regia* can also be used for surface analysis. However, it is yellow in color and makes visual estimation of the palladium content difficult.

14. G.H. Ayres, and E.W. Berg, "Separation of Palladium from Platinum, Iridium, and Rhodium with Dimethylglyoxime", *Analytical Chemistry*, **25** (1953) 980-981.
15. Palladium samples were kindly provided by Vittorio Violante.
16. Y. Arata, and Y.C. Zhang, "Anomalous production of gaseous 4He at the inside of 'DS cathode' during D2O-electrolysis", *Proc. Jpn. Acad., Ser. B*, **75** (1999) 281.
17. M. Balcerzak and K. Pcrgol, "Selective Determination of Platinum and Palladium in Iodide Media by Derivative Spectrophotometry", *Chem. Anal.* (Warsaw), **48** (2003) 87.