Accuracy in Trace Analysis

Graphite Furnace AAS: Application of Reduced Palladium as a Chemical Modifier

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Chemical modification techniques are widely used in graphite furnace atomic absorption spectrometry (GFAAS). Palladium is a very effective chemical modifier and can be used to stabilize many elements to several hundred degrees higher than the temperatures possible with current methods [1–9]. Of the elements tested, the greatest temperature shifts are achieved for the semi-metallic elements such as As, Se, Te, Bi, Sb, Pb, Tl, Ga, Ge and P. Ash temperatures can be raised 400–800 °C higher than current methods allow. Temperature shifts are somewhat less for the transition elements and ash temperatures can be raised 200–500 °C. Palladium has no similar effect on elements in Groups I and II of the Periodic Table. The change in stability is believed to be due to the formation of an intermetallic species. This improvement in stability permits more efficient removal of matrix constituents during the ash step and vaporization into a hotter environment during the atomize step. Background and interference problems are thus reduced or eliminated.

Steps taken to guarantee that palladium is present as the reduced metal as early as possible greatly improve performance of the modifier. The palladium modifier solution can be pre-injected and the graphite tube heated to 1000 °C. Such a method has been used to stabilize mercury [10]. It is assumed that at this temperature palladium metal is present on the graphite surface. The sample can then be introduced. The addition of a reducing agent such as 5% hydrogen in 95% argon, ascorbic acid, or hydroxylamine hydrochloride also appears to guarantee that the palladium is present as the metal early in the temperature program. The use of hydrogen as a reducing agent appears to be the method of choice for a number of reasons. It is cleaner, leaves no residue, and is less subject to contamination. It is also easy to use. A pre-mixed gas of 5% hydrogen in 95% argon can simply be introduced into the furnace. More importantly, the problem encountered with high concentrations of nitric acid is eliminated with the use of hydrogen.

Reduced palladium metal allows the retention of the analyte element on the graphite surface until a higher gas phase temperature is achieved. This appears to give many of the analytical advantages normally associated with platform atomization while using the simpler wall atomization technique.

Investigations to elucidate the mechanism of palladium chemical modification have been conducted. Also, comparison of palladium modifier methods with current modifier methods in spike recovery studies from difficult matrices was accomplished.

Scanning electron micrographs of graphite surfaces with palladium deposits obtained by different reduction methods were obtained to investigate whether the physical form of palladium influenced the modifier behavior. It was found that reduced palladium metal was indeed present on the graphite surface after reduction and that the most effective reduction method was the use of 5% hydrogen in 95% argon with a palladium solution containing 1% glycerol. The scanning electron micrograph of the surface produced under these conditions is shown in figure 1. The palladium particles are considerably smaller and more highly dispersed than those produced by other methods. The average particle diameter is 0.05–0.15 μm. The smaller particles result in a great increase in palladium surface area. Spike recovery studies from difficult matrices showed that smaller, highly dispersed particles produced improved interference performance.

The interference performance of a palladium/hydrogen/glycerol method for tin was compared with the performance of a commonly used method. The commonly used method requires the use of the platform and chemical modifiers of ammonium dihydrogen phosphate and magnesium nitrate. Wall atomization was used for the palladium method. The results of this study are listed in table 1. While both methods performed well in concentrated HCl, in most instances the palladium gave slightly better interference performance. It was significantly better in overcoming interferences from NaCl and seawater matrices. Other elements have been tested in the same matrices and, in virtually every instance, palladium gave as good as or better interference performance (wall) as did the currently used methods (platform).

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Table 1. Tin recoveries from interferent matrices

Interferent	Current method	Palladium method
	200 μg NH₄H₂PO₄ 10 μg Mg(NO₃)₂ Platform	20 μg Pd 150 μg glycerol 5% hydrogen Wall
5 μL 2.5% NaCl (125 μg)	22%[a] 26%[b]	91%[a] 110%[b]
5 μL 5.0% NaCl (250 μg)	0 0	92% 107%
5 μL Seawater	0 0	87% 99%
5 μL concentrated HCl	97% 92%	96% 100%
5 μL concentrated HNO₃	79% 87%	92% 93%
5 μL 20% H₂SO₄	39% 58%	60% 79%
5 μL 0.5% Na₂SO₄ (25 μg)	87% 85%	101% 101%
5 μL 1.0% Na₂SO₄ (50 μg)	82% 85%	103% 100%

[a] Peak height.
[b] Peak area.

The palladium modifier method has been utilized with numerous real samples as well as synthetic interferent matrices to test its applicability. The direct determination of selenium in biological fluids has shown excellent accuracy using palladium modification. Thallium has been accurately determined in brackish waters, soil digests and digested fish tissue. Work with other real samples is continuing.

In many situations, quite low concentrations of palladium may be used and accurate results still obtained. Table 2 compares recommended chemical modifier concentration ranges. The use of lower modifier concentrations decreases the possibility of analyte contamination and associated analysis problems.

In summary, reduced palladium chemical modification for graphite furnace AAS has been shown to be very useful. It can be used to improve difficult graphite furnace analyses. It has been applied to over 20 analyte elements and in each case has produced beneficial effects. It does not require the added complexity of platforms as it produces the same effects chemically. Reduced palladium may be as close to a "universal" modifier as possible for graphite furnace AAS.

Table 2. Recommended modifier concentration ranges (μg/mL)

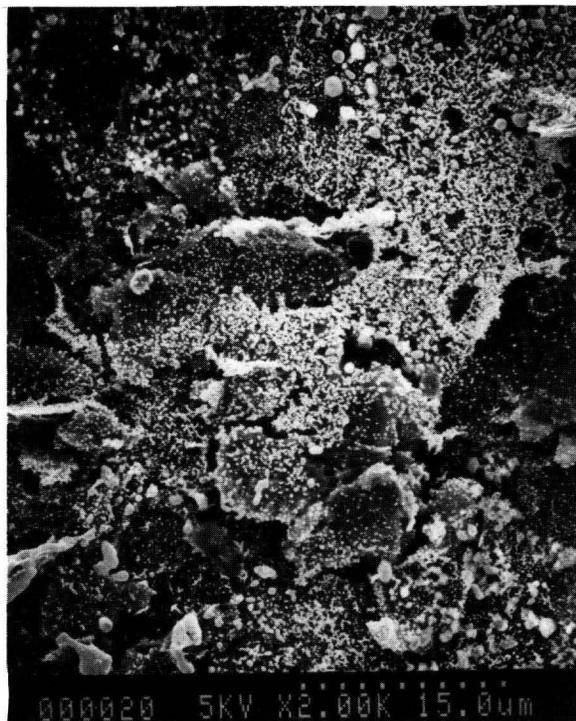| Modifier	Element	Current methods	Palladium method
Nickel	As	Up to 5000	50–1000
	Se	Up to 5000	50–1000
Mixed PO₄+[Mg(NO₃)₂]	Cd	Up to 20,000[1000]	50–1000
	Pb	Up to 20,000[1000]	50–1000
	Sn	Up to 20,000[1000]	50–1000
Mg(NO₃)₂	Fe	Up to 5000	50–1000
	Mn	Up to 5000	50–1000

Figure 1. Scanning electron micrograph of reduced palladium metal on graphite surface (20,000x magnification).

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The Determination of Trace Elements in Uranium Oxide (U₃O₈) by Inductively Coupled Plasma Emission Spectrometry and Graphite Furnace Atomic Absorption Spectrometry

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The observations and data presented here are drawn from a larger project which has as its objective the certification of a set of reference materials, known as CRM 123 (1–7), for the 18 trace elements contained in each of the seven levels which make up the set. Level 7 is high purity U_3O_8. Portions from the bulk of this same material were used as the base material for all the other concentration levels, which were made by adding known concentrations of impurity elements. CRM 123 (1–7) is a replacement for a previous reference material of the same type called CRM 98 (1–7). When that reference material was certified the workhorse methods were flame atomic absorption and spectrophotometric methods. Both graphite furnace atomic absorption (GFAA) and inductively coupled plasma emission spectrometry (ICP) had become established methods of analysis since then. The characterization of CRM 123 (1–7) provided an opportunity to take advantage of the greater sensitivity these newer methods could provide. In general the two techniques are complementary rather than competitive. A look at the characteristics of each method shows why we should have different expectations for each.

GFFA has a small linear dynamic range. The sensitivity for uranium is low; therefore, direct analysis without prior separation of uranium is possible. Volatile elements are the most sensitive analytes, so this should be a good method for cadmium, for example. A search of the literature [1–4] showed that the trail had already been blazed and that accurate results could be achieved in a 0.1 N nitric acid medium as long as the standards are matrix-matched for uranium as well. The amount of uranium present affects sensitivity. For cadmium there was no particular pattern for the sensitivity