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A COMPARISON OF TWO SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM IN TITANIUM-BASE ALLOYS

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Cleveland, Ohio

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ABSTRACT

This report compares extraction procedures using 1-nitroso-2-naphthol and dimethylglyoxime for the spectrophotometric determination of palladium in titanium-base alloys. Dimethyglyoxime has greater selectivity but lower sensitivity, similar precision (about 25 ppm at the 0.2 percent level), is faster and covers a wider range of palladium contents than does 1-nitroso-2-naphthol. The dimethylglyoxime procedure has no interferences by any of the common or potential alloying elements, for example, cobalt, niobium, and tantalum; thus it is well suited to the determination of 0.1 to 1.0 percent palladium in titanium-base alloys. Selectivity is improved by the presence of nitrate.

A COMPARISON OF TWO SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM IN TITANIUM-BASE ALLOYS

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SUMMARY

This report compares procedures using 1-nitroso-2-naphthol and dimethylglyoxime (DMG) for the spectrophotometric determination of small amounts of palladium in titanium-base alloys. The two reagents and methods are compared as to selectivity, sensitivity, precision of results, and speed of analysis. The effect of the presence of various ions commonly found in titanium-base alloys on the determination of palladium is shown for each method.

Several alloys have been analyzed for palladium by both methods, and the results show about equal precision. At the 0.2 percent level, the standard deviation is about 25 ppm.

While each reagent possesses certain advantages, either one is suitable for determining low levels of palladium in most of the commercially available titanium-base alloys. Although 1-nitroso-2-naphthol is the more sensitive reagent (its molar absorptivity is 23 000 compared to 1700 for DMG), DMG merits more attention than it has received. The procedure using DMG is faster, equally precise, and conveniently covers a wider range of palladium contents than does 1-nitroso-2-naphthol. Alloys containing cobalt or niobium and tantalum are better analyzed for palladium by DMG than by 1-nitroso-2-naphthol.

INTRODUCTION

The purpose of this report is to aid the analyst in the selection of a procedure for determining palladium in titanium alloys. Other elements which may be present include aluminum, chromium, cobalt, copper, iron, manganese, molybdenum, niobium, tantalum, tin, vanadium, and zirconium.

Small amounts of palladium, for example, 0.1 to 0.2 percent, have been added to titanium-base alloys to increase resistance to stress corrosion. Certain structural components in supersonic aircraft and submarines are candidates for use of these alloys. A use of increasing importance is in construction of large-scale desalination plants. These alloys have been used for some time in chemical plant equipment exposed to hydrochloric and sulfuric acids.

Palladium may be determined in a variety of ways. Large amounts (5 to 25 mg) are usually determined gravimetrically by precipitation with dimethylglyoxime (DMG) from a weak acid (0.2M HCl) solution. This procedure is nearly specific (gold and selenium are reduced to the metal and platinum is partially precipitated). Palladium dimethyglyoximate is of definite composition and can be dried and weighed in the same way as the nickel compound.

Small amounts of palladium may be determined spectrophotometrically, usually after separation from other colored ions by solvent extraction of a palladium complex into a water-immiscible solvent. Beamish (ref. 1) lists about 50 colorimetric reagents for palladium through 1962 and others have appeared more recently. Two common organic reagents that form extractable complexes with palladium are 1-nitroso-2-naphthol and DMG. These were chosen for study because the first has already been successfully applied to titanium alloys and the second has its high specificity to recommend it.

The first part of this report, DISCUSSION OF 1-NITROSO-2-NAPHTHOL, presents a summary of the early uses of 1-nitroso-2-naphthol as an analytical reagent followed by its more recent use as a spectrophotometric reagent for palladium. A description of the present work includes the effect of reaction conditions on the spectrophotometric determination of palladium in titanium-base alloys. The precision, sensitivity, and effect of diverse ions are also shown for the method. Because of the interference caused by cobalt, niobium, and tantalum, it is recommended that alloys containing these elements be analyzed for palladium with dimethylglyoxime. The recommended analytical procedure is described in appendix A.

The second part of this report, DISCUSSION OF DIMETHYLGLYOXIME, gives a brief history of the early use of dimethylglyoxime as an analytical reagent. The use of other reagents containing the oxime group as spectrophotometric reagents for palladium are reviewed. In the present work, the suitability of dimethylglyoxime for the spectrophotometric determination of palladium in titanium-base alloys is examined. The low sensitivity is shown to be adequate for determining 0.1 to 1.0 percent palladium. The high selectivity of the reagent is even further improved by the presence of nitrate. The tolerance of the method to different reaction conditions, its superior speed, and its satisfactory accuracy and precision make it an ideal reagent for this application. The recommended analytical procedure is described in appendix B.

DISCUSSION OF 1-NITROSO-2-NAPHTHOL

Feigl (ref. 2, p. 252) states that if organic reagents that form colored precipitates with metal ions were arranged in the chronological order of their discovery, the list would be headed by 1-nitroso-2-naphthol. The compound was prepared by Ilinski and von Knorre (refs. 3 and 4) in 1884, and almost at once it was found to be a precipitant for cobalt. Later, von Knorre (refs. 5 to 8) recommended it as a reagent for cobalt and ferric iron. Schmidt (ref. 9) proved that it is a sensitive precipitant for palladium, and Bellucci and Savoia (ref. 10) found that it precipitates zirconium. Copper and gold (ref. 11) are precipitated but none of the other platinum metals. Thus, 1-nitroso-2-naphthol is a selective reagent whose value rests on the fact that maintenance of certain conditions permits the realization of specific tests and quantitative determinations.

Either 1-nitroso-2-naphthol or 2-nitroso-1-naphthol can be used for determining 0.5 to 5 ppm of palladium (ref. 1). Cheng (ref. 12) found that the two naphthol derivatives have about equal sensitivity but preferred 2-nitroso-1-naphthol because the interference by cobalt(II) and iron(III) was completely eliminated by (ethylenedinitrilo) tetraacetic acid disodium salt (EDTA) for 2-nitroso-1-naphthol but not for the 1,2-isomer. In Cheng's procedure, the naphtholate complex is formed at a pH of 1.5 to 3.5 in the presence of EDTA, the solution is made basic with ammonium hydroxide, and the complex is extracted with toluene.

Alvarez (ref. 13) used the orange toluene extracts of palladium 1-nitroso-2-naphtholate from an acid solution. Excess reagent was scrubbed out of the extract with dilute base. The color intensity is greater when the extraction is made from neutral or weakly acidic solutions than from strongly acidic or alkaline media. The complex is stable in 1.5N acid but is partly destroyed in strongly acidic or alkaline solutions.

Ross, Kesser, and Kucera (ref. 14) used 2-nitroso-1-naphthol for determining less than 1 percent palladium in uranium-fission element alloys and found that uranium, ruthenium, molybdenum, zirconium, rhodium, zinc, and cadmium do not interfere. Their procedure adopts some of the features of the methods of Cheng and Alvarez: the complex is formed at a pH of 1 to 2 in the presence of EDTA, extracted with toluene, scrubbed free of excess reagent with 1N sodium hydroxide and finally centrifuged before measurement.

Baird, Valent, and Miles (ref. 15) selected the 1,2-isomer as most suitable for determining palladium in titanium alloys. Their extensive study showed no interference from up to 100 percent titanium, 8 percent aluminum, about 1 percent copper and iron, 4 percent molybdenum, 11 percent tin, 4 percent vanadium, and 5 percent zirconium. They found that chromium, if oxidized to valence six, interferes at any level and that this may occur by heating to heavy sulfuric-perchloric acid fumes. They proved that this interference can be eliminated by adding a few crystals of ferrous ammonium sulfate after fuming. Alloys containing as much as 11 percent chromium were satisfactorily analyzed by this expedient. These authors do not use EDTA in their procedure. The complex is formed in a solution containing 20 milligrams sample and 0.5 gram citric acid by adding 1 milliliter 0.05 percent 1-nitroso-2-naphthol in ethanol. The solution is mixed and the color allowed to develop for 2 hours. A 25-milliliter portion of toluene and 1 milliliter (1+1) ammonium hydroxide are added and shaken for 30 seconds; then the layers are allowed to separate for 15 minutes. The aqueous layer is discarded, and the toluene layer is transferred to a small beaker. The beaker effectively traps water droplets and prevents them from transferring to the cells. A portion of the toluene extract is transferred to 1-centimeter cells and the absorbance measured at 430 nanometers against a reagent blank.

Kodama (ref. 16) used 1-nitroso-2-naphthol and the 2, 1-isomer in perchloric or sulfuric acid solutions and extracted the palladium complex with chloroform. Chloride is reported to be an interference.

It was observed in the present work that the sensitivity to 1-nitroso-2-naphthol decreases with increasing chloride concentration (see fig. 1). The extent of this interference was found in tests in which potassium chloride, in amounts up to 1 gram, was added to solutions containing 10 milligrams titanium and 10.81 or 21.62 micrograms palladium. Under the conditions of the procedure used, the extraction of palladium decreases

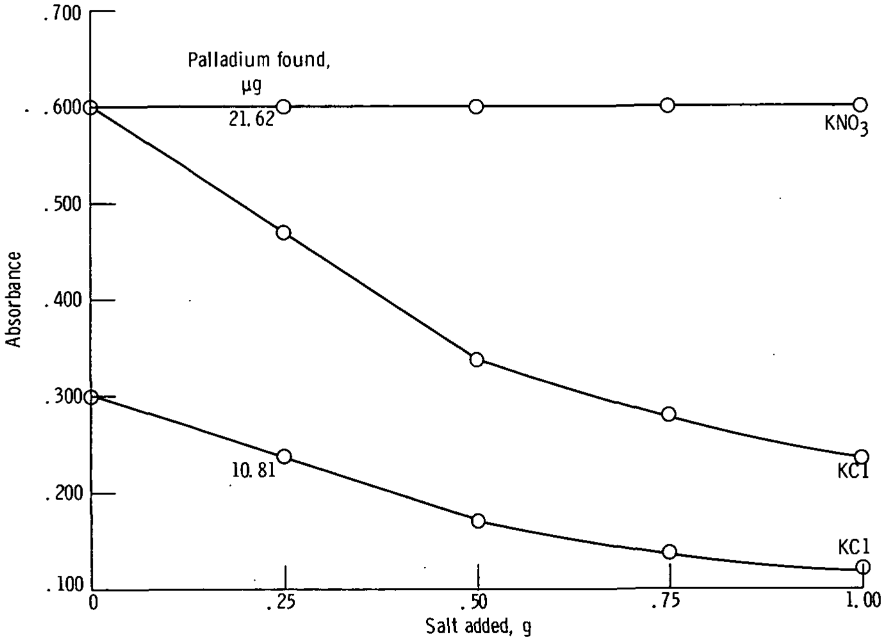

Figure 1. - Effect of potassium chloride and potassium nitrate on 1-nitroso-2-naphthol procedure (10 mg titanium present). Beckman Model B spectrophotometer; 425 nanometers; 2-centimeter cells; 15 milliliters toluene.

linearly up to 0.5 gram of KCl added, then, as KCl separates out of solution, at a lesser rate up to 1 gram. In contrast, the addition of up to 1 gram potassium nitrate has no effect on the extraction of palladium with 1-nitroso-2-naphthol. In the adopted procedure, the solution of the alloy is fumed with sulfuric-perchloric acids before extraction; thus chloride, fluoride, and nitrate are removed. The use of a small amount of fluoboric acid along with hydrochloric or sulfuric acid is very advantageous for the dissolution of titanium alloys because of its good solvent properties.

In the procedure described here, the pH of the solutions to be extracted is not adjusted. The method of preparation controls the pH within the desired range. The color intensity of the complex is independent of pH in the range 1 to 4. It is recommended that pH adjustment be avoided because of possible hydrolysis of titanium with sodium hydroxide, or possible hexammine complexation of palladium (analogous to that of cobalt (ref. 2, p. 259)) with ammonium hydroxide. The usual pH at the time of extraction with this procedure is 1.5±0.5.

After the reagent is added, a short period of standing is necessary to form the 1 to 1 complex before extracting with toluene (see table I). The absorbance is slightly greater with a standing period of 30 minutes than with 10 minutes; standing periods greater than 30 minutes gave no further increase in absorbance.

By performing tests with known amounts of palladium, it was found that sensitivity was improved when 0.1 milliliter 0.5 percent 1-nitroso-2-naphthol was used, instead of

TABLE I. - EFFECT OF TIME OF STANDING[a]

Time, min	Absorbance[b]	
	Ti-Al-blank[c]	Ti-Al-Pd standard[d]
10	0.020	0.323
30	.020	.333
60	.019	.332
120	.019	.334

[a] After adding 0.1 ml 0.5 percent 1-nitroso-2-naphthol in ethanol before extracting with toluene.

[b] Measured at 425 nm in 2-cm cells and 15 ml toluene.

[c] 6 mg Ti + 0.3 mg Al.

[d] 6 mg Ti + 0.3 mg Al + 11.29 μg Pd.

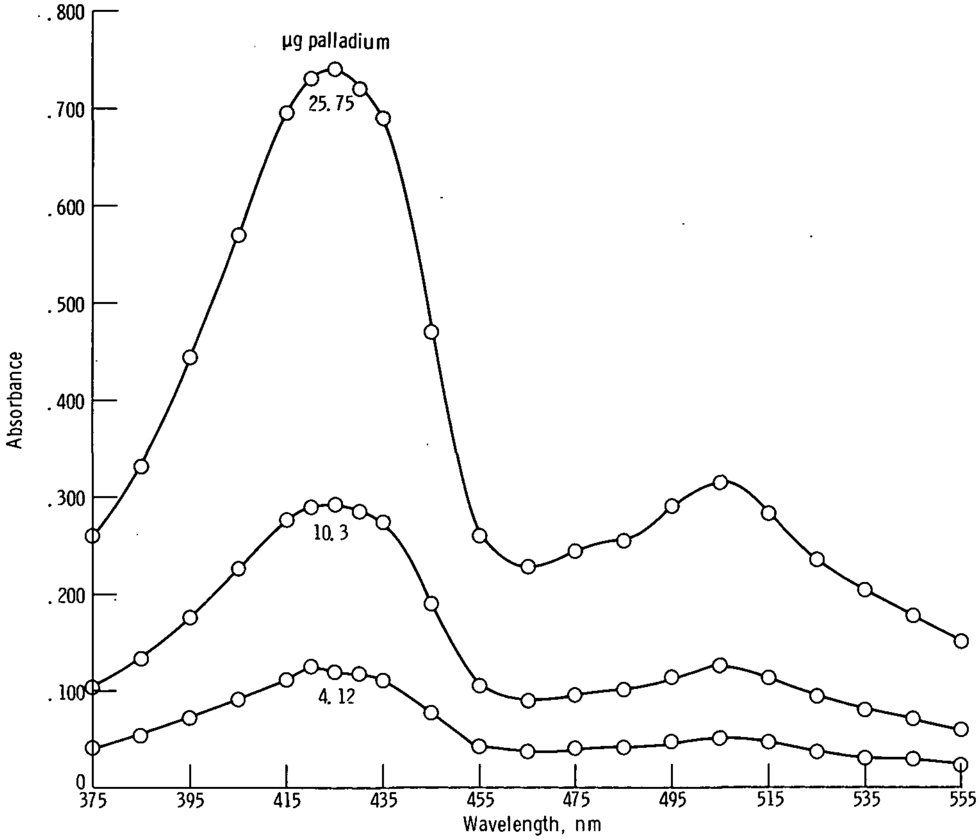

Figure 2. - Absorption spectrum of palladium-1-nitroso-2-naphtholate in toluene. Beckman Model B spectrophotometer; 2-centimeter cells; 15.00 milliliters toluene.

1 milliliter 0.05 percent reagent. Keeping the volume of alcohol as small as possible apparently increases the extraction efficiency.

Any excess reagent is also extracted into toluene, but it can be removed without affecting the palladium complex by scrubbing the extract with 2 percent NaOH solution. This reduces the blank to a low reproducible value equivalent to 0.6 to 0.7 microgram palladium. A trial in which (1+1) ammonium hydroxide was used as a wash solution gave a much higher blank value.

The extract is centrifuged to remove suspended water droplets and the absorbance is measured at 425 nanometers with toluene in the reference cell. Beer's law is obeyed, and the molar absorptivity is about 23 000 (figs. 2 and 3). The absorbance of the colored complex is quite stable - there is no change in 3 days.

As would be expected, in view of the introductory remarks, cobalt interferes in the palladium determination by 1-nitroso-2-naphthol at greater than trace levels (see

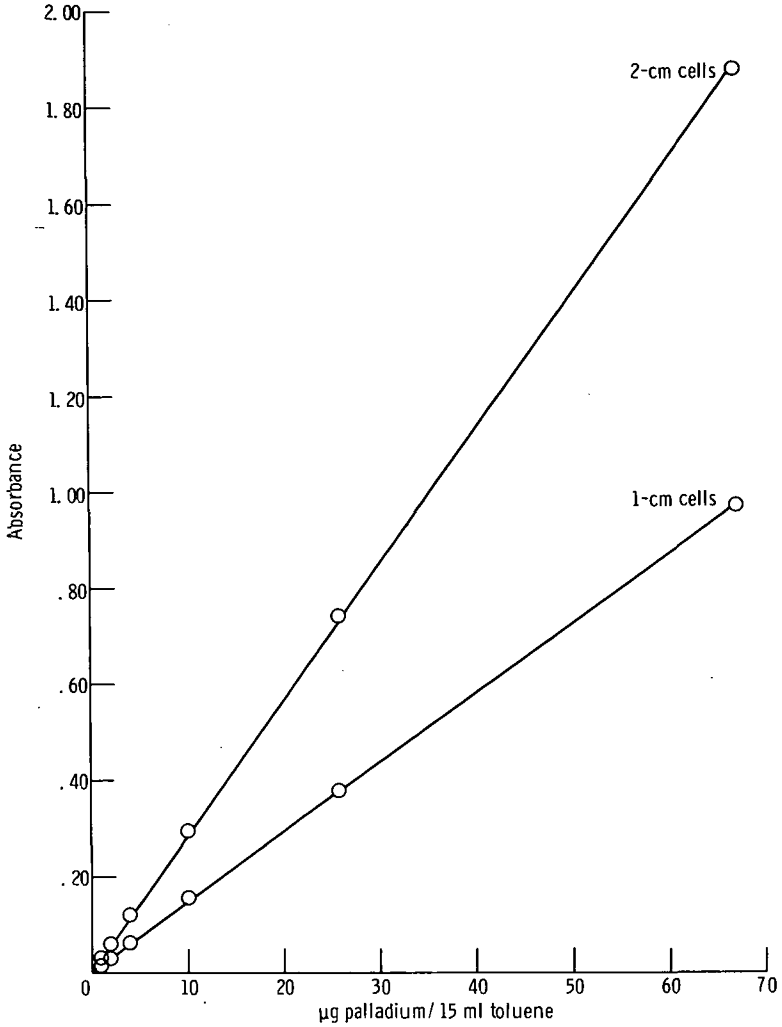

Figure 3. - Calibration curve for palladium-1-nitroso-2-naphtholate in toluene. Beckman Model B spectrophotometer; 425 nanometers; 1- and 2-centimeter cells.

table II). EDTA does not prevent this interference except at the very lowest levels; it is not very effective as a masking agent because of its low solubility in the solutions used.

Fortunately, cobalt does not occur in any of the common titanium alloys. Recently, however, the alloy Ti-6Al-4V-3Co has been introduced (refs. 17 and 18) and is reported to have certain advantages over the same alloy without cobalt. The determination of palladium in alloys containing cobalt requires the use of another reagent such as the 2,1-isomer or dimethylglyoxime. A procedure using the latter reagent is described in the next section of this report.

Aluminum, boron, and other common elements do not interfere. For example, addition of 1- to 2-milligram amounts of chromium(III), copper(II), iron(III), manganese(II), molybdenum(VI), tin(IV), vanadium(V), and zirconium(IV) to 10 to 20 milligrams tita-

TABLE II. - EFFECT OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH 1-NITROSO-2-NAPHTHOL

Ion added[a]	Palladium added, μg	Palladium found, μg	Deviation, μg
2 mg Al(III)	21.62	21.77	+0.15
2 mg Cr(III)	21.62	21.56	-.06
2 mg Cr(VI)	21.62	21.87	+.25
2 mg Cr(VI) + 50 mg FAS[b]	21.62	21.45	-.17
10 μg Co(II)	28.83	28.77	-.06
100 μg Co(II)	28.83	28.59	-.24
1 mg Co(II)	28.83	26.18	-2.65
10 μg Co(II) + EDTA[c]	21.62	21.28	-.34
100 μg Co(II) + EDTA[c]	21.62	21.15	-.47
1 mg Co(II) + EDTA[c]	21.62	19.20	-2.42
2 mg Cu(II)	21.62	21.59	-.03
2 mg Fe(II)	21.62	21.45	-.17
50 mg FAS	21.62	21.25	-.37
2 mg Fe(III)	21.62	21.49	-.13
2 mg Mn(II)	21.62	21.73	+.11
2 mg Mo(VI)	21.62	21.52	-.10
2 mg Ni(II)	21.62	21.52	-.10
2 mg Sn(II)	21.62	20.26	-1.36
2 mg Sn(IV)	28.83	28.77	-.06
2 mg V(V)	21.62	21.49	-.13
2 mg Zr(IV)	21.62	21.69	+.07

[a] Each solution contains 12.5 mg Ti(IV).
[b] FAS = ferrous ammonium sulfate.
[c] 2 ml 3 percent EDTA solution.

nium(IV) cause no difficulty in the determination of 10 micrograms palladium. Addition of 1 to 2 milligrams nickel(II) increases the blank slightly in the absence of EDTA but the sensitivity to palladium is unchanged. When 2 milliliters 3 percent EDTA are present, the blank is normal. This effect is probably due to traces of cobalt in the nickel solution. Addition of 1 to 2 milligrams tin(II), fumed with sulfuric acid alone, causes low results for palladium. With the same amount of tin(IV), fumed with sulfuric and perchloric acids, recovery is normal.

Results of the recovery of palladium added to four titanium-base alloys are presented in the following table:

Alloy	Sample weight extracted, mg	Palladium added, μg	Palladium found, μg	Percent recovery
Ti-6Al-4V	4.48	11.29	11.36	100.6
Ti-4Al-4Mn	4.02		11.33	100.3
Ti-5Al-2.5Sn	4.41		11.29	100.0
Ti-8Al-2Nb-1Ta	.75		10.89	96.5

Samples of NBS 173 (Ti-6Al-4V), NBS 174 (Ti-4Al-4Mn), Ti-5Al-2.5Sn, and Ti-8Al-2Nb-1Ta were dissolved in hydrochloric and fluoboric acids. Aliquots of each were spiked with palladium before fuming with sulfuric and perchloric acids. Somewhat low recovery of palladium occurred when added to a solution of Ti-8Al-2Nb-1Ta. During acid fuming, a precipitate formed which did not dissolve completely on warming with citric acid. It is recommended that palladium be determined in this alloy with dimethylglyoxime.

The precision obtainable in the analysis for palladium with 1-nitroso-2-naphthol is indicated by the results for a titanium-base alloy that was procured from Ledoux & Company, Teaneck, N. J.

Two separate samples of the alloy, about 0.4 gram, were dissolved in 50 milliliters hydrochloric acid and 4 milliliters fluoboric acid, oxidized by dropwise addition of nitric acid and then diluted to 100 milliliters. Two separate 10.00-milliliter aliquots from one solution and a 10.00-milliliter aliquot from the other solution were fumed with sulfuric and perchloric acids and diluted to 100 milliliters. Aliquots of the fumed diluted solutions were then analyzed by the usual 1-nitroso-2-naphthol procedure. Results are as follows:

Sample aliquot		
1a	1b	2
Palladium found, ppm*		
1926	1898	1925
1913	1891	1873
1917	1909	1894
1891	1880	1952
1916	1918	1929
1944	1944	

*Arithmetic mean,
$\bar{x}$ = 1913 ppm.
Standard deviation,
σ' = 23 ppm.

TABLE III. - RESULTS OF ANALYSIS OF TITANIUM-BASE ALLOYS FOR PALLADIUM BY 1-NITROSO-2-NAPHTHOL

Alloy		
Ti-3Al-0.2Pd	Ti-0.4Pd	Ti-0.8Pd
Palladium found, ppm		
2032	4115	8101
2002	4066	7954
2032	4109	8048
2028	4129	8056
2055	4219	8230
2071	4219	8172
2066	4123	7868
2073	4114	7898
[a]2045 [b]24	[a]4137 [b]23	[a]8041 [b]110

[a] Arithmetic mean, $\bar{x}$.
[b] Standard deviation, σ.

Results obtained in the analysis of titanium-base alloys made at the Lewis Research Center are shown in table III to indicate precision at three different levels of palladium content.

In summary, 1-nitroso-2-naphthol is a sensitive and selective reagent for the determination of palladium. It is suitable for accurately determining less than 1 percent of this element in most of the existing and potential titanium alloys.

DISCUSSION OF DIMETHYLGLYOXIME

The reactivity of dimethylglyoxime with nickel and palladium salts was first observed by L. Tschugaeff (ref. 19) in 1905. The following year, K. Kraut (ref. 20) used the reagent to detect nickel and measure its distribution in nature. In 1907, O. Brunck (ref. 21) used DMG for the separation and gravimetric determination of nickel in the presence of iron, cobalt, zinc, manganese, aluminum, and chromium. Wunder and Thüringer (refs. 22 to 25) separated palladium from nickel, platinum, rhodium, and iridium as well as from copper and iron with DMG in 1913. Since that time, a great many procedures using DMG have appeared in the literature (ref. 26, pp. 55-61).

The behavior of DMG (other dioximes act similarly) toward metal ions illustrates the dependence of the activity of the dioxime group on the reaction conditions. Since DMG precipitates nickel only from a weak acid or ammoniacal solution, but precipitates palladium from a dilute mineral acid solution, it is almost a specific reagent for palladium. In hydrochloric acid solution (refs. 26, p. 40 and 27), gold is reduced to the metal by the reagent and platinum is partially precipitated, either as the metal or as a greenish complex compound, on boiling the solution. The presence of a small amount of nitric acid has been reported (ref. 28) to prevent reduction of gold to the metal and of platinum(IV) to platinum(II). Platinum(II) dimethylglyoximate is also extracted by chloroform.

F. Feigl (ref. 2, p. 274) states that it is incorrectly recorded in the literature that palladium dimethylglyoximate is soluble in ammonia, and thus, no precipitate appears when DMG is added to an ammoniacal palladium solution. Unpublished studies of F. Feigl and H. A. Suter revealed the following: No precipitate appears, even after 3 to 4 hours standing at room temperature, when the reagent is added to a strong ammoniacal solution containing colorless $[Pd(NH_3)_2]^{2+}$ ions. On longer standing, and especially with warming, the solution turns yellow, and incomplete precipitation of palladium dimethylglyoximate results. The 1 to 2 compound can be isolated by precipitation from an acid solution and, after washing, is only slightly soluble in ammonia even on warming.

A further qualification of the precipitation specificity of DMG in ammoniacal solution is necessary when iron(III) and cobalt(II) are present together. At higher concentrations of these ions in a solution that also contains tartrate, brown-red $FeCoC_{12}H_{19}N_6O_6$ is precipitated, even though these ions if alone are not precipitated. Cobalt salts give brown-violet soluble complex compounds, while ferric salts remain unchanged.

An ammoniacal copper solution gives a red-brown color with DMG, and a violet shade if oxidizing agents are present. Ferrous salts in tartrate solution develop a red color when treated with DMG and ammonia. The solution becomes colorless when the ferrous ion is oxidized.

Both palladium and nickel can be precipitated by DMG from acetic acid solutions. According to Feigl (ref. 2, p. 274), the specific precipitability of palladium(II) ions from acid solutions holds only for nitric acid solutions.

Yellow palladium dimethylglyoximate dissolves (ref. 2, pp. 99 and 276) in potassium hydroxide solution and the subsequent addition of a ammoniacal nickel solution produces no red precipitate; in this case, DMG is masked because it remains linked with the palladium.

A sensitive and selective cobalt reaction is based on the fact that the addition of alkali sulfide to ammoniacal cobalt solutions containing DMG does not produce a precipitate of cobalt sulfide; instead, a red-violet color develops.

The dimethylglyoxime precipitation of nickel is incomplete in the presence of large amounts of nitrate, and pink solutions are formed. Feigl (ref. 2, p. 278) showed that nickel is oxidized from valence two to four. Many oxidants dissolve nickel dimethylglyoximate suspended in fixed base or ammonia and produce a pink solution.

The color reaction resulting from the formation of soluble nickel(IV)-dimethylglyoximate is about 50 times as sensitive as the precipitation of the familiar red nickel(II)-dimethylglyoximate. This was made the basis of a colorimetric method for small amounts of nickel by Rollet (ref. 29). The remarkable stability of nickel(IV)-dimethylglyoximate is shown by the fact that it is unaffected by cyanide ions, while nickel(II)-dimethylglyoximate is soluble in KCN.

In recent years, colorimetric methods of high specificity for palladium have been developed in which separation is achieved by chloroform extraction with various dioximates. The absorbance of the usually yellow extract is then measured. O. Menis and T. C. Rains (ref. 30) found α-furildioxime to be a very sensitive and highly selective reagent for palladium using a chloroform extraction procedure. Nioxime (refs. 31 to 33) (1, 2-cyclohexanedione dioxime) and its 4-methyl- and 4-isopropyl- derivatives (refs. 34 and 35) show high sensitivity and specificity for only nickel and palladium. Ayres and Martin (ref. 36) determined palladium by chloroform extraction with glyoxime, the simplest of the dioximes. R. S. Young (ref. 28) determined palladium in silver assay beads by dithizone titration after separation with DMG using chloroform extraction.

Ayres and Tuffly (ref. 37) found the extraction procedure unsatisfactory for 10- to 20-milligram amounts of palladium; but Fraser, Beamish, and McBryde (ref. 38), were able to completely extract up to 1 milligram of palladium from solutions containing 15 grams of lead. Beamish (ref. 1) states that Kodama preferred dimethylglyoxime to 1-nitroso-2-naphthol when interference from chloride was to be avoided. However, Sandell (ref. 39) considers dimethylglyoxime not very suitable for palladium because of its low sensitivity. Nielsch (ref. 40) has reported on the determination but did not discuss possible interferences or its technical applications.

In the present work, dimethylglyoxime was chosen for study because of its high selectivity for palladium with reaction conditions that are compatible with solutions of titanium and its alloys.

The reagent was found to have adequate sensitivity to determine 0.1 to 1.0 percent palladium in all of the common titanium alloys. The molar absorptivity is 1700 (liters) $(\text{moles})^{-1}(\text{centimeters})^{-1}$, and Beer's law is obeyed. The precision is about 25 ppm at the 0.2 percent level. Cobalt, niobium, and tantalum do not interfere at a 3, 2, and 1 percent level, respectively. There is no interference by chloride or other common ions. The procedure is faster than with 1-nitroso-2-naphthol because fuming with sulfuric and perchloric acids is not necessary. Less than 5 micrograms up to nearly 1 milligram palladium may be extracted and determined by measurement of the absorbance of its dimethylglyoxime complex in chloroform (figs. 4 and 5). This compares with a range

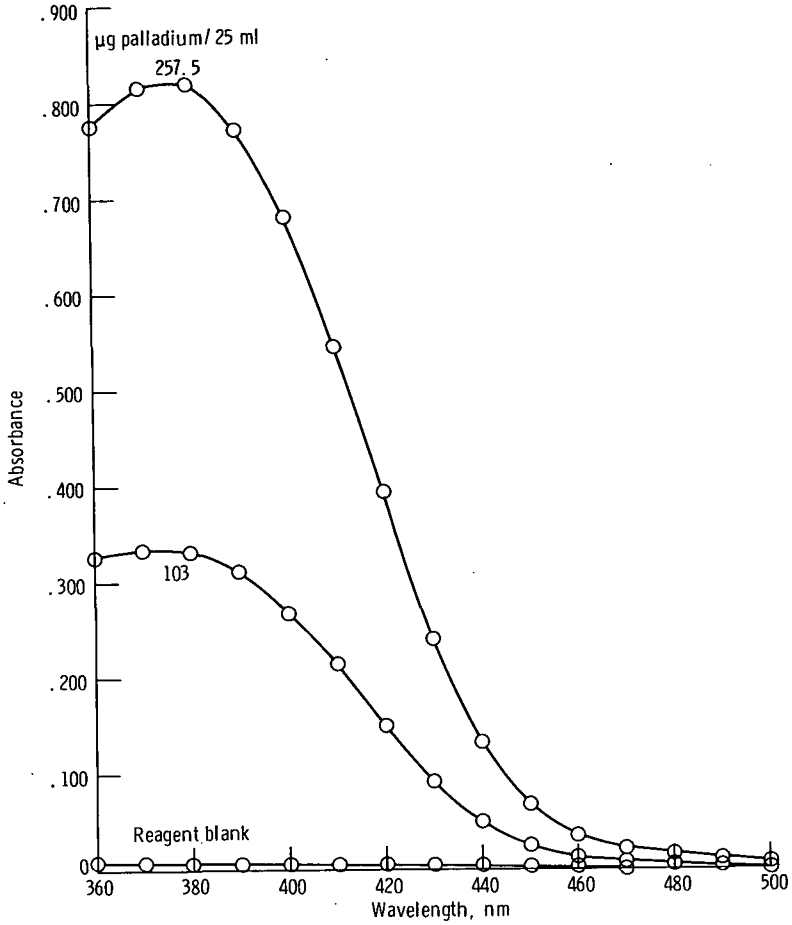

Figure 4. - Absorption spectrum of palladium dimethylglyoximate in chloroform. Beckman Model B spectrophotometer; 5-centimeter cells.

of about 1 to 65 micrograms palladium when the 1-nitroso-2-naphthol complex is extracted with toluene and its absorption measured at 425 nanometers by the procedure described previously (fig. 3). (However, it appears possible, by using a secondary absorption peak at 505 nanometers, to extend this range several-fold, fig. 2.) Also, of course, the volume of solvent may be increased.

The blank in the DMG procedure is low and constant, about 0.010 absorbance unit using a 5-centimeter cell, equivalent to about 3 micrograms palladium. Although most of the complex is separated in the first extract, three 7- to 8-milliliter portions of chloroform are used in the procedure and are sufficient for all but the highest amounts of palladium.

The procedure has been applied to the determination of 0.2 to 0.8 percent palladium in several titanium-base alloys. The effect of many common ions has been investigated.

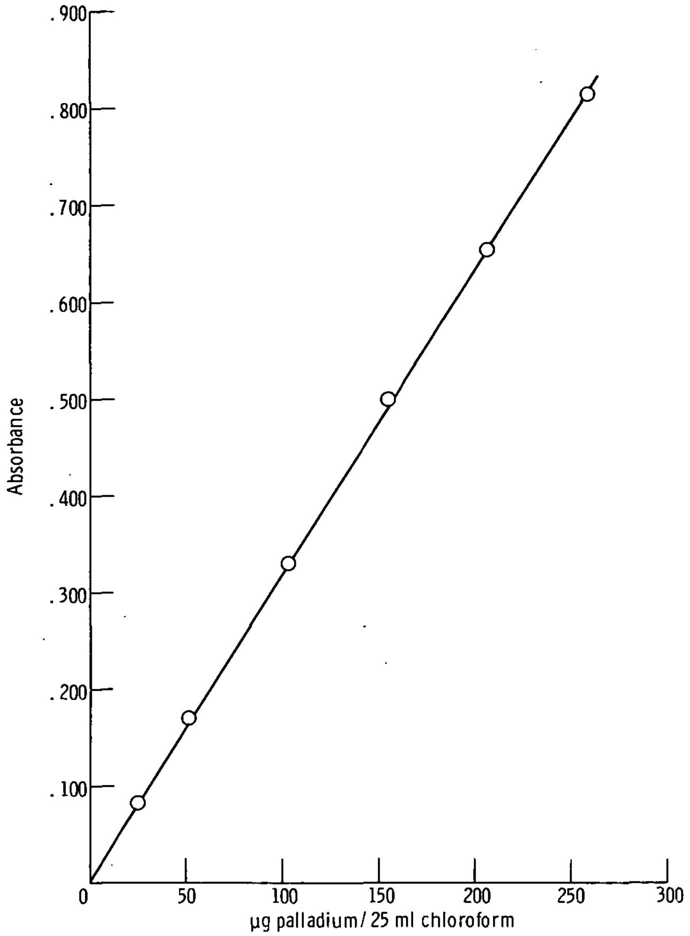

Figure 5. - Calibration curve for palladium dimethylglyoximate extracted with chloroform. Beckman Model B spectrophotometer; 380 nanometers; chloroform reference; 5-centimeter cells.

A nominally Ti-0.18Pd alloy was obtained from Ledoux & Company, Teaneck, N. J., for testing the procedure. Two ~0.4-gram samples were dissolved in hydrochloric acid and a little fluoboric acid, then oxidized with nitric acid. Aliquots of these solutions were analyzed for palladium by the DMG procedure. The results, in ppm palladium found, were 1895, 1859, 1878, and 1898. Several titanium-palladium alloys prepared at the Lewis Research Center have been analyzed for their palladium content by the DMG procedure. The nominal compositions of these alloys and the results of the analysis are shown in table IV.

The data in this table indicate erratic results in the presence of ammonium hydroxide, probably because of formation of competing complexes. Precision is satisfactory, however, when there is no pH adjustment. Samples prepared according to the procedure

TABLE IV. - RESULTS OF ANALYSIS OF TITANIUM-BASE ALLOYS FOR PALLADIUM BY DIMETHYLGLYOXIME - EFFECT OF AMMONIUM HYDROXIDE

Alloy					
Ti-3Al-0.2Pd	Ti-0.4Pd	Ti-0.8Pd	Ti-3Al-0.2Pd	Ti-0.4Pd	Ti-0.8Pd
pH adjusted to 2.0 with NH_4OH			No pH adjustment (pH ~ 1.5)		
Palladium found, ppm					
2312	4056	8123	2013	4119	7976
2086	4330	7959	2052	4084	7998
1964	4573	8874	2073	4233	7896
1964	4602	9246	2073	4206	7933
			2085	4257	8102
			2085	4283	7938
			2044	4141	8049
			2044	4141	8233
			[a]2064 [b]27	[a]4183 [b]72	[a]8016 [b]110

[a] Arithmetic mean, $\bar{x}$.

[b] Standard deviation, σ.

have a pH of about 1.5 at the time of extraction.

In order to assess the accuracy of the DMG extraction procedure for the determination of palladium, three alloys analyzed by the previous method were also analyzed by the 1-nitroso-2-naphthol method and the results compared.

The data in table V indicate satisfactory agreement, although results are slightly higher by the DMG method than by the 1-nitroso-2-naphthol method. Also, compare the data in table IV with that in table III. The sample C-358, when fumed with sulfuric and perchloric acids, shows about the same result by the DMG method as the same sample by the 1-nitroso-2-napthol method. This may indicate that fuming causes slightly lower results. Adjusting the samples to a pH of 2.0 with ammonium hydroxide appears to have no adverse effect on the results obtained by the 1-nitroso-2-naphthol method. The effect of various common ions on the determination of palladium by extraction of its DMG complex with chloroform was investigated with the following results.

The data in table VI indicate significant deviations only with 5 milligrams copper (II), 10 milligrams iron(III), and 5 milligrams nickel(II). The aforementioned tests were carried out using a KCl-HCl buffer. In order to find out whether use of a KNO_3-HNO_3 buffer would improve the specificity of the DMG procedure, various foreign ions were

TABLE V. - COMPARISON OF THE RESULTS OF ANALYSIS TO TITANIUM-BASE ALLOYS FOR PALLADIUM WITH DIMETHYLGLYOXIME AND 1-NITROSO-2-NAPHTHOL

Dimethylglyoxime method			1-Nitroso-2-napthol method[a]		
Alloy					
C-349	C-354	C-358	C-349	C-354	C-358
Palladium found, ppm					
2017	4096	8284	1932	3984	8090
1985	4096	8284	[b]1961	[b]4010	[b]8106
1969	4053	8135	[b]1945	[b]4013	[b]8096
1969	4053	8149	1955	4011	8109
		[a]8080			[b]8086
		[a]8080			8100
[c]1985	[c]4075	[c]8169	[c]1948	[c]4004	[c]8098

[a] Samples were fumed with sulfuric and perchloric acids.

[b] Samples were adjusted to a pH of 2.0 with ammonium hydroxide.

[c] Arithmetic mean, $\bar{x}$.

TABLE VI. - EFFECT OF DIVERSE IONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM WITH DIMETHYLGLYOXIME

Foreign ion	Palladium added, μg	Palladium found, μg	Deviation, μg
100 mg Ti(IV)	28.8	28.8	0.0
40 mg Al(III)	28.8	28.5	-.3
10 mg Cr(III)	51.5	51.8	+.3
10 mg Co(II)	51.5	52.5	+1.0
5 mg Cu(II)	51.5	57.3	+5.8
2 mg Cu(II)	51.5	52.5	+1.0
10 mg Fe(III)	51.5	53.8	+2.3
50 mg Fe(II)	51.5	52.8	+1.3
5 mg Mo(VI)	28.8	29.2	+.4
5 mg Ni(II)	51.5	58.1	+6.6
2 mg Ni(II)	51.5	51.5	0.0
5 mg V(V)	51.5	52.6	+1.1
2 mg Zr(IV)	51.5	51.5	0.0
1 g citric acid	25.8	25.8	0.0
1 g tartaric acid	25.8	25.7	-.1
1 g oxalic acid	25.8	25.7	-.1
1 ml nitric acid, 70 percent	28.8	28.8	0.0
1 ml fluoboric acid, 48 percent	28.8	28.8	0.0

TABLE VII. - COMPARISON OF THE SPECIFICITY OF THE DIMETHYLGLYOXIME PROCEDURE FOR PALLADIUM USING CHLORIDE AND NITRATE BUFFER SOLUTIONS

Foreign ion	Percent recovery of 28 to 36 μg Pd	
	KCl-HCl buffer[a]	KNO_3-HNO_3 buffer[b]
5 mg Cu(II)	101.6; 103.9	100.0
5 mg Fe(III)	98.9	101.1
5 mg Ni(II)	101.6	98.9
5 mg Cr(III)	102.5	101.1
5 mg Co(II)	98.9	101.1
5 mg Mo(V)	101.4	100.0
5 mg V(V)	101.6; 102.7	100.0
5 mg Zr(IV)	96.1	100.0
20 mg Ti-6Al-4V	97.8	98.9
20 mg Ti-4Al-4Mn	97.8	97.8
20 mg Ti-5Al-2.5Sn	97.8	100.0
20 mg Ti-8Al-2Nb-1Ta	98.9	98.9

[a] 10 ml 0.05M KCl-0.06M HCl added as buffer.
[b] 10 ml 0.25M KNO_3-0.25M HNO_3 added as buffer.

tested for their effect on the recovery of palladium with the two different buffers (table VII).

The data in table VII indicates a higher degree of specificity for the extraction of palladium from weakly acid solutions of many ions when a nitrate buffer is present. The purpose of the buffer is to level out variations in salt content and acidity in the various samples. The volume extracted was 20 milliliters in all cases.

Tests of the recovery of palladium from chloride solutions of the noble metals gold, iridium, platinum, rhodium, and ruthenium showed interference by gold and ruthenium (4 mg metal added), but nearly normal recovery from the others. Gold caused a large positive interference, while ruthenium caused a negative interference because it precipitated during extraction.

The absorbance of the blank was found to increase, and the sensitivity for palladium to decrease, with increase in hydrochloric acid below a pH of 1.0. No pH adjustment is recommended as sodium hydroxide may precipitate titanium and ammonium hydroxide may affect the formation of the palladium-DMG complex. However, the palladium-DMG complex is completely extracted in the pH range of 1 to 6.

CONCLUSIONS

In summary, dimethylglyoxime is a highly selective reagent for the determination of palladium by chloroform extraction from weak mineral acid solution. Selectivity is improved by the presence of nitrate. Sensitivity is not high - the molar absorptivity is 1700 (liters)(moles)$^{-1}$(centimeters)$^{-1}$, compared to 23 000 for 1-nitroso-2-naphthol.

Dimethylglyoxime is well suited to the determination of 0.1 to 1.0 percent palladium in titanium-base alloys. None of the common or potential alloying elements interfere with the determination. The procedure using dimethylglyoxime is faster, equally precise, and conveniently covers a wider range of palladium contents than does 1-nitroso-2-naphthol. Samples containing cobalt or niobium and tantalum are better analyzed for palladium with dimethylglyoxime than with 1-nitroso-2-naphthol. Moderate amounts of any of the common mineral acids as well as citric, tartaric, and oxalic acids have no effect on the results.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, December 26, 1968,
129-03-14-04-22.

APPENDIX A

PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM IN TITANIUM-BASE ALLOYS WITH 1-NITROSO-2-NAPHTHOL

Principle

A colored complex is formed between palladium and 1-nitroso-2-naphthol which is extracted with toluene. The absorbance is measured at 425 nanometers and the palladium content found by comparison with a calibration curve.

Scope

This method may be applied to titanium alloys with a palladium content of 1 percent or less. Of the common alloying metals, chromium(VI) interferes; this interference can be overcome. If the elements cobalt or niobium and tantalum are present, it is better to use another procedure, for example, one using dimethylglyoxime which is described later.

Apparatus

The apparatus consists of the following:

(1) Spectrophotometer, such as the Beckman Model B
(2) Centrifuge and stoppered centrifuge tubes

Reagents

The reagents are as follows:

(1) Palladium standard solution, 1 milliliter $\Bumpeq$ 5 micrograms palladium - Weigh 100 milligrams palladium metal and dissolve in a few milliliters of aqua regia. Dilute to 100 milliliters with 0.6M hydrochloric acid. Transfer a 5.00-milliliter aliquot of this solution to a 100-milliliter beaker; add 5 milliliters 9M sulfuric acid and 2 milliliters perchloric acid; cover with a "Speedy-vap" watch glass and evaporate to perchloric acid fumes. Repeat the fuming twice, washing down the sides of the beaker between each fuming. Dilute this solution to 1 liter with

water and acid to obtain a concentration of 5 micrograms palladium per milliliter in 0.5M sulfuric acid and 0.25M perchloric acid.

(2) 1-Nitroso-2-naphthol, 0.5 gram Eastman practical grade reagent per 100 milliliters 95 percent ethanol - The solution is dark brown in color and stable to light.

(3) Citric acid, 50 grams of the granular monohydrate crystal dissolved in water and diluted to 100 milliliters

(4) (Ethylenedinitrilo) tetraacetic acid disodium salt (EDTA), 3 grams dissolved in water and diluted to 100 milliliters

(5) Sodium hydroxide, 20 grams ACS reagent dissolved in water and diluted to 1 liter

(6) Toluene, ACS reagent grade

Procedure

Weigh a sample of the alloy (0.4 to 1.0 g for a 0.1 to 0.2 percent Pd content) into a 100-milliliter teflon beaker. Cover the beaker and add 20 to 40 milliliters 6M hydrochloric acid and 1 to 2 milliliters fluoboric acid. Alternatively, 1.8M sulfuric acid may be used instead of 6M hydrochloric acid. Let stand or warm slightly until the reaction ceases. Add nitric acid dropwise (10 to 20 drops), and warm until the titanium is oxidized. The color of the solution changes from deep purple to clear yellow, or red-brown if much palladium is present. Transfer to a 100-milliliter volumetric flask and dilute to the mark, keeping the hydrochloric acid concentration about 20 percent by volume.

Transfer a 10.00-milliliter aliquot of the sample solution to a 100-milliliter beaker. Add 5 milliliters 9M sulfuric acid and 2 milliliters perchloric acid, cover with a "Speedy-vap" watch glass, and evaporate three times to perchloric acid fumes. Wash down the sides of the beaker between each fuming. Transfer the fumed sample aliquot to a 100-milliliter volumetric flask and dilute to the mark. If chromium is present, add a few crystals of ferrous ammonium sulfate.

Pipet a sample aliquot containing, preferably, 1 to 65 micrograms palladium into a 60-milliliter separatory funnel containing 1 milliliter 50 percent citric acid and 2 milliliters 3 percent EDTA solution. Dilute to about 15 milliliters with water. Carry a reagent blank through the procedure at the same time.

Add 0.1 milliliter 0.5 percent 1-nitroso-2-naphthol in ethanol. Mix and allow 10 to 15 minutes for the complex to form. Add exactly 15.00 milliliters toluene and shake for 1 minute. Allow the layers to separate for 1 minute, then discard the lower aqueous phase. Add about 15 milliliters 2 percent sodium hydroxide solution and shake for 30 seconds. Let the layers separate for 1 minute, then discard the yellow aqueous phase containing excess reagent. Drain the toluene extract into a stoppered tube and centrifuge for 1 minute to remove suspended water droplets. Measure the absorbance of the complex at 425 nanometers in a 1- or 2-centimeter cell with toluene in the reference cell.

Determine the palladium content by reference to a calibration curve prepared by carrying known weights of palladium through the procedure and plotting absorbance values against the weights of palladium used.

APPENDIX B

PROCEDURE FOR THE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM IN TITANIUM-BASE ALLOYS WITH DIMETHYLGLYOXIME

Principle

A colored complex is formed between palladium and dimethylglyoxime which is extracted with chloroform. The absorbance is measured at 380 nanometers and the palladium content found by comparison with a calibration curve.

Scope

This method may be applied to titanium alloys with a palladium content of 1 percent or less. None of the common alloying metals interfere with the determination of palladium.

Apparatus

The apparatus consists of a spectrophotometer, such as the Beckman Model B.

Reagents

The reagents are as follows:

(1) Palladium standard solution, 1 milliliter $\Bumpeq$ 10 micrograms palladium - Weigh 100 milligrams palladium metal and dissolve in a few milliliters of aqua regia. Dilute to 100 milliliters with 0. 6 to 1. 2M hydrochloric acid. Dilute a 10. 00-milliliter aliquot of this solution to 1 liter with 0. 25 to 0. 50M hydrochloric acid to obtain 10 micrograms palladium per milliliter.

(2) Dimethylglyoxime, 1. 0 gram ACS grade reagent per 100 milliliters 95 percent ethanol - The solution is colorless and stable.

(3) Citric acid solution, 50 grams of the granular monohydrate crystals per 100 milliliters water

(4) Potassium chloride buffer solution, 0.05M KCl-0.06M HCl - Dissolve 3.7 grams potassium chloride in water, add 5 milliliters hydrochloric acid and dilute to 1 liter with water.

(5) Potassium nitrate buffer solution, 0.25M KNO_3-0.25M HNO_3 - Dissolve 25.3 grams potassium nitrate in water, add 16.7 milliliters nitric acid and dilute to 1 liter with water.

(6) Sodium sulfate, anhydrous ACS reagent

(7) Chloroform, ACS reagent grade

Procedure

Weigh a sample of the alloy (0.4 to 1.0 g for a 0.1 to 0.2 percent Pd content) into a 100-milliliter teflon beaker. Cover the beaker and add 20 to 40 milliliters (1+1) hydrochloric acid and 1 to 2 milliliters fluoboric acid. Let stand or warm slightly until the reaction ceases. Add nitric acid dropwise (10 to 20 drops) and warm until the titanium is oxidized and the solution is clear. The color of the solution changes from deep purple to yellow, or red-brown if much palladium is present. Transfer to a 100-milliliter volumetric flask and dilute to the mark, keeping the hydrochloric acid concentration about 2.4M.

Transfer a sample aliquot containing, preferably, 5 to 350 micrograms palladium to a 60-milliliter separatory funnel containing 1 milliliter 50 percent citric acid solution. Add about 10 milliliters chloride or nitrate buffer solution, dilute to 20 milliliters with water and mix. The buffer used will depend on the ions present (see tables VI and VII). Carry a reagent blank through the procedure at the same time. Add 2 milliliters 1 percent DMG in ethanol and mix. Allow a few minutes for the complex to form; during this time, add about 0.5 gram sodium sulfate to 25-milliliter volumetric flasks which will receive the chloroform extracts.

Shake the sample solution with 7 to 8 milliliters chloroform for 30 to 60 seconds, carefully release the pressure by loosening the stopper, and drain the extract into the receiving flask. Repeat the extraction twice with portions of chloroform and combine with the first extract. Dilute to the mark with chloroform and mix. Any water droplets will be absorbed by the sodium sulfate.

Measure the absorbance of the complex at 380 nanometers in a 5-centimeter cell with chloroform in the reference cell. Determine the palladium content of the sample by reference to a calibration curve prepared by carrying known weights of palladium through the procedure and plotting aborbance values against the weights of palladium used.

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