

C H A P T E R - V I

SIMULTANEOUS SPECTROPHOTOMETRIC
DETERMINATIONS OF
COBALT AND PALLADIUM

6.1 INTRODUCTION

The use of molecular absorption spectroscopy for the simultaneous determinations in binary or ternary systems has attracted little attention of the analytical chemists mainly because of the fact that the absorption bands in visible region are usually broad and hence overlapping. It is of interest to investigate the systems, where there will be perfect additivity of spectral properties, with a view to develop suitable methods of simultaneous determinations.

The author, therefore has investigated the possibility of use of cinnamaldehyde guanylhydrazone (CAG) as a reagent for photometric simultaneous determinations of cobalt and palladium.

The literature is rich in chemistry of the Cobalt-Palladium alloy. Co-Pd is an important alloy because of its industrial uses. The chemistry of Co-Pd alloy is extensively investigated. Cobalt rich films¹ of Co-Pd alloys were produced with basal orientation. Co-Pd alloys are used for making magnetostrictive devices e.g. ultrasonic vibrators². An improved amorphous soft magnetic material of Co-Pd alloy is described which is particularly useful as a thin film for a magnetic recording and playback head³. The recording medium is composed of an alloy whose light reflectivity

changes by the heat of a laser beam. A quartz substrate may be coated with cobalt-palladium alloy film to give the recording medium⁴. A reliable and economical ceramic capacitor⁵ utilizes an internal electrode from Pd-Co alloy powders.

Bath for electroplating of Pd-Co alloys are described which are used for printed circuit boards⁶. An electroplating bath⁷ for depositing hard, corrosion resistant and wear resistant Pd-Co alloy is prepared. Control of unbalanced electrolysis⁸ in the electrodeposition of Pd-Co alloy of predetermined composition i.e. Co \rightarrow 0 to 40% and Pd \rightarrow 60 to 100% was studied. Electrodeposition^{9,10} of Pd-Co alloys and their physicochemical and physicomechanical properties¹¹ from sulphate baths have been studied by many workers.

Magnetostriction¹² of Pd-Co alloys and structural, magnetic and electrical properties of thin film of Pd-Co layered structures have been studied by Carcia et al.¹³. Literature also shows the electronic structure¹⁴ and magnetic properties¹⁵ of Co-Pd films with a low cobalt content and of single crystal films of Co-Pd system alloys.

Onset of magnetic order¹⁶ in the giant moment system in Co-Pd alloys have been studied. Magnetization measurements¹⁷ of dilute Pd-Co alloys show that as the concentration

of cobalt impurities is reduced; the ordering changes from ferromagnetic character to single impurity behaviour. Such behaviour can be attributed to fine structure splitting. Magnetocrystalline anisotropy¹⁸ and magnetostriction of Pd-Co alloys and perpendicular¹⁹ magnetic anisotropy in Pd-Co thin film layered structures were studied by many workers. The effect of annealing of the ferromagnetic crystalline anisotropy constant K^{20} of Pd-Co alloys was studied in connection with a short-range order structure.

Bolshikh²¹ worked on catalytic decomposition of hydrogen peroxide on Pd-Co alloy, Pd-Co catalysts on activated graphite support²² are more active in some liquid phase hydrogenations than any of the unalloyed metals.

NMR²³ of Co^{59} was measured in ferromagnetic Pd-Co alloys. The Mossbauer effect^{24,25,26} of Pd-Co alloy with impurities were determined. The Kondo resistivity²⁷ was measured of hydrogenated Pd-Co alloys. Ordered phases in Pd+Co alloys system were studied by linear sweep voltametry²⁸. The samples were heated at 500°C for 3 hours and the existance of Pd_3Co , PdCo and $PdCo_3$ ordered phases were noted.

6.2 EXPERIMENTAL

6.2.1 Standard Solutions :

Standard Palladium (II) Solution :

A stock solution of Palladium (1 mg/ml) ($0.9398 \times 10^{-2} \text{M}$) was prepared by dissolving A.R. grade palladium chloride in 100 ml distilled water containing few mls of concentrated hydrochloric acid. Further dilutions for experimental purposes were done with distilled water.

Standard Cobalt (II) solution :

Standard cobalt solution 1 mg/ml ($1.697 \times 10^{-2} \text{M}$) was prepared from cobalt nitrate hexahydrate and the solution was standardized with EDTA volumetrically. Further dilutions for experimental purposes were made by diluting the stock solution with distilled water.

Reagent Solution :

A stock solution of 0.01 M reagent (CAG) was prepared by dissolving 0.188 gms of CAG in 100 ml ethyl alcohol (1.88 mg/ml).

Buffer Solution :

Buffer solution of pH 12 was prepared by dissolving appropriate amount of sodium hydroxide and borax.

6.2.2 Recommended procedure

An aliquot of the solution which contains upto 10 μ g palladium (II) and 20 μ g cobalt (II) was taken. Then 3.5 ml of 0.01 M reagent (CAG) solution was added which provides desired excess quantity to complete the complex formation. The pH of the solution was adjusted to 11 by adding 1 ml of sodium hydroxide and borax buffer solution of pH 12 and was diluted upto the mark with ethyl alcohol. The absorbances of the Pd (II) and Co (II) complexes respectively were measured at 370 nm and 410 nm, and were substituted in the simultaneous equation developed on the basis of spectral measurements.

6.3 RESULTS AND DISCUSSION

6.3.1 Spectral Characteristics :

Table 6.1 summarizes the spectral characteristics of Pd (II) and Co (II) complexes of CAG.

Table 6.1 : Properties of the complexes.

Complex	λ_{max} nm	Molar extinction coefficients		Validity of Beer's law
		370 nm	410 nm	
Co (II)	410	1.031×10^3 $1 \text{ mole}^{-1} \text{cm}^{-1}$	1.532×10^3 $1 \text{ mole}^{-1} \text{cm}^{-1}$	7.0 ppm
Pd (II)	370	7.455×10^3 $1 \text{ mole}^{-1} \text{cm}^{-1}$	3.408×10^3 $1 \text{ mole}^{-1} \text{cm}^{-1}$	8.0 ppm

Figure 6.1 shows the absorption spectra of Pd(II)-CAG complex, Co(II)-CAG complex and the mixture of Pd(II) and Co(II) complexes. The reagent does not absorb in the visible region. The observations are given in table 6.2.

Table 6.2 : Absorption spectra of Pd (II)-CAG complex, Co (II)-CAG complex and mixture of Pd (II)-CAG and Co (II)-CAG complex.

Wavelength, λ , nm	Absorbances		
	Pd(II)-CAG	Co (II)-CAG	Mixture of Pd (II)-CAG & Co (II)-CAG
360	0.62	0.30	0.93
365	0.66	0.33	1.02
370	0.70	0.35	1.05
375	0.65	0.38	1.03
380	0.62	0.40	1.02
385	0.54	0.43	0.97
390	0.48	0.45	0.93
400	0.38	0.50	0.88
410	0.32	0.52	0.84
420	0.24	0.50	0.74
430	0.18	0.44	0.62
440	0.14	0.39	0.53
450	0.11	0.34	0.45
460	0.09	0.30	0.39
470	0.07	0.26	0.30
480	0.06	0.22	0.28
490	0.05	0.18	0.23
500	0.04	0.15	0.20

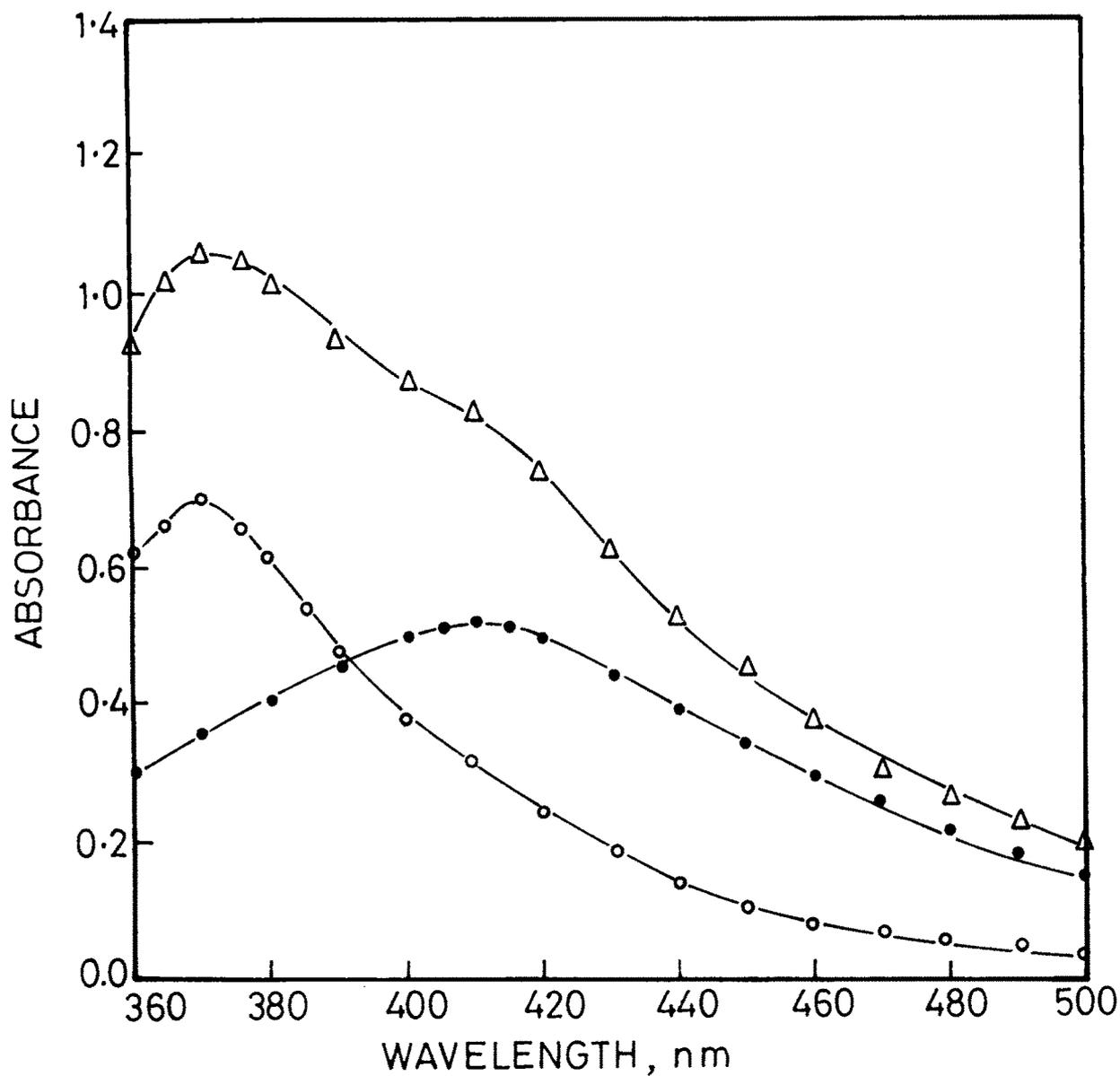


FIG. 6.1 - ○—○ ABSORPTION SPECTRUM OF PALLADIUM-CAG COMPLEX ($9.40 \times 10^{-5} \text{ M}$).
 ●—● ABSORPTION SPECTRUM OF COBALT-CAG COMPLEX ($3.392 \times 10^{-4} \text{ M}$).
 △—△ ABSORPTION SPECTRUM OF MIXTURE OF PALLADIUM-CAG AND COBALT-CAG COMPLEXES.

The method for the simultaneous determination is developed on the basis of

- i) well separated absorption maxima of the complexes.
- ii) sufficiently high values of extinction coefficients of the complexes.
- iii) no absorption by the reagent in the visible region.
- iv) stability of the complexes of the two metals at pH 11 and
- v) additivities of the absorbances of the complexes.

Equations (1) and (2) are used to develop the equations (3) and (4).

$$(1) \quad A_{410} = \epsilon_{410}^{\text{Pd}} \times [\text{Pd}] + \epsilon_{410}^{\text{Co}} \times [\text{Co}]$$

$$(2) \quad A_{370} = \epsilon_{370}^{\text{Pd}} \times [\text{Pd}] + \epsilon_{370}^{\text{Co}} \times [\text{Co}]$$

$$(3) \quad A_{410} = 3.408 \times 10^3 [\text{Pd}] + 1.532 \times 10^3 [\text{Co}]$$

$$(4) \quad A_{370} = 7.455 \times 10^3 [\text{Pd}] + 1.031 \times 10^3 [\text{Co}]$$

Equations(3) and (4) are used to develop the equations (5) and (6) which are used for the simultaneous determinations of the two constituent elements.

$$(5) \quad [\text{Co}] \times 10^4 = 9.426 A_{410} - 4.308 A_{370}$$

$$(6) \quad [\text{Pd}] \times 10^4 = 1.937 A_{370} - 1.303 A_{410}$$

Determination of Cobalt (II) and Palladium (II) in
synthetic mixtures :

Several synthetic mixtures of Co(II) and Pd(II) were prepared and analysed in triplicate. The results of analyses are summarized in table 6.3.

Table 6.3 : Results of analysis of synthetic mixtures :
 [Mixture of 10 μg Pd + 20 μg Co] + 3.5 ml
 reagent, CAG (0.01 M) + 1 ml buffer (pH = 12),
 diluted to 10 ml with ethyl alcohol.

Obs. No.	Quantity taken	Absorbances at	Quantity found	Relative Standard deviation		
	Pd $\times 10^{-4}$ M	370 nm	Pd $\times 10^{-4}$ M	Pd(II)	Co(II)	
	Co $\times 10^{-4}$ M	410 nm	Co $\times 10^{-4}$ M			
1	0.62	0.72	0.626	2.45	+0.19	+0.21
2	0.68	0.70	0.678	1.89	+0.34	-0.15
3	0.63	0.65	0.62	1.81	-0.27	+0.48
4	0.70	0.64	0.69	1.201	-0.45	+0.51
5	0.72	0.58	0.706	0.517	+0.12	-0.32
6	0.60	0.60	0.59	1.56	-0.39	+0.29

Determination of Cobalt and Palladium in alloys

Solutions of alloys containing cobalt and palladium were prepared. Suitable aliquots were taken and analysed as outlined in general procedure. The results are summarised in table 6.4.

Table 6.4 : Analysis of Co + Pd alloys

Sample	Composition of the alloys	Weight of the sample mg	Expected,mg		Found,mg	
			Co(II)	Pd(II)	Co(II)	Pd(II)
A	60% Co (II) 40% Pd (II)	20.0	12.0	8.0	12.17	7.89
B	70% CO (II) 30% Pd (II)	10.0	7.0	3.0	6.90	3.13

6.4 INTERFERENCES :

This method is applicable to the analysis of binary alloys and also to solutions containing Pd(II) and Co(II) free from interfering metals, e.g. gold, platinum, iron. Organic materials such as urea, thiourea seriously interfere but can be destroyed by first boiling with concentrated nitric acid and then with concentrated sulphuric acid to white fumes.

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