

THIOSEMICARBAZONES AS ANALYTICAL REAGENTS: A SELECTIVE SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM

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ABSTRACT

Salicylaldehyde thiosemicarbazone has been proposed as a new reagent for the rapid and selective estimation of 1.0–7.2 ppm of palladium. The reagent instantaneously and quantitatively forms a yellow-orange species with palladium at room temperature in the pH range 1.8–4.0. The coloured species is extractable in oxygenated solvents. Various photometric parameters have been worked out for quantitative estimation of palladium(II) and possible analytical applications (the estimation of palladium in hydrogenation catalysts, dental alloy, jewellery metal, electrical standard resistor and thermocouple) have been reported. The reliability of the method has been worked out with the aid of statistical analysis.

INTRODUCTION

THIOSEMICARBAZONES containing aldehydes or ketones have been employed as analytical reagents for the estimation of metal ions, including platinum group elements^{1–6}. However, most of these reagents have limited usefulness for the estimation of palladium, owing to lack of sensitivity, complex formation at elevated temperature, stability of complex with time, more interference from other associated metal ions, etc.

In this paper a method for the spectrophotometric determination of palladium is described. The method has been used in the determination of palladium in small samples of hydrogenation catalysts, dental alloy, jewellery metals, electrical standard resistor and thermocouple.

This photometric method is based on the instantaneous formation of a yellow, water-insoluble Pd(II) complex of salicylaldehyde thiosemicarbazone (SATSC), which is easily extractable into oxygen-containing solvent in the pH range 1.8–4.0.

MATERIALS AND METHODS

Reagents and apparatus

A suitable concentration (~0.01 M) of stock solution of palladium(II) was prepared from PdCl₂ (Arora Metthey, India) in minimum volume of 0.1 M HCl and standardized gravimetrically by DMG method⁷. The stock solution was further diluted suitably according to experimental requirements. Standard solutions of diverse ions were prepared from reagent-grade salts; the noble metal compounds

were standardized by adopting well-established procedures^{8,9}. For the interference study, alkali salts were used for solutions of the anions, and nitrates and chlorides for solutions of the cations. SATSC (m.p. 235°C) was synthesized by the procedure of Sah and Daniels¹⁰. A stock solution of SATSC (0.01 M) was prepared in ethanol. Walpole buffer solutions were prepared by mixing 0.1 M HCl and 0.1 M sodium acetate to maintain the desired pH values. Absorbance measurements were performed in a Varian model DMS-80 UV/vis spectrophotometer provided with 1 cm matched quartz cells. The pH measurements were made with an Elico digital pH meter model LI 120 provided with a glass-calomel combination electrode.

Spectrophotometric determination of palladium

To a solution containing 1.0–7.2 ppm of palladium(II), 3 ml of buffer (pH 3.0±0.1) and 1 ml of 0.01 M reagent were added. The mixture was shaken for 1 minute. To this 10 ml of cyclohexanol was added and the mixture was shaken vigorously for 2 min. The two phases were allowed to separate; the organic phase separated was dried over sodium sulphate and the absorbance measured at 405 nm against reagent blank.

Spectrophotometric determination of palladium in hydrogenation catalysts

An accurately weighed sample was dissolved in nitric acid or aqua regia, according to the support, and heated on a water bath, if necessary. The cooled

solution was diluted to 100 ml in a calibrated flask. Suitable aliquots were analysed for palladium as described above.

RESULTS AND DISCUSSION

Absorption spectrum of Pd(II)-SATSC extracted into cyclohexanol

The complex in cyclohexanol was found to absorb maximally at 405 nm; the reagent has absorption maximum at 352 nm. All the present studies were made at 405 nm, where the reagent showed negligible absorption. The absorption maximum does not shift with the changing concentration of palladium(II).

Optimum conditions for Pd(II)-SATSC extraction

The influence of pH over the extraction percentage was studied using an aqueous solution of 4 ppm of Pd(II) with 1 ml of SATSC (0.01 M) and extracting each time with an equal volume of organic phase. The remaining palladium in aqueous phase after extraction was determined by applying the recommended procedure. The results showed that the extraction was almost null for pH lower than 1.0, whereas the extraction was complete in the pH range 1.8–4.0. Of the various oxygen-containing solvents for extraction tried, cyclohexanol was found to be more effective since the complex showed maximum absorbance in this solvent. Shaking for 30 sec was sufficient. An at least 2-fold excess of reagent was necessary for maximum colour development, and even a 100-fold excess had no adverse effect. The order of addition of reagent did not affect the absorbance of the complex. There was no influence on the absorbance when complexation was effected at higher temperature. Cyclohexanol extract remained spectrophotometrically stable for 24 h. The influence of aqueous:organic phase volume ratio on the absorbance was studied to increase the sensitivity of the method proposed. It was observed that a v_w/v_o ratio of 5 allows the quantitative determination of lower concentrations of palladium in the aqueous phase. Since the reagent (SATSC) was prepared in ethanol, the permissible ethanolic content in aqueous phase should be less than 35%; beyond 45% the two phases were miscible in all proportions.

Stoichiometry of the extracted complex

A simple graphical test was adopted for confirming single or multiple species formation. As per

Coleman's analysis¹¹; a series of sets of wavelengths were selected from the absorption spectra and the absorbance values obtained for each set of wavelengths at varying Pd(II) concentration were plotted. Linear plots passing through the origin confirm single species formation. The combining ratio of Pd(II) with SATSC was investigated by Job's method¹² and further verified by mole-ratio method¹³ as 1:1. The isolated solid complex was subjected to various physicochemical studies³, which indicated that the complex is $[Pd(II)(SATSC)Cl_2]$.

Beer's law range and sensitivity of the method

The system obeys Beer's law at 405 nm over the range 1.0–7.2 ppm of palladium. The molar absorptivity of the system was found to be $6.4 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The corresponding Sandell's sensitivity of the method was $0.017 \mu\text{g}/\text{cm}^2$. The optimum concentration range, evaluated by Ringbom's method, was 1.3–6.5 ppm. The formation constant of Pd(II)-SATSC was calculated to be 3.3×10^8 from the curve obtained from Job's method.

Interference by other ions

The recommended procedure was followed to study interference due to various ions in aqueous solutions containing 4 ppm of palladium(II). Of the various cations and anions tested individually in the estimation of Pd(II), no interference was observed in the presence of 100, 50, 25, 10, 5 and 2-fold excess of EDTA, NH_4^+ , Co(II), Ca(II), Ba(II), chloride, fluoride and nitrate; sulphate, oxalate, Al(III) and acetate; Zn(II), Ni(II) and Mn(II); Fe(II, III), W(VI), Mo(IV), thiocyanate and iodide; Cu(II), Ir(III), Rh(III), Cr(III), Au(III) and Ru(III); and Pt(II) respectively. Thus, by the recommended method, Pd(II) can be determined in the presence of greater number of diverse ions, including moderate amounts of most of those that are commonly associated with palladium in real and synthetic samples (except Pt(II), which can also be overcome by precipitating palladium¹⁴ prior to photometric estimation of Pd(II) as the SATSC complex).

Analytical applications of the method

In order to assess the analytical usefulness of the proposed method, synthetic mixtures simulating the compositions of dental alloy, jewellery metal, electrical standard resistor and thermocouple were made and the palladium content was determined in each (table 1). The method developed was also

Table 1 Estimation of palladium in dental alloy, jewellery metal, electrical standard resistor and thermocouple

Metal constituent	Concentration (ppm)		Palladium found* after isolation of Pd(II)	Error (ppm)
	I	II		
Dental alloy				
Palladium	2.0	4.0	2.07 (4.18)	+0.07 (+0.18)
Platinum	2.0	4.0		
Copper	5.0	100		
Zinc	5.0	10.0		
Jewellery metal**				
Palladium	2.8	5.6	2.72 (5.67)	-0.08 (+0.07)
Ruthenium	0.2	0.4		
Electrical standard resistor				
Palladium	4.0	6.0	4.20 (5.82)	+0.20 (-0.18)
Platinum	4.0	6.0		
Thermocouple				
Palladium	3.0	6.5	3.25 (6.33)	+0.25 (-0.17)
Platinum	9.0	19.5		

*Average of four determinations. **Direct determination (without isolation of palladium).

applied to the determination of palladium in small samples of hydrogenation catalysts. The results are shown in table 2, and compared with those obtained by atomic absorption spectroscopy (A.A.S).

Reliability of the proposed method

The precision of the present method was evaluated by determining the same amount (40 µg/10 ml or 4 ppm) of Pt(II) in solution in 10 different samples. The mean absorbance was found to be 0.530 with a standard deviation of 0.016. The correlation coefficient was 0.9984, which indicates excellent linear relationship between the measured signal and the true concentration.

Table 2 Spectrophotometric estimation of palladium with SATSC in hydrogenation catalysts

Catalyst (Fluka)	Found (%)	
	AAS method	Proposed photometric method*
Pd/asbestos	4.40	4.37
Pd/activated charcoal	9.42	9.37
Pd/CaCO ₃	5.60	5.78
Pd/BaSO ₄	9.78	9.94

*Average of 5 determinations.

Use of SATSC for the estimation of palladium(II) has the following advantages: simplicity, good sensitivity, high stability, insensitivity to temperature, rapidity and very good selectivity. The entire procedure extraction and assay takes only 10–15 min.

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ANNOUNCEMENTS

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