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STUDY OF THE REACTIONS OF THE PLATINUM(IV) CHLORO COMPLEXES BY UV SPECTROPHOTOMETRY

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Abstract

A sensitive spectrophotometric method which is based on the formation of the complex of platinum(IV) with Cl^- anions (0.1 M HCl) by measuring the absorbance at 260 nm has been elaborated. The method exhibits linear response in the range of 0.4 -1.4 $\mu\text{g ml}^{-1}$ and provides easy determination of this metal from low to higher concentration at affordable cost. No significant interferences were observed from a majority of the investigated ions, with the exception of Cu(II) and Fe(III).

Keywords: Platinum; UV spectrophotometry; Chloroplatinates; Determination

Introduction

The interest in the determination of platinum group metals (PGM) has rapidly increased due to use of PGM based-catalyst in automobile industry. The PGM compounds e. g., chloroplatinates are not highly toxic but may cause allergic reactions [1,2].

The use of spectrophotometric methods in PGM analysis is limited due to low sensitivity. However, many new highly specific and sensitive organic reagents are being synthesized and various highly sensitive methods are being developed with molar absorptivities of 10^5 - 10^6 or even higher [3,4]. The author [5] presented detailed information of reagents used in spectrophotometric determination of PGM.

The present study describes a simple and sensitive method for the spectrophotometric determination of platinum(IV), which is based on the formation of the complex of platinum(IV) with Cl^- anions (0.1M hydrochloric acid).

Experimental

Apparatus

The UV spectra were recorded between 190 and 350 nm on HP 8452 A diode array computer controlled spectrophotometer (Hewlett Packard), equipped with thermostated cell compartment. The advantage of using this spectrophotometer is the possibility of measuring full spectra, rather than just the absorbance of a single wavelength. The measurements were performed using 1 cm quartz thermostated cell. A combined glass electrode and a pH meter were used for the pH measurement.

Reagents

All reagents were of analytical purity or suprapur quality. Water was deionised before use. A platinum standard stock solution (2.41 mg ml^{-1}) was prepared by dissolving platinum wire in aqua regia ($\text{HCl} + \text{HNO}_3$, 3+1) [6]. The residue was dissolved in a few drops of 1 M HCl. The solution obtained was diluted to 50 ml with 0.1 M HCl. The platinum(IV) solution was standardized by a complexometric method [7]. Working standards were prepared by serial dilution of the stock solution with 0.10 M HCl. Hydrochloric acidic solution (0.1 M) was used as a blank solution.

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Procedure

According to the procedure, to a suitable aliquot of the solution containing 10.0 - 30.0 μg of platinum, sufficient diluted hydrochloric acid was added and the solution was diluted with water to 25 ml. A portion was transferred to a glass cell and the absorbance of the complex at 260 nm against a reagent blank prepared similarly without platinum was measured.

Results and Discussion

Effect of Some Experimental Parameters

To find the working range and to elaborate the analytical procedure, the reaction conditions and reagent concentrations must be optimized and therefore, parameters such as the reaction time, temperature, pH, hydrochloric acid concentration and concentration of metal were studied.

To evaluate the effect of reaction time the solution (25 ml) containing PtCl_6^{2-} ions in hydrochloric acid solution was investigated for different periods of time (up to 30 min.) at room temperature. It was found that for this period of time the absorbance at 260 nm was constant. The effect of temperature in the range 15-30 $^{\circ}\text{C}$ was also investigated. The absorbance change with temperature for the reaction of the complex formation was negligible at 25 $^{\circ}\text{C}$ and a room temperature (15-25 $^{\circ}\text{C}$) was chosen for measurement.

The influence of pH on the formation of PtCl_6^{2-} complex ions was determined by measuring the UV spectra at different HNO_3 concentrations for $5 \cdot 10^{-5}$ M Pt(IV) in 0.1 M KCl solutions. The absorption band of PtCl_6^{2-} ions between 0 and 3 does not change markedly around 260 nm. Thus, pH between 0 and 3.0 should be used for measurements since the absorbances were highly reproducible at these pH values.

The effect of hydrochloric acid concentration was studied in the range of 0.01M-2M. In order to find the optimum concentration of this acid, the absorbance change with concentration of the chloride ion was measured. The results showed that the absorbance of the complex is maximal at 0.1M HCl. Therefore, a final concentration of 0.1 M HCl acid was selected as the optimum.

Effect of Foreign Ions

The spectral interference of several cations and anions on the determination of platinum in solution was studied in detail. Different amounts of ions were added to 0.4 $\mu\text{g ml}^{-1}$ of the Pt metal solution. Concentrations of interfering ions are taken as maximum tolerance limits when the relative error exceeds 1.5 %. The tolerance limits for the different studied ions are listed in Table 1.

Table 1. Interference of various cations and anions on the measurement of 2.0×10^{-5} M platinum (IV) at 260 nm.

Interfering ions tolerance limit ^a molar ratio Pt : Me
Zn(II), Pb(II), Mn(II) 1000
Cd(II), Co(II), Ni(II) < 1000
Cu(II), Sb(III) 100
Fe(III), Pd(II) < 10
I ⁻ < 1
NO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} > 1000
NH_4^+ > 1000

^a An error of 1.5 % was taken as the maximum tolerance limit.

No significant interferences were observed from the major of the studied ions. However, several ions such as Cu(II), Fe(III) and Pd(II) interfere significantly with the determination. Cu(II) forms a strong chlorocomplex which interferes with the absorbance of the complex. It was observed that the interference of Fe(III) ions is more serious and a higher signal even at 1.12 mg l^{-1}

level was obtained (Fig.1). Pd(II) ions do not interfere with the analytical response of platinum in a molar ratio smaller than 10. But, in the presence of a higher concentration of Pd(II) ions (molar ratio > 10) the platinum signal is enhanced. High concentrations of anions given in Table 1 with the exception of I⁻ ions do not interfere.

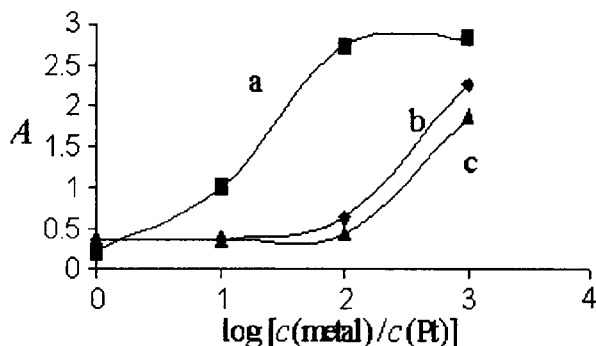


Figure 1. The influence of interferences of: a-Fe(III), b-Cu(II), c-Sb(III) on the absorbance of 2.0×10^{-5} M Pt(IV) at 260 nm.

Conclusion

The developed spectrophotometric method can be used for the determination of Pt(IV) in hexachloroplatinate complexes of K, Na, Pt(II), Fe(II), Ni(II), Co(II), Mn(II), Pb(II), Cu(II). Since this method is based on the detection of the platinum chloro complexes in UV region below 300 nm, this may cause problems if the decomposition of the organic constituents is not quantitative and small amounts of other inorganic anions, which absorb at the used detection wavelength, are present in the sample.

Acknowledgements

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