

A New Spectrophotometric Determination of Uranyl ion with p-chlorotrifluorobenzoyl acetone*

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(Received 12th February, 1985)

Summary: A new colorimetric estimation of uranyl ion is described. The procedure involves the reaction of uranyl ion with p-chlorotrifluorobenzoyl acetone in acetic medium. The condition for analytical measurement is given too. Common cations that might interfere are studied. Detection limit and reproducibility are given to evaluate the applicability of this method.

Introduction

There is a growing concern for the determination of uranium in different samples, therefore, different organic reagents and dyes were described for spectrophotometric determination of uranium. Table (1) summarise the analytical characteristic of most important methods. Despite the large number of dyes and organic reagents mentioned for uranium, there is still a demand for a simple direct spectrophotometric method to estimate uranium for a wide range of concentration.

Experimental

Apparatus

A Pye unicam SP6-400 uv-spectrophotometer was used for absorptiometric measurement. The pH meter used for pH adjustment was pH DIGI 520.

Reagent

P-chlorotrifluorobenzoyl acetone was prepared by condensation of ethyltrifluoroacetate with p-chloro benzoyl acetone in the presence of sodium

ethoxide. The following general procedure for B-diketonates was adopted [11].

Procedure

Prepare a suspension by dissolving 7.88 g (0.1446 mole) of sodium ethoxide (Prepared spontaneously from sodium metal and dry ethanol) in 100 ml of ethanol (Previously dried in sodium). Add gradually 19.9 ml (0.140 mole) of ethyltrifluoroacetate, then shake the solution for 10 minute. Add then gradually with vigorous shaking 11.83 g (0.1407 mole) of p-chlorobenzoyl acetone for 15 minute. Leave the mixture 24 hours in a dark place and keep it in dry place. Acidify the mixture by addition of 10% H₂SO₄ and extract the -diketone from the mixture by ether using rotary evaporator.

Optimum condition

The optimum condition for the formation of yellow colour was studied and maintained throughout the studies.

*Part of this work has been submitted to the 12th Iraqi Chemical conference held at Baghdad 2-4 Feb. 1985

Table-1: Analytical characteristic of uranium (IV)

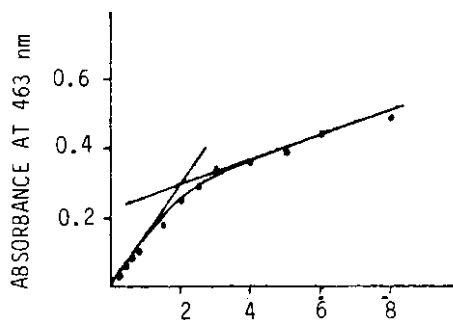
Reagent	medium	max.nm	E_{\max} $1.\text{mol}^{-1}.\text{cm}^{-1}$	range of deter- mination(ppm)	Reference
Thiocyanate	acidic	380	2.9×10^3	-	[1]
Dibenzoyl methane		395	2.0×10^4	-	[2]
Rhodamine 6G	-	-	-	0.04 - 4	[3]
Arsenazo I	pH 7.5-9	596	-	1 - 300	[4]
Arsenazo III	6-8 M HCl	665	1.27×10^5	-	[5]
Chlorophosphonazo	-	670	7.96×10^4	-	[6]
PAN	Ammonical	560	2.30×10^4	-	[7]
PAR	-	530	2.30×10^4	-	[8]
8-hydroxy quinoline	pH 6 - 8	400	-	-	[9]
Eriochrom cyanine R	-	570	-	13 - 125	[10]

There were no large effect of the pH on the stability of the yellow colour. The optimum pH was found [4-7].

The effect of reagent concentration to metal was studied by adding different concentration of reagent to fixed concentration of uranium. It was found that the composition of the complex is (UO_2R_2) as indicated from fig (1). 2 ml of the reagent (0.025 M) was found optimum to give maximum complex formation, therefore, this volume was maintained through the subsequent steps.

The effect of time on complex formation was also studied and found that the absorbance should be measured

after 5 minutes and the colour was stable for three hours.



number of moles of reagent: no. of moles of metal.

Fig.1: Study of stoichiometry of reagent to metal ion for uranyl-P-chlorotrifluoro-benzoyl acetone.

The order of addition was examined by preparing three different solutions containing 80 ppm uranium, 2 ml of reagent (0.025 M) and acetone in different orders. The highest absorbance was achieved when the order is acetone: uranium: reagent.

The confirmatory with beer's law was studied using the optimum conditions mentioned above. The results are given in fig (2). Beer's law is hold up to 1000 ppm, and this range is too wide to allow uranium to be determined.

Procedure for determination of uranyl ion (10-1000 ppm)

Prepare a series of solution containing different concentration of uranyl (10-100 ppm) by serial dilution of the stock uranium solution in 10 ml. Volumetric flask. Add acetone to each flask before addition of uranium solution, then add 2 ml of p-chlorotrifluorobenzoylacetone to each flask and finally complete the volume in each flask at 463 nm against blank solution (the blank solution is the solution of uranyl ion only). Plot the values of net absorbance vs. amount of uranyl concentration. Results are shown in fig. (2). The graph shows that beer's law is obeyed up to 1000 ppm.

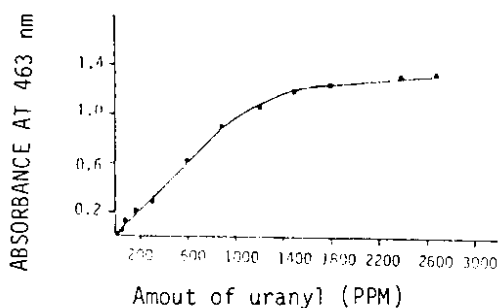


Fig.2: Calibration graph for determination of uranyl-P-chlorotrifluorobenzoyl acetone (10-1000 ppm).

Study of Precision and detection limit

To test the reproducibility of the method, ten replicate determination of 100 ppm uranium were done. The relative standard deviation was found $\pm 0.85\%$. The confidence interval from the mean value 100 ppm lies in the range 99.80 to 100.12 ppm.

Effect of foreign substances in uranyl ion determination

In order to study the applicability of the method, the determination of uranium was studied in the presence of related inorganic metal ions. Table (2) shows the result of interferences of ten fold concentrations of ten inorganic metal ions. Most metal ions show increase in the absorbance values, particularly, ferrous, ferric and copper (II) ions, because these ions form strong complexes with p-chlorotrifluorobenzoyl acetone. Hence, its possible to study the analysis of mixture of uranyl with other metal ions, this will be discussed in future publications. Nickel (II), silver (I), and manganese (II) are less effective on absorbance values. Addition of EDTA to the solution containing ferrous ions (10 fold) eliminates the interference and restored the value of absorbance. The main reason for interference is attributed to the activity of p-chlorotrifluorobenzoyl acetone towards most metal ions. This phenomenon were mentioned for dibenzoylmethane [12].

Discussion

P-chlorotrifluorobenzoyl acetone was not described in the literature as reagent for uranyl. Dibenzoyl methane was studied previously for uranium and the finish was extraction-spectrophotometric (II). The present study demonstrate a simple direct spectro-

Table-2: Effect of selected common ions on absorbance of uranyl complex.
The amount of each interferent is 10 fold mass excess of uranyl concentration.

Interferent	Colour	Absorbance	Concentration of uranium found from calibration (ppm)
0	yellow	0.15	143
Fe ⁺² (1)	purple	0.24	2300
Fe ⁺³ (2)	orange	1.19	14000
Cu ⁺²	green	0.355	345
Ni ⁺²	yellowish-green	0.15	143
Ce ⁺	Faint yellow	0.10	93
Mn ⁺²	yellow	0.19	183
Pb ⁺²	yellow	0.175	168
Ag ⁺	yellow	0.17	163
Co ⁺² (3)	yellow-orange	0.58	570
Cr ⁺³	yellow-green	0.50	490

(1) If 1 ml. of 1M EDTA added to the reaction mixture in order of: uranyl: Fe⁺²:EDTA: Reagent:acetone, the absorbance was found 0.15.

(2) Similar to (1), the absorbance was 0.21

(3) Similar to (1), the absorbance was 0.36.

photometric method which can be applied for determination of uranyl ion for 10 to 1000 ppm. With $\pm 0.85\%$. The measurement can be made within 5 minute. The disadvantages of interference can be controlled by addition of EDTA or any other masking agent.

The simplicity of the reaction and stability of the complex prepared in acetone makes the method suitable for uranium determination in different samples such as ore radioactive minerals and water.

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