

Chapter 5

ANALYTICAL USES OF BENZOYLACETANILIDE

Benzoylacetanilide $C_6H_5 \cdot CO \cdot CH_2 \cdot CONHC_6H_5$ has been introduced as an organic reagent in the analysis of metal ions by Sarkar and Das¹. This reagent has been prepared from ethyl-benzoylacetate by a slight modification of the method due to Allen and Humphlett² as described in Section 5A. Ethyl benzoylacetate was in turn prepared from ethyl acetoacetate following a standard method³.

Benzoylacetanilide is obtained as stable colourless crystals melting at 106 - 106.5°C. The reagent is readily soluble in ethanol, chloroform, ether and benzene, though the solubility in water is low. The acid dissociation of benzoylacetanilide in 75% aqueous acetone (v/v) has been reported⁴; the pK_a is 9.96. The ultraviolet absorption spectra of the reagent in isobutylmethyl ketone solution showed λ_{max} at 340 nm. At wave-lengths higher than this the absorbance shows a steep decrease to zero.

Sarkar⁴ observed that under suitable conditions benzoyl-acetanilide forms precipitates with beryllium (colourless), mercury(II)(colourless), aluminium (colourless), iron(III) (red), vanadium(IV) (green), titanium(IV) (orange-yellow), molybdenum(VI) (yellow) and forms extractable chelates with iron(III) (red), titanium(IV) (yellow), molybdenum(VI) (yellow) and vanadium(IV) (blue-green) in suitable solvents. It also gives colouration with uranyl salts (yellow). The use of benzoylacetanilide in the

spectrophotometric determination of uranium(VI) has been described in Section 5-1. Analytical procedures for different metal ions based on the remaining observations have been reported earlier (section 4.3.1).

5A. Method of Preparation

A mixture of 105.7g (0.55 mole) of ethyl benzoyl acetate and 46.6g (0.5 mole) of freshly distilled aniline was heated to 135°C on an oil bath and allowed to reflux under an air-condenser for 6-7 hours. Then, 300 ml of xylene was added and slightly heated, if necessary, to form a clear solution. When the solution was cold enough 100 ml of petroleum ether (35 - 60°C) was added, the mixture was stirred and cooled to 15°C. The crystalline product was filtered under suction and washed with petroleum ether (300 - 400 ml). The yield was 99 - 100 g (83 - 84 %).

5.1. Spectrophotometric Determination of Uranium(VI) with Benzoylacetanilide

Many organic reagents bonding through oxygen atoms have been found to give colour reactions with uranyl ion and have been used in the colorimetric determination of this ion. However, the problem of avoiding the interference due to other ions, particularly that of chromate always caused difficulties. Thus, dibenzoyl - methane⁵ can be made specific for uranium(VI), if chromate and chloride are absent and a prior extraction with suitable reagents is performed. Alternatively, reduction of chromate with iron(II) followed by differential colorimetry has been suggested⁶. Among other potentially less selective reagents, the selectivity of thenoyl trifluoroacetone and rhodamine combination toward uranium(VI) seems to be satisfactory when EDTA is used to mask the diverse ions⁷.

Benzoylacetanilide, in the present investigation, has been found to be a good reagent for uranium(VI), as the yellow complex formed may be extracted easily in isobutyl methyl ketone and the absorbance can be measured at 390 nm against the pure solvent. However, the main advantage lies in the selectivity of the reagent toward uranyl ion, when magnesium - EDTA is used as the masking agent. Thus, the determination of very small quantity of uranium(VI) (1.0 to 40.0 µg per ml of solvent) is possible in the presence of considerable amounts of a variety of ions commonly associated with uranium including Fe^{3+} , Cr^{3+} , Th^{4+} , Zr^{4+} , VO^{2+} , CrO_4^{2-} and MoO_4^{2-} .

EXPERIMENTAL

5.1.1. Reagents and Chemicals

Benzoylacetanilide solution - A 0.5% ethanolic solution of the reagent ($2.1 \times 10^{-2} \text{ M}$) was prepared and a total of 2.0 ml of this was used for each determination.

Uranium(VI) solution - Uranyl nitrate (E.Merck) solution was purified by precipitation with ammonia in the presence of EDTA and then dissolving the precipitate in dilute nitric acid. The metal content was determined using N-benzoyl phenylhydroxylamine⁸, and the solution was suitably diluted.

Diverse Ions - Stock solutions of various ions were prepared from potassium chromate, sodium tungstate and molybdate, ammonium vanadate, and nitrate, chloride or sulphate of the remaining metals. The metal contents of these solutions were determined by conventional methods including titrations with EDTA.

Magnesium - EDTA Solution - A stock solution of disodium -EDTA was prepared (50 mg of Na_2EDTA per 1 ml of water). Magnesium sulphate solution containing an equivalent amount of Mg^{2+} per ml was also prepared. When required, 2 ml portions of each were mixed.

Pyridine Solution - A 10% solution of freshly distilled pyridine in water was used for the adjustment of pH. When stored in coloured bottles, this solution could be used for the spectrophotometric determination of uranium upto at least two weeks.

5.1.2 Apparatus

Spectrophotometer - The optical measurements were carried out in a Hilger & Watts H700 Uvispek spectrophotometer using 1 cm quartz cuvettes for wave-lengths below 380 nm and 1 cm glass cuvettes above 380 nm.

pH - Meter - A battery operated bench model cambridge pH-meter was used for the adjustment of acidity.

5.1.3. Determination of Uranium(VI)

A known quantity of the standard uranium(VI)(25 to 500 µg) solution was mixed with 1 ml of benzoylacetanilide solution and diluted to 10 ml. The pH of the mixture was first raised to 4.0 with aqueous ammonia and finally adjusted between 6.5 and 7.0 by the dropwise addition of the pyridine solution. After waiting for 10 minutes, 5 ml of isobutyl methyl ketone was added and shaken well. The organic layer was collected in a 10 ml measuring flask, while the aqueous layer was used for a second extraction with another 1 ml portion of the reagent solution and 5 ml more of isobutyl methyl ketone. These two extracts were combined and the absorbance was measured at 390 nm against the reagent blank or against pure solvent after removing the last traces of water with anhydrous sodium sulphate.

5.1.4 Studies of Different Variables and Results

A. Absorbance Curves - The absorbance values in the range 330 to 490 nm were recorded for uranium(VI)- benzoylacetanilide extracts of different concentrations, as well as of the reagent blank. The

data obtained for the useful range as presented in Figure 5.1-1., indicated that a flat maximum was exhibited around 375 nm beyond which the absorbance value gradually decreased. As the reagent had slight absorption at 375 nm, the subsequent measurements were carried out at 390 nm, where pure isobutyl methyl ketone could be used as the reference without any effective loss in sensitivity.

B. Selection of the Extracting Solvent - Several oxygenated solvents were tried, but only isobutyl methyl ketone and tri-n-butyl phosphate were found to extract the uranium complex quantitatively in one or two steps. A 9:1 mixture of these two solvents could also be used. Due to the lower cost and ease in the purification and recovery pure isobutyl methyl ketone was selected.

C. Effect of pH - A set of uranium(VI) (200 µg) solutions containing the reagent was adjusted to different pH-values and the complex was formed and extracted. Qualitative tests for uranium(VI) with ferrocyanide were performed with the aqueous layers left after the extraction. The results confirmed that the process was quantitative above pH 6.5 when pyridine was used to control the pH. The effect of pH on the process of extraction has been presented in Figure 5.1-2. When only aqueous ammonia was used to adjust the pH, the extraction was maximum (about 91%) between pH 6.8 and 7.0. The low extraction was probably caused by the local concentration of ammonia resulting in the formation of some diuranate. However, the adjustment of pH with ammonia in the initial stage and finally with pyridine was easier resulting in quantitative transfer of the complex into the organic layer.

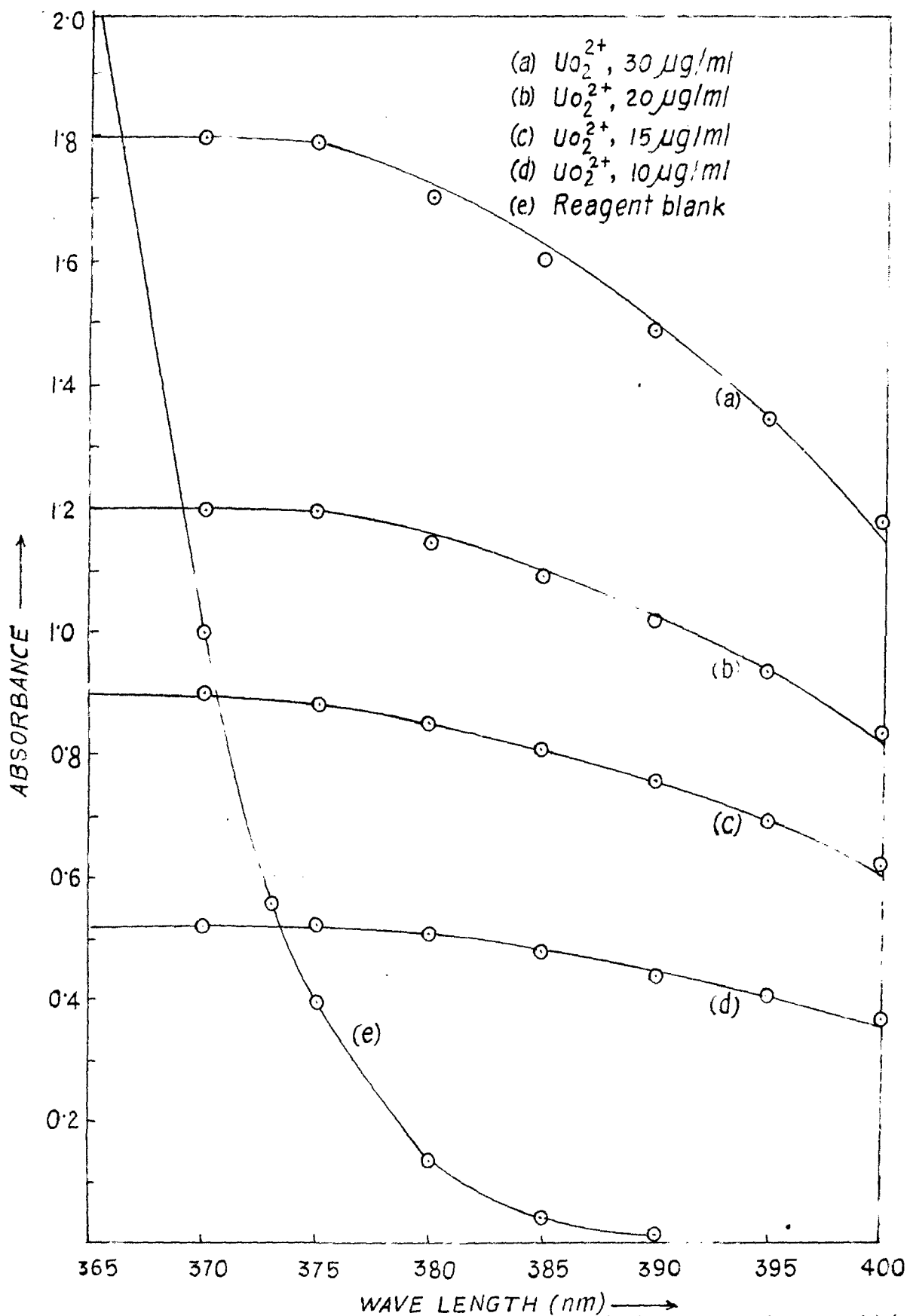


Fig 5.1-1. Absorbance curves of Uranium (VI) - Benzoylacetylacetonate in Isobutyl methyl Ketone.

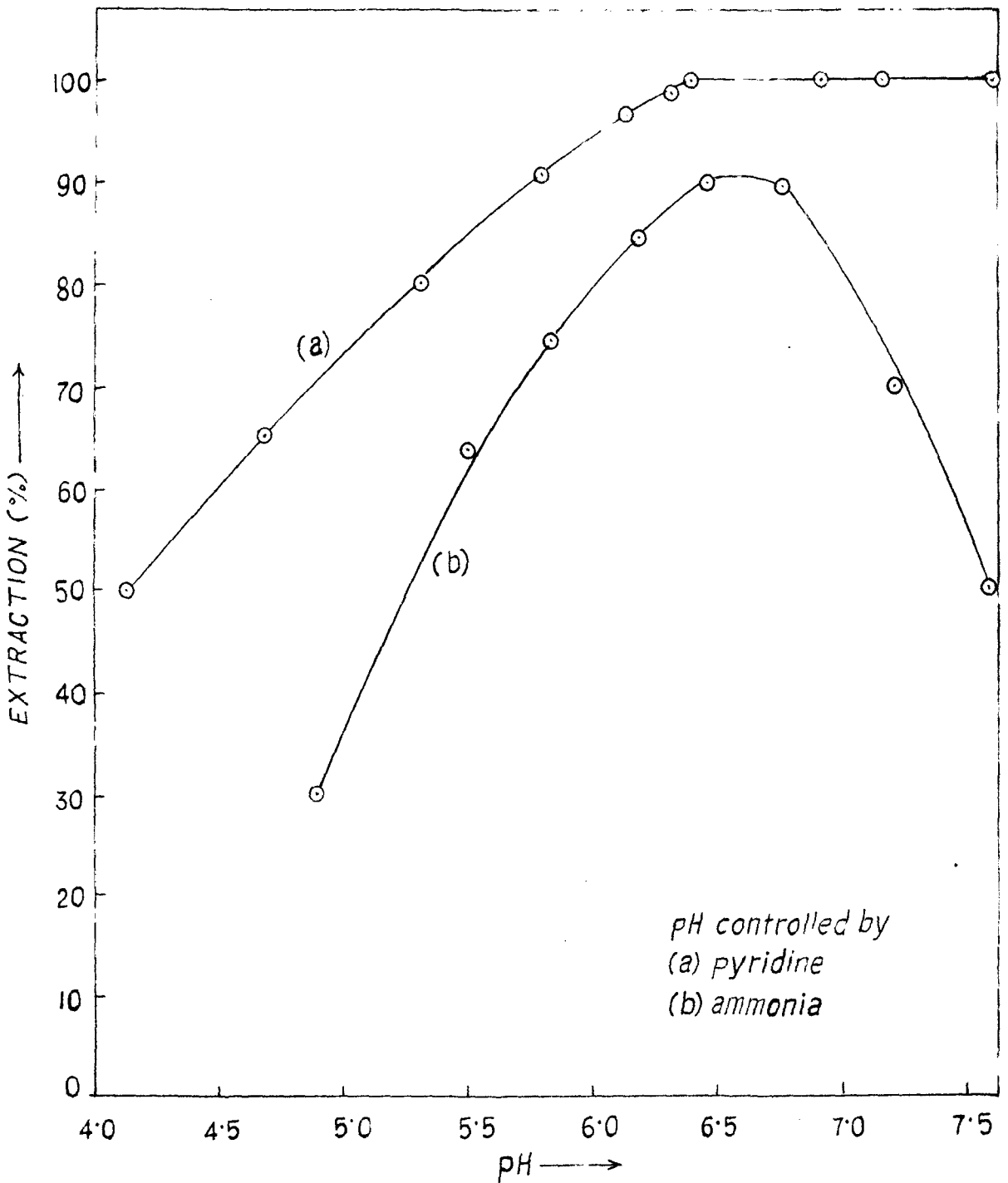


Fig. 5.1-2. Effect of pH on the extraction of Uranium (VI) - Benzoylacetanilide in Isobutyl methyl Ketone.

D. Effect of the Concentration of the Reagent - Using 1.0 to 20.0 mg of the reagent for each extraction keeping all the other conditions identical, it was observed that 10 mg of the reagent in two 5 mg installments, as described under 5.1.3., were necessary and sufficient when the complex was allowed to form in the aqueous layer before the addition of isobutyl methyl ketone.

E. Effect of Number of Extractions - From the experimental results presented in Table 5.1 - I it was concluded that the uranium(VI) complex was transferred into the isobutylmethyl ketone layer almost completely in a single step. A second extraction ensured a quantitative transfer.

Table 5.1 - I

Effect of Number of Extractions

Wave-length : 390 nm

U(VI) taken, (μg)	First Extraction		Second Extraction	
	Absorbance	U found(μg)	Absorbance	U found (μg)
12.5	0.64	12.25	0.02	0.30
15.0	0.75	14.50	0.03	0.50
20.0	1.00	19.50	0.04	0.70

F. Stability of the Complex - The absorbance values of several extracts were recorded just after the transfer and at intervals of 15 minutes thereafter. The curves in figure 5.1-3 show that the complex was stable in isobutyl methyl ketone upto 3 hours.

G. Conformity to Beer's Law - The absorbance values at 390 nm of the uranium(VI)- benzoylacetanilide complex extracted in isobutyl methyl ketone were recorded starting with varying amounts of uranium. Beer's law was found to be valid for solutions containing upto 40 µg of uranium(VI) per millilitre of the ketone as evident from the results presented in Figure 5.1 - 4.

H. Effect of Sequestering Agents - The determination of uranium was carried out after adding sufficient quantities of different sequestering agents. Experimental results as presented in Table 5.1-II show that there was no interference due to the presence of triethanolamine, ethylenediamine and magnesium -EDTA and these substances could be used for masking other ions during the estimation of uranium(VI).

Table 5.1 - II

Effect of Sequestering Agents

U(VI) taken : 12.5 µg/ml

Wave-length : 390 nm

Sequestering agent	Absorbance	U found(µg/ml)	Rel.Error(%)
Mg-EDTA (≡ 0.1g Na ₂ EDTA)	0.65,0.645	12.5,12.4	nil, -0.8
Triethanolamine,0.5 ml	0.65, 0.65	12.5, 12.5	nil, nil
Ethylenediamine,0.2 ml	0.65, 0.65	12.5, 12.5	nil, nil

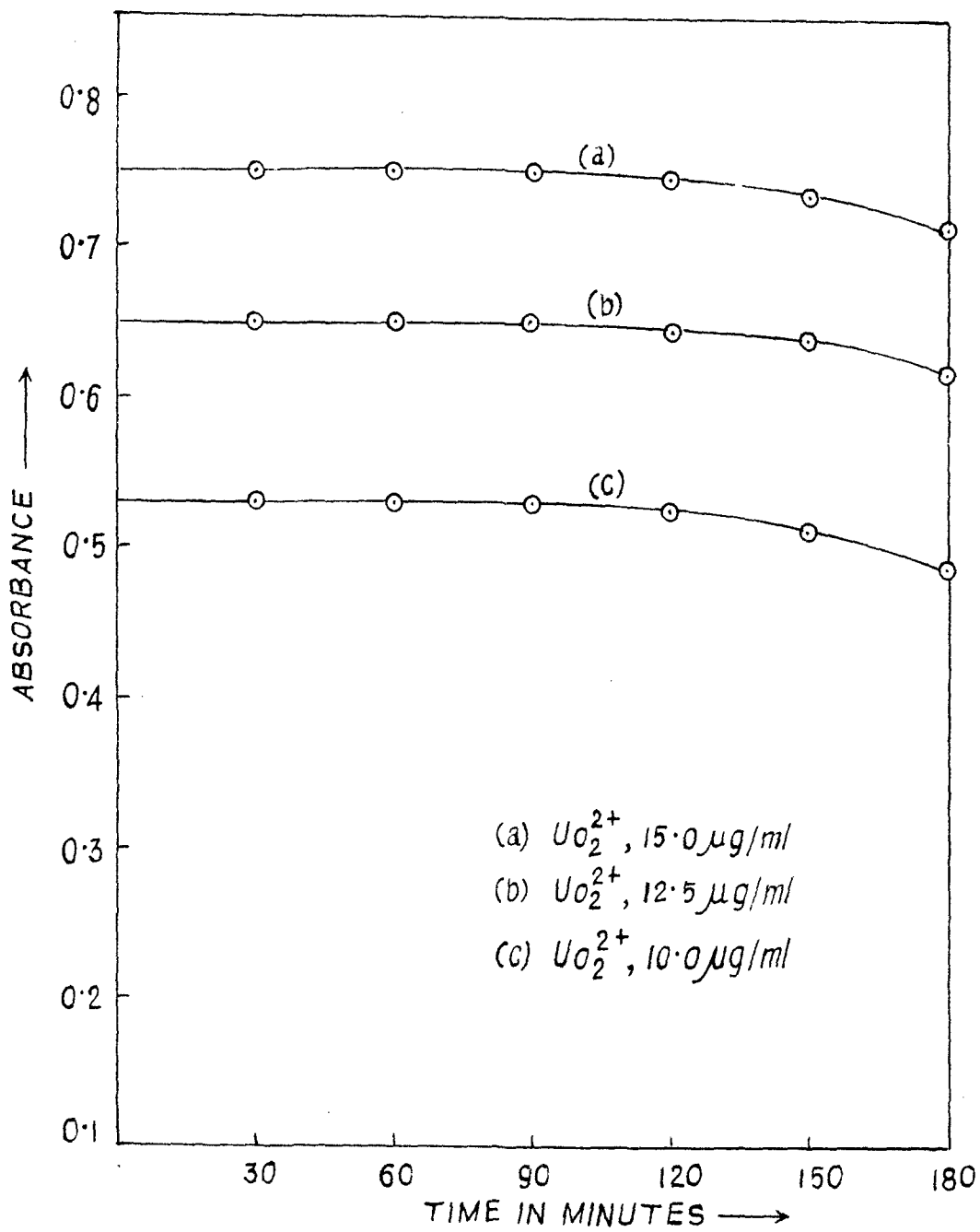


Fig. 5:1-3. Stability of Uranium (VI)-Benzoylacetylacetonate in Isobutyl methyl Ketone

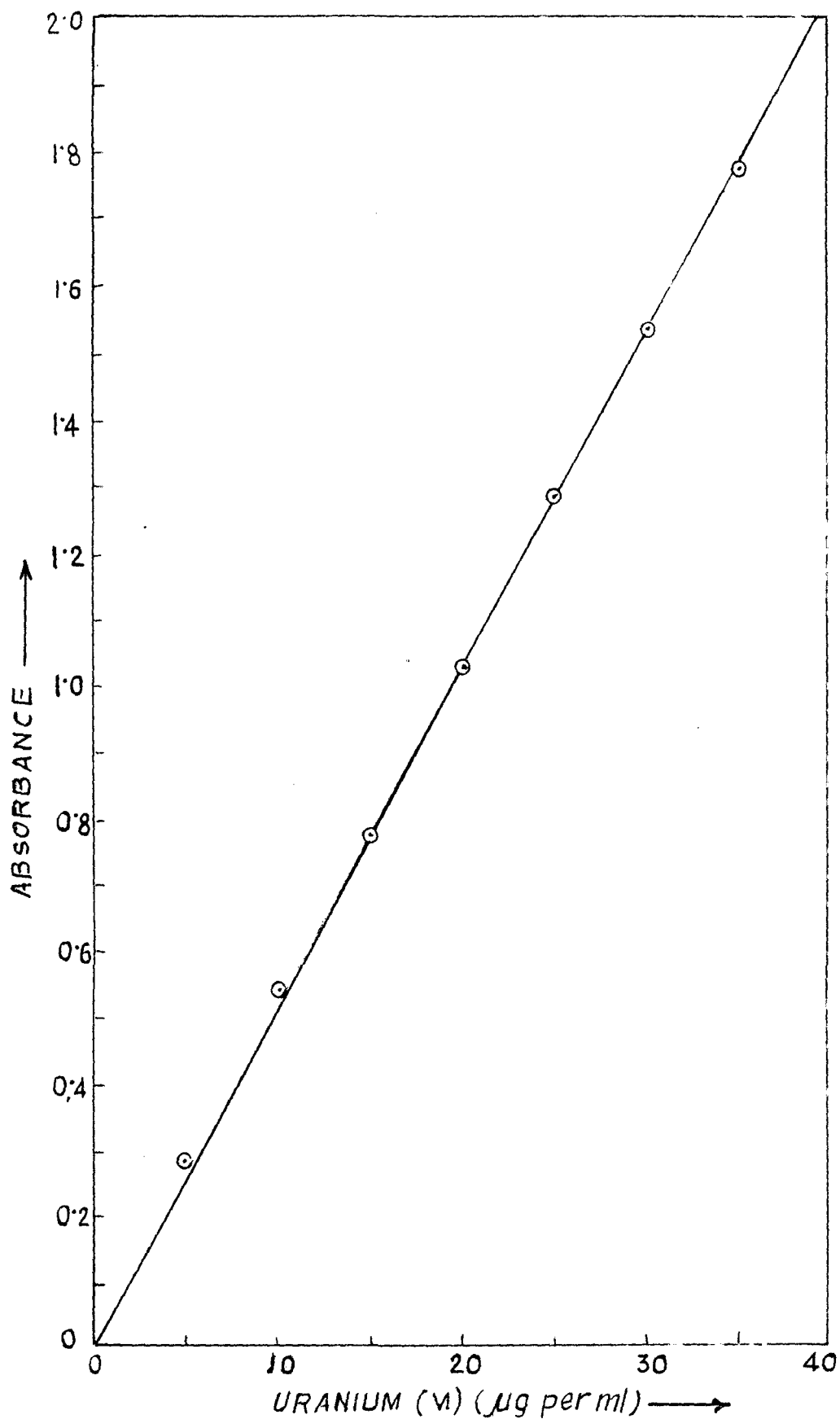


Fig. 5.1-4. Absorbance of Uranium (VI) Benzoyl-acetanilide against concentration.

However, sulphosalicylic, thioglycolic, nitrilotriacetic, tartaric, oxalic, citric and phosphoric acids as well as fluoride ion were found to prevent the formation of the uranium(VI) - benzoylacetylacetonide complex.

I. Effect of Diverse Ions - A known quantity of uranium(VI) (200 μg) was mixed with desired amounts of Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Bi^{3+} , Fe^{3+} , Al^{3+} , Ce^{3+} , Th^{4+} , VO^{2+} , Zr^{4+} , CrO_4^{2-} or MoO_4^{2-} solution, 4- ml of the magnesium - EDTA solution was added to it and the mixture was boiled for about 5 minutes. After cooling, the pH of the mixture was adjusted and the extraction was worked out as described in section 5.1.3. The absorbance values of these extracts showed that there was no interference due to the presence of the ions mentioned above in quantities upto five times the molar quantity of uranium(VI) . The results are given in Table 5.1 - III.

Table 5.1 - III.

Determination of Uranium(VI) in the presence of Diverse Ions

U(VI) taken : 12.5 µg/ml

Wave-length : 390 nm.

Diverse ion (mg)	Absorbance	U found(µg/ml)	Rel. Error(%)	
Ca ²⁺	2.0	0.65, 0.65	12.5, 12.5	nil, nil
Sr ²⁺	2.0	0.65, 0.65	12.5, 12.5	nil, nil
Ba ²⁺	2.0	0.655, 0.65	12.63, 12.5	+1.0 nil
Mg ²⁺	2.0	0.655, 0.65	12.63, 12.5	+1.0, nil
Hg ²⁺	0.5	0.648, 0.65	12.44, 12.5	-0.5, nil
Cu ²⁺	0.5	0.645, 0.645	12.38, 12.38	-1.0, -1.0
Cd ²⁺	0.5	0.65, 0.645	12.5, 12.38	nil, -1.0
Zn ²⁺	0.5	0.655, 0.648	12.63, 12.44	+1.0, -0.5
Mn ²⁺	0.5	0.663, 0.648	12.81, 12.44	+2.5, -0.5
Co ²⁺	0.5	0.655, 0.648	12.63, 12.44	+1.0, -0.5
Ni ²⁺	0.5	0.65, 0.648	12.5, 12.44	nil, -0.5
Pb ²⁺	0.5	0.648, 0.64	12.44, 12.25	-0.5, -2.0
Bi ³⁺	0.5	0.663, 0.645	12.81, 12.38	+2.5, -1.0
Fe ³⁺	0.5	0.65, 0.64	12.5, 12.25	nil, -2.0
Al ³⁺	0.5	0.655, 0.645	12.63, 12.38	+1.0, -1.0
Ce ³⁺	0.5	0.65, 0.645	12.5, 12.38	nil, -1.0
Th ⁴⁺	0.5	0.65, 0.645	12.5, 12.38	nil, -1.0
Zr ⁴⁺	0.5	0.645, 0.645	12.38, 12.38	-1.0, -1.0
VO ²⁺	0.5	0.645, 0.64	12.38, 12.25	-1.0, -2.0
CrO ₄ ²⁻	0.5	0.645, 0.645	12.38, 12.38	-1.0, -1.0
MoO ₄ ²⁻	0.5	0.65, 0.64	12.5, 12.25	nil, -2.0

However, the absorbance values were low in the presence of

tungstate and vanadate.

J. Optimum Concentration Range and Sensitivity

According to Sandell's⁹ definition the optimum concentration range was found to be 4.5 to 12.5 μg of uranium per millilitre of the solvent. The sensitivity of the reaction was 0.019 μg per cm^2 , while the practical sensitivity, based on the detection of 0.01 absorbance unit was 0.19 μg of uranium per cm^2 corresponding to the measurements at 390 nm.

5.1.5. Molar Absorptivity and Standard Deviation

The molar absorptivity at 390 nm was $12,414 \pm 4.0\%$, while the relative standard deviation for the determinations was $\pm 0.70\%$.

5.1.6. DISCUSSION

Benzoylacetanilide has been found to be a very good reagent for uranium(VI) as small amounts of this ion (1.0 to 40.0 μg per ml of isobutyl methyl ketone) can be determined spectrophotometrically after extracting the complex from aqueous solutions buffered above pH 6.5 with pyridine. The procedure is simple as the pure solvent can be used as reference when the absorption measurements are done at 390 nm. The principal advantage of the procedure developed lies in the determination of uranium(VI) in the presence of ions like CrO_4^{2-} , MoO_4^{2-} , Fe^{3+} , Ce^{3+} , Th^{4+} , Zr^{4+} and VO^{2+} without prior separation using magnesium-EDTA as masking agent. Uranium has also

been determined in the presence of Ca^{2+} , Sr^{2+} , Ba^{2+} , Mg^{2+} , Hg^{2+} ,
 Cu^{2+} , Cd^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Pb^{2+} , Bi^{3+} , and Al^{3+} .

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