

TABLE 1 — MICRODETERMINATION OF ASPARTIC AND GLUTAMIC ACIDS

Aspartic acid (μg)		Glutamic acid (μg)	
Taken	Found	Taken	Found
266	269	294	300
	271		297
	274		300
133	136	147	150
	138		153
	138		153
67	69	74	77
	67		79
	69		77

study are presented in this note. Only one carboxylic group of the aspartic and glutamic acids was found to react with sodium phenobarbitone. Further, the potentiometric titrations of hydrochloric acid by sodium phenobarbitone gave sharp inflexions at one equivalence between pH 4.5 and 7.0. The method described is accurate, less time consuming and gives reproducible results (Table 1). However the determination of the individual acid in their binary mixture is not feasible because of interference.

The reagents used were aspartic acid (E. Merck), glutamic acid (E. Merck), sodium phenobarbitone (K. Light), and bromocresol purple (BDH).

Procedure — An aliquot (0.5 ml) of 0.001M aspartic or glutamic acid was diluted with distilled water to about 15 ml, and 1 or 2 drops of 0.0053% solution of bromocresol purple added to it. The resulting yellow solution was titrated against 0.001M sodium phenobarbitone to the first faint pink colour. The results are given in Table 1.

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Phenylazoacetaldoxime, a New Reagent for the Estimation of Co(II or III)

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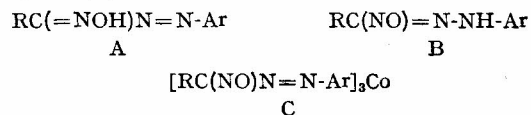
The title reagent has been successfully used for the gravimetric determination of Co(II or III). Co(III)-oxime complex absorbs strongly in UV-visible region in benzene. This has led to the development of a spectrophotometric method for the determination of microquantities of Co(III). Phenylazo-*p*-tolualdoxime is equally effective for the determination of cobalt.

THE commonly used reagents for the estimation of cobalt are oximes¹⁻⁷. A new class of azo-oximes (A, R=alkyl or aryl) found to have a very

high affinity for Co²⁺ and Co³⁺ was synthesized by Bamberger *et al.*⁸. In this paper some of the analytical applications of this class of azo-oximes are reported. These compounds, commonly known as C-nitrosohydrazones (B), actually exist as oximes (A)⁹.

The reaction between cobalt (II or III) salts and arylazo-oximes (A), leads to the formation of complexes of the type tris(arylaazo-oximate)cobalt (III) (C)⁹ which have a dark red colour, show intense absorption bands in UV and visible region and are completely insoluble in aqueous medium. The precipitation of cobalt with arylazo-oximes in the aqueous medium is quantitative.

The arylazo-oximes (A) were prepared by the revised procedure of Bamberger *et al.*^{8,9}. Phenylazoacetaldoxime (A, R=CH₃, Ar=C₆H₅, m.p. 117°), phenylazobenzaldoxime (A, R=Ar=C₆H₅, m.p. 133°) and phenylazo-*p*-tolualdoxime (A, R=C₆H₄CH₃, Ar=C₆H₅, m.p. 132°) were used for the estimation of Co(III). A slight excess of arylazo-oxime (A), dissolved in aq. ammonia (1:1) was added dropwise with continuous shaking to Co(II) salt solution in water and pH of the solution adjusted to ~8 by adding aq. ammonia. The dark brown precipitates were digested on a water-bath for 30 min, the precipitates filtered, heated to a constant weight and washed with 5% ammoniacal solution till these were completely free of the precipitating reagent. The precipitates were finally washed with doubly distilled water and dried overnight at 140° and cobalt estimated from the weight of the precipitated complex (C).



The anions NO₃⁻, SO₄²⁻, CH₃COO⁻, Cl⁻, ClO₄⁻ do not interfere with the estimation of Co(III). However, the transition metals like Fe, Mn, Ni, Cu do interfere. The method is particularly useful for the determination of Co(II) and Co(III) in their coordination complexes. The aqueous solution of the Co³⁺ or Co²⁺ was obtained from the complex of cobalt (II or III) after digesting several times with an acid mixture containing conc. HNO₃, conc. H₂SO₄ and conc. HClO₄. This solution was then used for the estimation of the metal gravimetrically by arylazo-oximes as described above. The estimation of cobalt by this method was successfully carried out from its complexes of hydroxyazophenols, salicylaldehydes and *o*-hydroxyacetophenimines. The % error was always less than 0.5. This method gives better results than α -nitroso- β -naphthol method for the gravimetric estimation of cobalt¹⁰. The tris(phenylazoacetaldoximate) Co(III) chelate (C, R=CH₃) gives intense red purple colour in benzene; λ_{max} 490, 390, 315 (ϵ 11300, 14000, 41500). These solutions obey the Lambert-Beer's law over a wide range of concentrations. All these three bands were successfully employed for the estimation of cobalt spectrophotometrically.

Co²⁺ in aqueous solution was precipitated by aq. ammoniacal solution of phenylazoacet-

doxime. The precipitates obtained after digestion were filtered in a sintered funnel, rendered free from the reagent by washing with 5% ammoniacal solution and finally with distilled water. The precipitates were dried for 2-3 hr at 140° and thereafter dissolved completely in a known amount of benzene. The optical density of this solution was then measured at 490, 390 or at 315 nm. From the optical density, the concentration of the complex (C, R=CH₃) and hence of cobalt was calculated. The percentage error by this method generally does not exceed ± 2.0 .

The other arylazo oxime tried successfully for the spectrophotometric determination of cobalt was phenylazo-*p*-tolualdoxime (A, R=C₆H₄CH₃, Ar=C₆H₅). The cobalt (III) complex of this reagent shows maximum absorption at 510 ($\epsilon=10200$) and 325 nm ($\epsilon=73500$). This reagent has a slight advantage, since the charge transfer band at 325 nm ($\epsilon=73500$) is best suited for analysing the micro-quantities of cobalt. By using this band 1 μ g/ml of cobalt in solution can be conveniently estimated. All the spectrophotometric measurements were carried out on a Hilger and Watts spectrophotometer.

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Extractive Spectrophotometric Determination of V(V) Using Salicylhydroxamic Acid

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A rapid and accurate extractive spectrophotometric method for the determination of V(V) in geological samples, based on the extraction of the coloured complex between V(V) and salicylhydroxamic acid at pH 3 by methyl isobutyl ketone is described. Vanadium(V) present in ppm levels in geological samples has been successfully determined.

RAY and Bhaduri¹ have studied the reaction of vanadium(V) with salicylhydroxamic acid (SHA) and have used this reaction for colorimetric

as well as extractive spectrophotometric determination of vanadium.

As versatile analytical procedures for the determination of minor and trace quantities of vanadium in geological materials and related industrial products are not abundant^{2,3} an attempt has been made to utilize the sensitive colour reaction of vanadium(V) with SHA for the development of a rapid and accurate procedure for the extractive spectrophotometric determination of V(V) in various types of rocks, minerals, ores, refractories, etc., using methyl isobutyl ketone (MIBK) for the extraction of the coloured complex at \sim pH 3.

Salicylhydroxamic acid was prepared and purified by standard method⁴ and 1 g of the purified product was dissolved in 100 ml of ethyl alcohol. The buffer solution used (pH = 3.0) was prepared as follows:

Monochloroacetic acid (19 g) was dissolved in water (50 ml). An aliquot (25 ml) of this solution was neutralized with 2N caustic soda solution and the remaining monochloroacetic acid solution added to the neutralized solution.

The absorption measurements were made on a Unicam SP500 spectrophotometer. pH of the experimental solutions, after the addition of buffer, were measured with a Beckman pH meter (model zeromatic II). Decomposition of the samples was done by the usual sodium carbonate fusion method and the solution for analysis was made by leaching the Na₂CO₃ melt with water and acidifying with dil. H₂SO₄.

Determination of vanadium by extraction with MIBK—To an aliquot of the sample solution (20 or 50 ml) was added the buffer solution (2 ml) and the pH adjusted to 3.0 ± 0.1 . Salicylhydroxamic acid reagent solution (15 ml) was added to this and mixed thoroughly. The coloured complex was extracted with a measured 10 ml portion of MIBK. The organic layer was allowed to separate and transferred to a stoppered bottle containing anhydrous sodium sulphate. Optical density of the organic layer was then measured at 480 nm against the process blank. The amount of vanadium was found out from the calibration curve prepared from the standard vanadium solution following the procedure of extraction as described above. The results of these experiments are recorded in Table 1.

The vanadium-SHA colour reaction is dependent on pH and monochloroacetic acid buffer (pH 3.0) has been found to give satisfactory results.

TABLE 1 — ANALYSIS OF V(V) IN GEOLOGICAL SAMPLES

Description of sample	Source	Vanadium in ppm	
		SHA method	Reported val.
Basalt	Nancy ⁵	250	240
Biotite (mica Fe)	do	160	160
Granite	do	35	36
Peridotite	USGS ⁶	37	31.2
Andesite	do	120	125
Basalt	do	400	399