

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 $\mu\text{g/ml}$ 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 $\sim \text{pH } 3$.

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 ($\text{pH} = 3.0$) 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 ($\text{pH } 3.0$) 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

Aqueous-ethanol medium has been found to produce stable colour. Interfering ions like Fe^{3+} , Ti^{4+} , etc., are removed during carbonate fusion and subsequent aqueous extraction. The vanadium present in the solution reacts immediately with SHA under the experimental conditions and full colour is developed immediately which remains stable for more than 24 hr. This procedure is particularly suitable for the estimation of vanadium in bauxite, magnetite, ilmenite, etc. In view of purity, availability, good solvent property and better extraction efficiency, methyl isobutyl ketone (MIBK) has been preferred as the extracting solvent to alcohols or esters used by other workers. The coloured complex can be quantitatively extracted by a single extraction with MIBK at pH 3, which makes the procedure simple and rapid. The method is sensitive as well as accurate and can be applied successfully for the determination of vanadium in various types of rocks, minerals, ores, etc., where vanadium is present in the p.p.m. level.

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Rapid Separation & Simultaneous Spectrophotometric Determination of U(VI) Using N-*m*-Tolyl-*o*-methoxybenzohydroxamic Acid

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A method is presented for rapid liquid-liquid extraction and simultaneous spectrophotometric determination of U(VI) in the presence of various anions and cations which are usually associated with it using N-*m*-tolyl-*o*-methoxybenzohydroxamic acid (TMBHA) in chloroform. The effect of various parameters such as pH reagent concentration, volume of mother liquor, foreign ions, etc., on the extraction and determination of uranium is discussed. The sensitivity of colorimetric determination of U(VI) with the present method is about 8 times more than the sensitivity of the most sensitive hydroxamic acid method used hitherto.

THE first detailed examination of N-phenylbenzohydroxamic acid (PBHA) as a reagent for uranium was carried out recently¹. It was found that in the extraction of U(VI), many cations interfered and the colour of the extracted U(VI)-PBHA complex with $\lambda_{\text{max}} = 510$ nm was suitable

only for the determination of milligram quantities of uranium, the molar absorptivity at λ_{max} being as low as 230. The selectivity was also low and no attempt was made to counter the interference of various common and less-common metals which are associated with uranium in minerals and fission products. Subsequently N-phenyl-2-naphthohydroxamic acid (PNHA) was prepared and tried as a reagent for U(VI)². PNHA, though proving highly sensitive and selective for V(V)³, came off as only a marginal improvement on PBHA in case of U(VI), in both sensitivity and selectivity.

N-*m*-tolyl-*o*-methoxybenzohydroxamic acid (TMBHA) is now presented as a reagent more selective than either PBHA or PNHA and about eight times more sensitive than PNHA for the extractive colorimetric determination of U(VI).

All the chemicals used were of reagent grade unless specified. Conductivity water was used for all purpose. A stock solution of U(VI) was prepared by dissolving uranyl nitrate (0.5 g) in water (1 litre) and standardizing the solution for uranium⁴.

TMBHA was prepared by the method of Gupta and Tandon⁵, and recrystallized repeatedly, m.p. 110° (lit.⁵ m.p. 111°). The reagent is very stable if stored out of contact of light and air. A 0.1M solution of TMBHA in ethanol-free doubly distilled chloroform was used for extraction work.

pH measurements were carried out with a radio-meter pH meter type PHM-29. The absorption spectra were recorded on a Perkin-Elmer model 402 spectrophotometer and measurements at a constant wavelength were done with a SF-4 (USSR) spectrophotometer. All optical measurements were carried out using matched quartz cells with 10 mm path-length.

Extraction procedure—An aliquot solution of U(VI) containing 15 to 950 $\mu\text{g}/\text{ml}$ of uranium was adjusted at pH 4.4-5.2 with the help of dil. NaOH or HNO_3 . To it was added TMBHA solution (4 ml) in chloroform and the two phases equilibrated for about 5 min, kept aside for complete separation and the chloroform layer removed. The aqueous layer was again extracted with a fresh 4 ml portion of TMBHA for 5 min, the chloroform extract mixed with the first extract, dried (Na_2SO_4), and made up to 10 ml with TMBHA solution. The absorbance of the orange-yellow extract was measured against TMBHA solution as blank. The extracts containing 15-90 $\mu\text{g}/\text{ml}$ of uranium were measured at 360 nm and those containing 80-950 $\mu\text{g}/\text{ml}$ of uranium were measured at 520 nm. A calibration curve was set by extraction-colorimetric determination of several known amounts of uranium and plotting the optical density values against concentration of uranium. The results were found reproducible within $\pm 0.5\%$.

The absorption spectra of uranium extract of TMBHA in chloroform against reagent (TMBHA solution in chloroform) blank exhibits a sharp peak at 360 nm and a broad peak at 518-522 nm. Beer's law is obeyed in the range 15-90 $\mu\text{g}/\text{ml}$ of U(VI) at 360 nm and 80-950 $\mu\text{g}/\text{ml}$ of U(VI) at 520 nm; the molar absorptivities being 2×10^3 at 360 nm and 285 at 520 nm. Thus uranium, if present in concentrations less than 90 $\mu\text{g}/\text{ml}$ can be determined