amino form —NH_2 group is hydrogen bonded to the neighbouring nitrogen. The formation of uranyl chelate may be considered as merely a substitution of UO_2^{2+} for the hydrogen bonded hydrogen atom.

$\log K_1$ is lower but $\log \beta_2$ is higher than the pK of melamine. The presence of two identical ligands around UO_2^{2+} to fulfil the maximum coordination number of uranyl ion renders 1:2 chelates more stable.

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Separation & Determination of Rhenium by Extraction of Its Thiocyanate with Chloroform

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A simple method both for separation and determination of rhenium has been worked out. Perrhenate ion, ReO_4^-, on reduction in acid solution, forms a coloured complex with thiocyanate which is extractable into chloroform in the presence of alcohol. Rhenium is determined by measuring the absorbance at $\lambda_{max} = 430$nm. W(VI), U(VI), V(V), Pt(IV), Pd(II) and many other elements do not interfere in the method.

MANY methods for the extractive spectrophotometric determination of rhenium have been proposed. In the most commonly used thiocyanate-tin(II) chloride method[1], though the structure of the rhenium species[2] is undecided, yet the colour of the complex in aqueous sulphuric acid, aqueous hydrochloric acid, ether or isoamyl alcohol, has been made the basis of its spectrophotometric determination in microgram amounts. These methods face serious interference from several elements specially molybdenum and tungsten. However, the former can be removed by selective reduction with mercury in HCl and pre-extraction of its thiocyanate complex or by other methods[3-5], but no method is specifically available for tungsten. With this problem in view, the Re-thiocyanate reaction has been studied and a method has been developed for the determination of rhenium and its separation from tungsten and other elements. The results are reported in this note.

A standard stock solution of rhenium containing 1 mg Re/ml was prepared by dissolving weighed amount of 'specpure' potassium perrhenate (Johnson-Matthey). Lower concentrations at the μg/ml level were made by suitable dilution. Solutions of other ions were prepared by dissolving their sodium or potassium salts (C.P. or A.R. grade) in distilled water. An aqueous solution of potassium thiocyanate (20%) was used. Stannous chloride dihydrate (30g) was dissolved in 20 ml of 1 : 1 HCl by heating, solution was cooled and finally made upto 100 ml.

Procedure — Solution containing microgram amounts of rhenium and milligram amounts of any other ion, hydrochloric acid (2ml, 10M), ethyl alcohol (10 ml), potassium thiocyanate (1 ml, 20%) and stannous chloride (1 ml, 30%) was taken in a 100 ml separatory funnel and diluted to 20 ml with distilled water. It was gently mixed and allowed to stand for 5 min. The yellow coloured rhenium thiocyanate complex was extracted once with an equal volume of chloroform for 1 min. The solvent was filtered through a dry filter paper to remove any hanging water droplets and taken in a 25 ml volumetric flask and made upto the mark with chloroform. Absorbance measurements were made on a Hilger & Watts 'Spekker Absorptiometer' using Kodak filter No. 1 (λ_{max}, 430 nm) and 1 cm cells against chloroform blank.

The interference of other ions was studied under similar conditions. For separation purposes, the metal ion can be recovered from the solvent by back-extracting twice with an equal volume of water each time for 1 min. The combined back-extracts were made slightly alkaline and H_2O_2 (1–2 ml, 6%) was added and boiled to oxidize the reduced metal ion/s. Excess of H_2O_2 was removed by boiling in acid medium.

The elements were determined by appropriate conventional methods[6].

Rhenium(VII), in acid media, forms a yellow complex with thiocyanate on reduction with stannous chloride. The coloured species is extractable into chloroform only in the presence of ethyl alcohol. In hydrochloric acid medium, the extraction of rhenium increases with increase in acidity. It is maximum at 1M HCl and then tends to level off at higher acidities. Chloroform does not extract any rhenium even under optimum conditions unless ethyl alcohol is present in the aqueous phase. The extraction of rhenium changes from 12.5 to 100% as the alcoholic content is increased from 4 to 10 ml or more (per 20 ml). With 0.2 ml of potassium thiocyanate (20%), the extraction of rhenium is 80%, and with 1-2.5 ml, it is 100%. The extraction is 60% with 0.5 ml stannous chloride (30%) and increases to 100% with 1–2 ml of the reagent.

In view of the above data, the optimum conditions for the quantitative extraction of rhenium are the presence of 1M HCl, 10 ml ethyl alcohol, 1 ml potassium thiocyanate, 1 ml stannous chloride in a total volume of 20 ml, a waiting time of 5 min and a single equilibration for 1 min with an equal volume of chloroform.

The effect of a number of foreign ions, often associated with rhenium, was studied. W(VI), Pt(IV), Fe(III), Co(II) and Pd(II), upto 0.5 mg/ml, are not at all extracted. Though U(VI), V(V), Se(IV), Cu(II) and Ni(II) are slightly extracted (0.5, 3.5, 2.5, 0.03, 0.08% respectively), they do not influence the absorbance of rhenium thiocyanate complex. Upto 200 mg each of sulphate, chloride, oxalate, tartrate in 20 ml of aqueous phase, no effect on the absorbance of rhenium was observed. Molybdenum interferes seriously and requires prior separation as in other methods. Rhenium was determined from a standard curve prepared using a similarly prepared blank.

The proposed method has been satisfactorily applied to a wide variety of synthetic and technical (reverberatory flue dust) samples. It is of special value when the sample contains tungsten and platinum metals.

The method has good reproducibility with a standard deviation of $\pm 8 \times 10^{-4}$.

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Micro-determination of Hafnium Using ^{32}P as Radioactive Indicator

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A simple method for micro-determination of hafnium in nitric acid medium using ^{32}P as radio-active indicator has been developed. Trace amounts of hafnium in the range 2×10^{-6} – 10^{-3} g have been coprecipitated as hafnium pyrophosphate with thallous iodide in the presence of excess of labelled pyrophosphate. The effects of acid concentration and the presence of foreign ions like Al^{3+}, Bi^{3+}, La^{3+}, Cr^{3+}, Fe^{3+}, Sn^{2+}, Ce^{3+} and Ti^{4+} on the determination of hafnium have been also studied.

ZIRCONIUM hydrogen orthophosphate has been successfully employed as a carrier for palladous iodide and silver iodide in the micro-determination of palladium[1] and silver by radiometric procedure thereby overcoming the solubility factor involved in such estimations. The estimation of zirconium as pyrophosphate with radioactive ^{32}P, using thallous iodide as a carrier has also been reported earlier[2]. Since zirconium and hafnium have very close chemical similarities, attempts have been made in the present investigation to determine microamounts of hafnium as hafnium pyrophosphate coprecipitating it with thallous iodide. The radioactive isotope ^{32}P was used as the radioactive indicator for determining hafnium as hafnium pyrophosphate.

Hafnium oxide used was procured from M/s Johnson and Mathey, England. The other chemical reagents used in the experiments were of AR grade. The radioactive isotope ^{32}P was supplied in the carrier free state by BARC, Trombay, as orthophosphoric acid. To prepare labelled pyrophosphate, ^{32}P isotope was thoroughly mixed with inactive disodium hydrogen phosphate solution, evaporated to dryness, and the dry mass was finally heated to 600°C for 6 hr to convert it to active $Na_4P^*_2O_7$ (ref. 3). A known amount of the labelled pyrophosphate, about 2-4 times the theoretical amount as required by the equation, $Hf(IV) + Na_4P^*_2O_7 \rightarrow HfP^*_2O_7$. was mixed with the solution containing hafnium. A solution of potassium iodide was then added. Hafnium was co-precipitated as pyrophosphate along with thallous iodide formed by dropwise addition of thallous sulphate to the solution. The mixture was thoroughly stirred and gently warmed for coagulation of the precipitate. It was then transferred to a 50 ml volumetric flask and the volume was made up to the mark. An aliquot of the solution was filtered out by means of a pipette with a filter paper cap at the end and the activity left in the solution after precipitation was measured by means of a G. M. counter. From the loss of activity due to ^{32}P in the solution and from a knowledge of pyrophosphate added, the total amount of hafnium present in the solution was computed, assuming that the complete uptake of hafnium pyrophosphate takes place by thallous iodide through co-precipitation.

For determination of hafnium in the presence of foreign ions, solution containing hafnium was thoroughly mixed with the solutions of the foreign ions in question separately and hafnium pyrophosphate was co-precipitated with thallous iodide following the procedure already discussed. Experimental results are shown in Table 1.

It is evident from Table 1 that in the experimental conditions, hafnium up to 2 γ can be estimated as pyrophosphate from a solution of nitric acid of 0.01 to 0.1N concentration with a fair degree of accuracy. However, the presence of any foreign ion in the medium has significant effect on the uptake of hafnium by the carrier. At this lower acidity, the error increases due to the interference of the foreign ions. Error caused by the presence of the foreign ions can however, be minimised to some extent by increasing the acid concentration to that in the range 0.1-1N. It was observed that from an acid solution of 0.1-1N, hafnium can be determined in the presence of varying amounts of foreign ions, e.g. Ce^{3+},