

ANALYSIS OF URANIUM IN THE URANIUM ORES OF INDIA

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The processing of Uranium Ore from Jaduguda, Bhatin and Narwapahar and Uranium concentrates from Surda, Rakha and Mosaboni copper concentrator plant tailings to produce mangesium Di-uranate commonly known as yellow cake involves different stages and needs to be analysed for its U_3O_8 content. The methods used for the analysis depends on the uranium content in the sample. The methods generally used are :

- (i) Radiometric Assay and Chemical Assay for feed sample
i.e. upto grinding section
- (ii) Colorimetric Method
- (iii) Fluorimetric for ion exchange barren and tailings
- (iv) By titrimetric method with $K_2Cr_2O_7$ for final product
i.e. yellow cake
- (v) Emission spectrometry for all types of samples

The brief description of different methods adopted are as follows:

(i) Radiometric Method : Generally Beta and Gamma counters are used for radiometric assay of the sample. The counting methods are generally used for the quick determination of the sample where approximate assessment is required. But before using the counting method it should be ensured that the ore samples are in radiometric equilibrium otherwise this method of analysis will be of little use. This method cannot be used for accoutability purposes.

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Beta Activity Measurement : Beta activity of the sample is measured by Geiger Muller Counter. The Geiger counting Tube consists of essentially two electrodes one usually a fine wire and the other concentric metal cylinder of about an inch diameter. The space between two electrodes is filled with a suitable gaseous mixture (usually Argon and ethyl alcohol) at a few cms. pressure and a potential of about 1000 V is applied across the electrodes. The voltage and the gas pressure are so adjusted that in the absence of ions in the gas no discharge take place. A Beta particle passing through the tube and producing one or more ion pairs initiates a cascade of ionisation. A comparatively large surge of current results. The electronic quenching circuit to which the tube is attached is designed so that after a very short period of current flow about (10^{-4} to 10^{-5} seconds) the current is interrupted and the tube is re-charged to enable it to detect another particle. The pulse is amplified and sealed down by a scaling circuit to allow high counting rates to be handled by mechanical recorder.

Gama-Activity Measurement : Since Gamma rays are not charged particles, they are not detectable directly by ordinary counting devices. Instead electrons ejected from matter by the passage of highly penetrating gamma rays can cause ionisation, which is then detected. The ordinary Geiger tube may be used to detect gamma - radiation in the presence of beta activity if a suitable absorber, such as metal plate, is interposed between the tube and the sample to filter out beta - particles. The intensity of gamma radiation is slightly diminished, and the electrons ejected from the absorber and tube walls are counted, the value given being proportional to gamma activity. Ionisation chambers, particularly when filled with gas under pressure, are also used for determining gamma-activity.

N.B: Most experiments with radio active indicators involve the comparison of a control sample with an unknown.

2. Colorimetric Method

(a) Determination of Uranium in samples Free from Interfering Elements with Peroxide in Alkaline Medium

- Reagents :**
- (i) Standard U_3O_8 solution 1 mg/ml
 - (ii) Sodium hydroxide 50% solution (w/v)
 - (iii) Hydrogen peroxide 20% solution (v/v)

Take suitable standard in the range of 1-2 mg/ml and sample solution for determination and blank. Add 5 ml of 50% NaOH and mix well. Add 1 ml of 20% H_2O_2 and make up the volume of solution to 50 ml with distilled water and keep for 15 minutes and filter through double No.40 filter paper. Measure the optical density of the sample solution thus prepared against standard and blank solution prepared in a similar manner. Measure optical density at 380 m μ in a spectrophotometer.

Extraction of *Uranium as Nitrate with TBP followed by Colorimetric Determination with Peroxide in Alkaline Medium* : This method is followed in UCIL generally for all the uranium ore and solution samples containing uranium with interfering elements etc.

Reagents:

- (i) T.B.P. 10% solution in distilled kerosene (v/v)
- (ii) Ferric nitrate - 5% solution
- (iii) Ammonium Nitrate saturated solution
- (iv) Sodium sulphate 5% solution (w/v)
- (v) Hydrogen Peroxide 20% solution (v/v)
- (vi) Sodium hydroxide 50% solution (w/v)
- (vii) Standard uranium solution 1 mg U_3O_8 /ml

Opening of the Ore and Extraction with TBP : 5.0 g of the ore is boiled with 50 ml (1:1) HNO_3 for 3-4 hours. In some ore hydrofluoric acid treatment is needed before addition of HNO_3 . Filter and wash properly. Evaporate the filtrate to dryness. Cool and add 5 ml of 5% Ferric nitrate solution. Extract the uranium from the nitrate solution with 50 ml of 10% TBP in kerosene in a 100 ml separating funnel and shake well for 10 minutes. Allow the layer to separate. Rundown the lower layer and reject it. Add 10 ml of saturated ammonium nitrate solution and shake for two minutes. Allow the layers to separate. Run down the lower layer and reject. Repeat the washing with ammonium nitrate solution.

Back Extraction of Uranium : Add 10 ml of sodium sulphate solution and shake well for 5 to 7 minutes. Allow the layer to separate. Run down the lower layer containing the uranium in to a clear 100 ml beaker. Repeat the back extraction with sodium sulphate solution twice and collect the aqueous layer in the same beaker.

Extraction for blank and standard to be proceeded in the similar manner.

Colorimetric determination should be carried with 50% NaOH and H_2O_2 as described earlier.

Spectrophotometric Determination of Uranium in Sulphuric Acid Leach solution : Uranium is separated from contaminants by solvent extraction from aluminium nitrate solution using ethyl acetate. Colour is developed by introducing an aliquot of the extract into an acetone pyridine solution of dibenzoyl methane. The absorbance of the coloured solution is measured using a spectrophotometer at 390 $\text{m}\mu$. This method is applicable for low concentration of uranium. The lowest range is about $10\mu\text{ g U}_3\text{O}_8$ in 10 ml of final coloured solution. The optimum range for the leach solutions is 0.1 to 1.0 g/l U_3O_8 .

Reagents :

- (i) Standard U_3O_8 solution 0.1 mg/ml
- (ii) Saturated aluminium nitrate 50%
- (iii) Ethyl acetate analar
- (iv) *Dibenzoyl methane solution* - Prepare 1% solution of dibenzoyl methane in pure distilled acetone
- (v) *Chromogenic Reagent* : To 40 ml of the dibenzoyl methane solution add 100 ml of analar grade pyridine, followed by 800 ml of pure distilled acetone. Dilute this solution to 1000 ml with distilled water

Procedure : Pipette out a suitable volume of leach liquor not exceeding 2 ml to contain between 0.05 mg and 0.50 mg U_3O_8 into 30 ml stoppered test-tubes. Add dilute ammonia dropwise till the precipitation of metal ions just begin. Add 5 ml saturated aluminium nitrate solution and mix thoroughly. Accurately pipette 10.0 ml of ethyl acetate into the test tube and shake for 2 minutes. Allow the phase to separate. With a dry pipette carefully introduce 1 ml of organic phase into 10 ml volumetric flask. Fill the volume upto the mark with the chromogenic reagents, mix and keep aside for 15 minutes and measure the absorbance. Treat blank and standard in the similar manner.

3, Fluorimetric Determination of Uranium

Fluorimetric determination of uranium in solutions has been in use right from the days of Manhattan Project in USA. It is one of the most sensitive wet chemical method available for this purpose. It involves the separation of uranium from the sample solution by extraction with ethyl acetate in presence of saturated solution of aluminium nitrate which acts as a salting out reagent. After extraction an aliquot (0.1 ml) of the extract is pipetted into platinum dish specially made for fluorimetric work and the solvent is evaporated under infrared lamp. The residue is fused with about 0.4gm of sodium

fluoride and sodium carbonate flux at a temperature of about 800°C for 3 minutes using muffle furnace. The melt is cooled and the fluorescence of the resultant bead is measured using Galvanek Marrision reflectance fluorimeter. Using a set of standards containing known amount of uranium, a calibration graph is obtained. Minimum and maximum range of estimation are 0.01 µg - 1 µg.

Reagent :

- (i) Sodium carbonate - sodium fluoride flux (4:1)
- (ii) Ethyl acetate
- (iii) Standard Uranium solution 10 µg U₃O₈ /ml

Modified fluorimetric method : Periodically, the analytical methods used in the laboratory are being reviewed with the aim of either improving the efficiency or reducing the cost and time of analysis. While reviewing the fluorimetric method a fresh approach has been made by substituting the solvent itself. While using ethyl acetate, extraction is done in the nitrate medium. Since most of our samples are in sulphuric acid medium it was thought to use a solvent which extract uranium in sulphate medium itself. Currently tertiary amine has got wide application in uranium industry. Alamine-336 was found very selective extractant for quantitative extraction of uranium.

The same solvent was selected for fluorimetric determination of uranium. Other procedure is same as described in ethyl acetate extraction system.

Reagent :

- (i) 1% alamine-336 (v/v) in benzene
- (ii) H₂SO₄ solution of 1.5 pH
- (iii) Sodium carbonate - sodium fluoride flux (4:1)
- (iv) Standard uranium solution 10 µg/ml.

Uranium is extracted from the aqueous solution by 1.0 percent solution of Alamine-336 in Benzene. An aliquot of the extract is evaporated and the residue fused with fluoride carbonate flux as usual as described above. Generally the old fluorimetric method has been used for the samples containing low U_3O_8 i.e. generally below 0.02% but using Alamine extraction in sulphate medium even our feed samples containing 0.04% to 0.10% U_3O_8 has been analysed and the results have been compared with colorimetric method of analysis. The daily feed samples of one month have been compared and the results are given in Table-I

Table - I

**Comparison of Analysis of feed samples of September 1993 by
Fluorimetric and Colorimetric Method**

Sample No.	% U_3O_8		Sample No.	% U_3O_8	
	Fluorimetry	Colorimetry		Fluorimetry	Colorimetry
1	0.070	0.072	14	0.049	0.050
2	0.071	0.071	15	0.059	0.058
3	0.069	0.070	16	0.057	0.058
4	0.074	0.076	17	0.063	0.062
5	0.072	0.075	18	0.056	0.055
6	0.069	0.068	19	0.057	0.056
7	0.066	0.069	20	0.050	0.053
8	0.064	0.064	21	0.054	0.058
9	0.056	0.056	22	0.052	0.054
10	0.061	0.062	23	0.046	0.045
11	0.058	0.061	24	0.050	0.047
12	0.058	0.061	25	0.069	0.70
13	0.065	0.067			

4. Titrimetric Determination of Uranium in the final product

The determination of uranium in yellow cake and other U-rich materials must often be carried out with a precision higher than that obtainable by fluorimetric, spectrophotometric or polarographic methods and in such cases titrametric methods are almost invariably used.

Although precipitation and complexometric titration method have been proposed for the determination of U (Kolthoff and Elving 1962), only redox methods are useful in practice. The most popular of them are those that use zinc or lead column for reduction of U^6 to U^4 , followed by titration of U^4 with standard $K_2Cr_2O_7$. The disadvantage of these methods is that metallic reductants such as Zn, Pb, Bi will also reduce ions other than U^6 and causes error in uranium determination. For this reason, a preliminary separation of uranium by chromatography, ion-exchange or solvent extraction has to be carried out.

In 1964 Davies and Gray published a titrimetric method of U which does not require column reductors, electronic instruments or an inert atmosphere, and is sufficiently selective to enable uranium to be determined without prior separation. This method involves the reduction of U^6 to U^4 by ferrous sulphate in concentrated H_3PO_4 medium. The excess Fe^{++} is then selectively oxidised by HNO_3 using molybdenum catalyst after addition of sulphuric acid and dilution with water. The U^4 is titrated with standard $K_2Cr_2O_7$ using barium diphenyl amine sulphonate indicator.

Reagents :

- (i) Sulphuric acid 1.5 M : Dissolve 150 g of sulphamic acid in one litre of cold water
- (ii) Phosphoric acid concentrated

- (iii) Ferrous sulphate 1.0 M: Add 100 ml of conc. H_2SO_4 to 750 ml water slowly, with stirring. Add 280 g of ferrous sulphate heptahydrate to the hot solution and stir till dissolved. Cool, dilute to 1 litre with water and mix. Ferrous sulphate hexahydrate (395 g) may be substituted for ferrous sulphate.
- (iv) Nitric acid 4 M sulphamic Acid 0.1 M reagents: Dilute 250 ml of conc. HNO_3 (sp.gr. 1.42) to 930 ml. with water. Add 70 ml of 1.5 M sulphamic acid and mix well.
- (v) Ammonium molybdate 1%
- (vi) Sulphuric Acid - Reagent grade only
- (vii) Barium diphenyl amine sulphonate 0.04% - Dissolve 0.2 g of barium diphenyl amine sulphonate in 200 ml of boiling water. Cool and dilute to 500 ml
- (viii) Standard $\text{K}_2\text{Cr}_2\text{O}_7$: 0.05 N

Procedure :

Transfer an aliquot of sample solution (less than 15 ml) containing upto 300 mg of U to a 500 ml conical flask

Sample volume must not exceed 15 ml, and should contain nitrate equivalent to 0.25 - 3.0 ml of 15 M, HNO_3

Optimum quantity of uranium is 150 - 200 mg

If the sample is likely to contain Mo, total nitrate in sample aliquot should not exceed the equivalent of 0.5 ml of 15 M HNO_3 .

Add 5 ml of 1.5 M sulphamic acid, 40 ml. concentrated phosphoric acid, 5 ml 1.0 M ferrous sulphate 5 ml. of "4 M HNO_3 /0.1 M sulphamic acid reagent' and 2 ml of 1% ammonium molybdate solution in the order given, stir well after each addition.

Wait until the dark brown colour which is produced in the solution has disappeared and a pale green colour is produced, then allow the solution to stand for a further 3 minutes.

The 3 min. standing time is important for high precision results, and should be timed with a stop clock.

Except for the 3 min. waiting time, the procedure once started, should be carried through without delay.

Add 25 ml of 9 M H_2SO_4 , 200 ml cold water and 2 ml of 0.04% barium diphenyl amine sulphonate solution in order given, mixing after each addition.

Within 10 min. of adding water, titrate with N/20 $\text{K}_2\text{Cr}_2\text{O}_7$ solution until the intense violet colour which lasts at least for one min. without fading.

The one min. fading time of the indicator is conveniently timed with stop clock.

Determine a blank by applying the procedure to a sample consisting of 10 ml of water plus 0.5 ml of 15 M HNO_3 . The blank value of 0.05 to 0.15 of N/20 dichromate is substrated from the titre.

$$\begin{aligned} \text{Uranium (mg) in sample aliquot} &= \text{Net titre} \times 5.951 \\ \text{As } \text{U}_3\text{O}_8 &= \text{Net titre} \times 7.01784 \end{aligned}$$

Emission Spectrometry : LABTAM ICP Plasma Scan was used for determination of uranium

Reagents :

- (i) Standard U_3O_8 - NBS, USA
- (ii) Nitric Acid, AR BDH
- (iii) Triton X-200, Sigma Chemical USA

Standard U_3O_8 Solution: Take 1.0 gm pure U_3O_8 standard sample in a 500 ml beaker. Add 20 ml con. HNO_3 and 100 ml of distilled water. Boil to dissolve completely, cool and make up the volume to 1000 ml.

Standard Ore Sample : Take 5 gms. of standard ore sample in a 400 ml beaker. Add 10 ml conc. HNO₃ and 100 ml of distilled water. Boil for 3 to 4 hours. Filter through No.41 filter paper and wash the residue with 1:99) hot acidified (HNO₃) water. Cool and make up the volume to 250 ml.

Different standard ore samples were analysed in ICP at different recommended wavelengths and the results were compared with chemical analysis. The values obtained in ICP and by chemical analysis at different wavelength are given in Table-II.

Table - II
Analysis of Standard Uranium Ores in ICP at
Different Wavelengths

Wavelength nm	Actual U ₃ O ₈ concn.ppm	Measured U ₃ O ₈ Conc. ppm	% U ₃ O ₈ ICP	% U ₃ O ₈ chemical
385.958	13.80	13.78	0.069	0.069
	11.20	11.26	0.056	0.056
	10.00	16.87	0.084	0.050
409.014	13.80	13.82	0.069	0.069
	11.20	11.26	0.056	0.056
	10.00	10.05	0.050	0.050
427.167	13.80	9.97	0.050	0.069
	11.20	8.86	0.044	0.056
	10.00	7.60	0.038	0.050
385.466	13.80	13.53	0.068	0.069
	11.20	10.64	0.053	0.056
	10.00	9.42	0.047	0.050

Both standard samples of Jaduguda ore were of same matrices, whereas the uranium Table concentrate of Surda was of different matrix.

The results in the table No.II show that although the Surda, Uranium Table Concentrate was having a different matrix (containing approximately 30% Magnetite) than the other two samples of Jaduguda Ore, it didn't have any effect at 409.014 nm in respect to the accuracy of the uranium analysis. Although spectral line 385.958 nm was better line for uranium analysis due to this higher SBR upto 1000 ppm of Fe content, but when iron was higher than 1000 ppm the spectral line of Fe 385.991 nm interfered at this wave length and gave higher result. That was why we had chosen the line 409.014 nm, where there was no interference of iron spectral lines in the analysis of uranium ores and Table concentrates. Hundreds of Uranium Ores and other samples of Uranium were analysed for U_3O_8 content and the method has now become a routine one for U_3O_8 estimations in place of chemical analysis which was more time consuming. However it had been observed that precision and accuracy of analysis was better in case of lower range of Uranium content, say between 0.5 ppm to 150 ppm but above 150 ppm the percent error was more than the maximum permissible limit of 0.3%. This was observed in case of Uranium concentrates which might be due to series of dilution.

Some of the uranium ores and concentrates of different grades were analysed in ICP at 409.014 nm and results were compared with its chemical analysis and are given in Table-III.

Table-III

**Comparison of Chemical and ICP-AES Analysis of
Different Ores and Concentrates**

Sample Code	Chemical Assay % U ₃ O ₈	ICP-AES Assay % U ₃ O ₈
1. Jaduguda Ore	0.06	0.068
	0.60	0.061
	0.064	0.064
	0.78	0.077
	0.054	0.053
	0.270	0.271
2. Bhatin Ore	0.043	0.041
	0.045	0.045
	0.050	0.049
	0.030	0.030
	0.38	0.039
3. Jajwal Ore	0.050	0.051
	0.051	0.051
	0.047	0.049
	0.052	0.051
	0.048	0.047
4. Rakha Uranium Table Conc.	0.052	0.052
	0.053	0.054
	0.055	0.056
	0.060	0.061
	0.073	0.072
5. Surda Uranium Table conc.	0.075	0.077
	0.063	0.062
	0.098	0.100
	0.080	0.082
	0.078	0.077
6. Magnesium Diuranate	68.81	69.32
	68.12	68.40

Interferences:

The effect of interference in Uranium analysis by ICP-AES were studied and it was found that the presence of Fe, Al, Ca, Mg, Si, Cu, Ni, Mo, Na, K, P, S and Mn has no effect on accuracy in the concentration range given in Table-IV

Table-IV

Element	Concentration/ppm
Fe	1000
Al	100
Ca	100
Mg	100
Si	100
Cu	100
Ni	100
Mo	50
Na	1000
K	50
P	100
S	100
Mn	100

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