Quality Control of Portuguese Uranium Concentrates

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The analytical chemistry of uranium concentrates implies, as is well known, an accurate determination of U_3O_8 as well as the various impurities. This paper presents the analytical diagram used routinely in our laboratory for the quality control of concentrates.

The schema includes gravimetric, potentiometric and spectroscopic methods. Uranium was separated from metallic impurity elements by solvent extraction. Fluoride was separated from the matrix element by a Dowex 50W-X8 ion exchanger on a 0.24M nitric acid medium and determined potentiometrically by a standard addition method.

Portugal, which was one of the first countries to explore its uranium ores, has considerable experience in the analytical chemistry of concentrates, ammonium and sodium diuranates, produced at Urgeiriça's plant, by chemical processing of the ores.

Analytical chemistry of concentrates implies an accurate determination of U_3O_8 and the various impurities. This work presents the analytical diagram used routinely in LNETI for the quality control of concentrates. The schema includes gravimetric, potentiometric and spectroscopic methods of analyses.

The matrix element is determined gravimetrically after extraction with 40% tributylphosphate (TBP) in white spirit from a nitric acid medium, re-extraction with 35% ammonium acetate solution, and precipitation as ammonium diuranate which is ignited to U_3O_8.

Silica and sulphate ion are determined gravimetrically from a perchloric acid solution to avoid interference from fluoride ions. Carbonate ions are also determined by gravimetry after absorption of CO_2 on a column of ascarite.

Iron is analysed either spectrophotometrically with formation of a complex with orthophenanthroline, or by flame atomic absorption spectrophotometry after extraction of uranium with 100% TBP, as described below.

Phosphate ions are determined spectrophotometrically using a yellow complex of molybdovanadophosphoric acid which absorbs at 390 nm.

Arsenium is evolved as arsine after reduction by stannous chloride. With silver diethyldithiocarbamate in pyridine medium, the metal forms a complex which absorbs at 545 nm.

Boron is determined on the ignited sample by optical emission spectrography using the Scribner and Mullin Carrier-Distillation Method. Ga_2O_3 is added as carrier and spectroscopic buffer [1].

Zirconium is concentrated and separated from uranium, which must be present as U (VI), by precipitation with cupferron in sulphuric acid medium and extraction with chloroform. Organic matter is eliminated and the ignited residue is submitted to spectrographic examination using the total combustion method. Elements Ga, Hf, Mo, Nb, Pd, Ta, Ti, V and W are also extracted during the procedure [1,2].

Trace metals Na, K, Mg, Fe, Mo, V and Ti are determined in the raffinate after extraction of uranium with 100% tributylphosphate (TBP) from a medium 6 *M* in nitric acid. Extraction efficiency is improved when the aqueous phase is again extracted, first with 20% TBP in CCl_4, then with the diluent to recuperate residual uranium. Yield is 99.9% [3].

After dilution of the raffinate, Na, K, Ca, Mg and Fe are determined directly by flame absorption spectrometry.

To analyse Mo and V using the same method the aqueous phase must be concentrated about five times and aluminium added to increase the proportion of free atoms in the flame, preventing formation of vanadium and molybdenum oxides which are refractories.

Titanium is also determined spectrometrically in the raffinate by formation of a yellow complex with H_2O_2, which absorbs at 410 nm. Vanadium and molybdenum when present in concentrations up to 25 and 100 ppm respectively do not interfere.

Halogens, expressed as chloride ions, are analysed in nitric acid medium either volumetrically (Charpentier - Volhard method), or titrating potentiometrically with a Ag_2S selective electrode as the end point indicator. Concentration of titrating silver nitrate solution is evaluated either mathematically constructing a Gran's plot or directly using Gran's paper.

Fluoride is determined potentiometrically with a selective electrode, in a nitric acid medium, after passing the sample through a column of ion exchanger DOWEX 50W-X8, H^+. The column is washed with water and the solution diluted 1:1 with acetic acid-acetate buffer [4].

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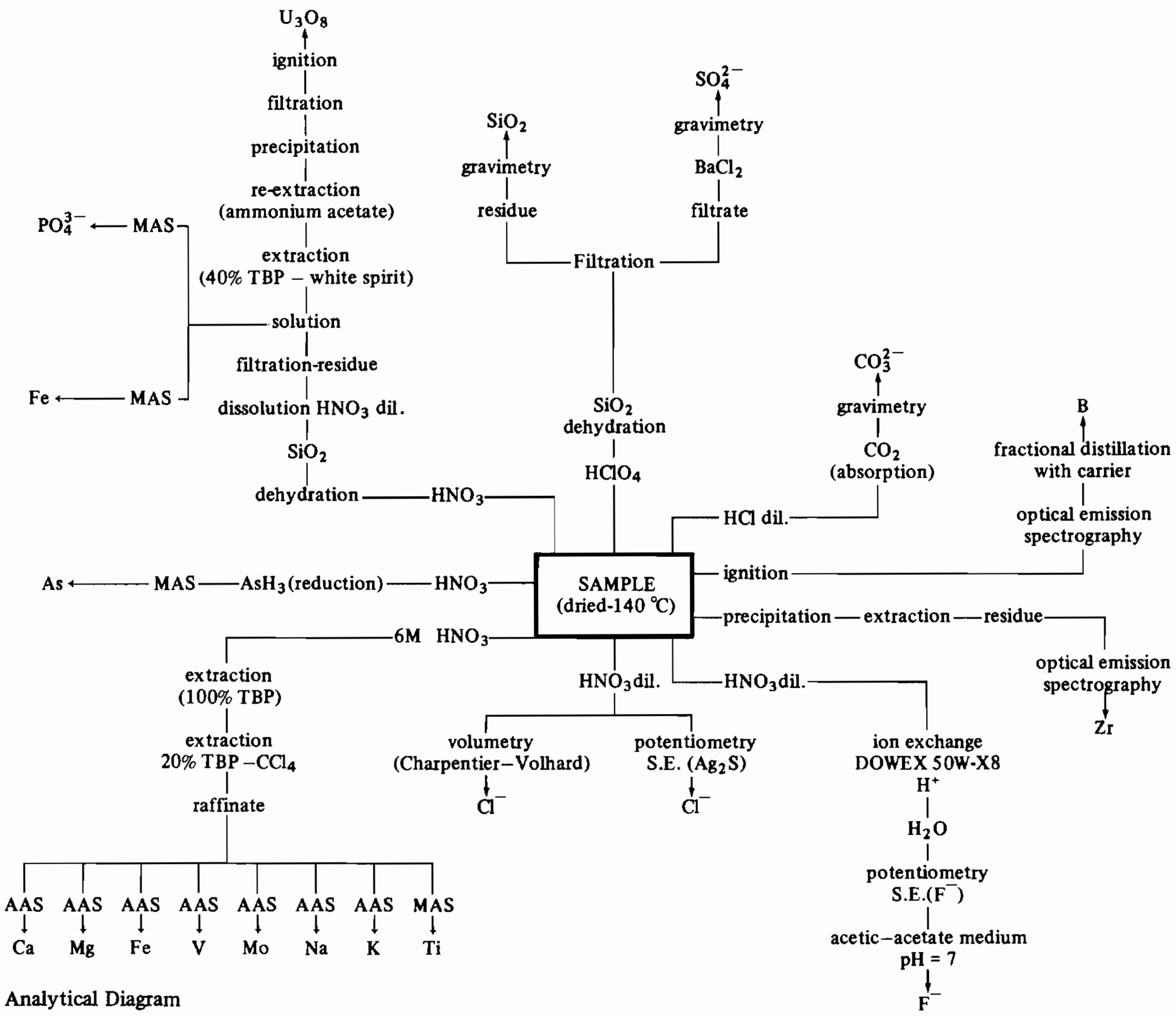

Analytical Diagram

TABLE I. Extraction Efficiency of Separation of Uranium from its Impurities

Yellow cake (reference)	U in organic phase %	U in aqueous phase %	Extraction efficience %	U total (U_{org} + U_{aq}) %	U total* %
1 C	77.51	0.062	99.9	77.57	77.45
2 C	77.08	0.080	99.9	77.16	77.25
3 C	77.61	0.076	99.9	77.69	77.55
4 C	77.91	0.055	99.9	77.97	77.72
5 C	76.99	0.065	99.9	77.06	76.92
10 C	76.91	0.053	99.9	76.96	76.96

*Uranium determined following the analytical schema.

Comparative Results by Different Methods

Uranium

Results of uranium determinations with the TBP solvent extraction method were compared with data obtained by absorption of the metal on a cellulose column followed by elution with ethyl acetate in nitric acid medium. The organic solvent is separated by distillation and the uranium is precipitated as ammonium diuranate, which is ignited to U_3O_8 [5].

In the Fig. 1 are represented the average data obtained by the two methods over five years on the same ammonium diuranate samples.

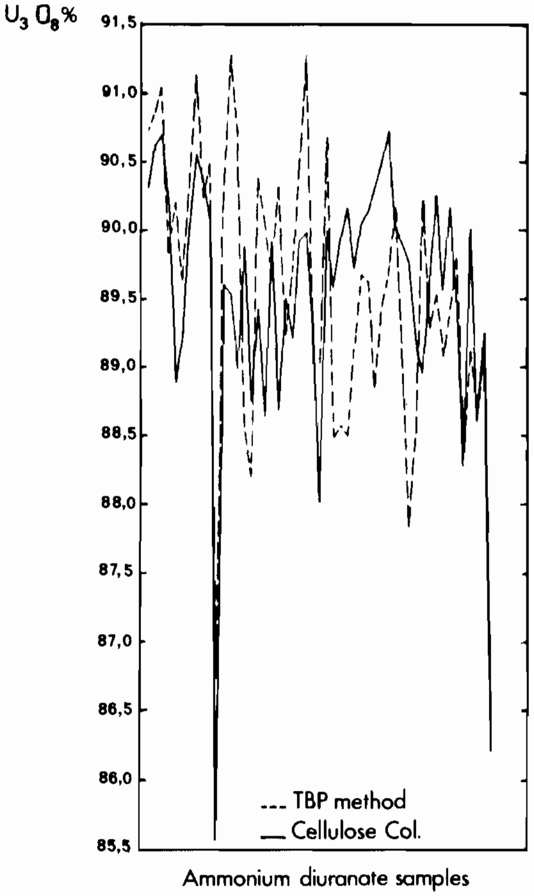

Fig. 1. Average data obtained by the two methods, processed on ammonium diuranate samples, over five years.

Fluoride

Fluoride ion concentration was determined either by a calibration curve prepared in the same conditions as the sample or by the standard addition method using three different additions and applying the iterative Newton method [6] to the non-linear function f (C) obtained by conjugation of the Nernst equation for the three experimental points with concentrations C, C + S_1 and C + S_2 and the e.m.f., E_c, E_1 and E_2

$$f(C) = (E_2 - E_1)\ln C + (E_c - E_2)\ln(C + S_1) + $$
$$+ (E_1 - E_c)\ln(C + S_2) = 0$$

Results were compared with data obtained after separation of fluoride ions by steam distillation of hydrofluosilicic acid, Table II.

Overall Data

Results obtained in LNETI using the analytical diagram proposed in this work are compared with data of another laboratory, Table III.

TABLE II. Comparative Results of Fluoride Ions Obtained on a Uranium Concentrate Sample.

Determination no	Distillation method F^-%	Ion exchanger method	
		Calibration curve F^-%	Standard addition F^-%
1	0.0067	0.0050	0.0069
2	0.0069	0.0050	0.0072
3	0.0062	–	–

TABLE III. Results of Uranium Concentrate Samples.

Constituent	Sample 8/79		Sample 9/79		Sample 8/80		Sample 5/81	
	LNETI	Other Lab.	LNETI	Other Lab.	LNETI	Other Lab.	LNETI	Other Lab.
U%	76.73	76.48	76.50	76.70	76.66	76.45	76.45	76.88
SiO_2 %	0.08	0.10	0.10	0.13	0.12	0.10	0.07	0.10
SO_4^{2-} %	1.43	1.54	1.36	1.44	1.10	1.13	1.32	1.34
CO_3^{2-} %	0.11	0.07	0.11	0.08	0.30	0.24	0.10	0.09
PO_4^{3-} %	0.11	0.10	0.14	0.11	0.14	0.14	0.17	0.17
As %	<0.001	<0.01	0.002	<0.01	0.004	0.01	0.028	0.02
Ti ppm	⩽5	<100	⩽5	<100	⩽5	<100	⩽5	<100
B ppm	≃5	<10	<10	<10	<10	<10	≃5	<10
Zr ppm	30–100	200	30–100	<100	≃100	<100	≃100	<100
Na %	0.3	0.24	0.3	0.26	0.3	0.28	0.3	0.28
K %	0.06	0.06	0.07	0.07	0.06	0.06	0.08	0.06
Ca %	0.04	0.05	0.04	0.04	0.05	0.04	0.03	0.03
Mg %	0.009	⩽0.01	0.009	<0.01	0.010	0.01	0.013	0.01
Fe %	0.05	0.03	0.06	0.04	0.12	0.09	0.06	0.04
V_2O_5ppm	16	<100	11	<100	16	<100	9	<100
Mo ppm	26	<100	25	<100	17	<100	17	<100
Cl^- %	0.02	0.02	0.02	0.02	0.03	0.01	0.02	0.02
F^- %	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

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