

## Comparative study of methods for determining metal elements in uranium tailings material

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This work presents a comparison of analytical results obtained for U, Th, K, and Fe in solid material from tailings pond, carried out within the CIPC's Tailings Management Program, with those achieved by instrumental neutron activation analysis. The validity of the techniques applied for dissolution and determination of elements in high silicate grade material, as the present case, can be assured by good agreement of the results.

### Introduction

Indústrias Nucleares do Brasil S/A (INB) is the Brazilian company responsible for producing material of the nuclear fuel cycle, from mining uranium ore to fabrication of fuel element. The uranium concentrate as uranium diuranate (DUA) has been produced since 1981 at Complexo Mineiro Industrial do Planalto de Poços de Caldas (CIPC), the only uranium ore facility in Brazil. Until present,  $2 \cdot 10^6$  metric tons of ore have been exploited resulting in  $44 \cdot 10^6$  m<sup>3</sup> of waste from mining activity, deposited as rock piles over an area of 1.73 km<sup>2</sup>.

CIPC is located in the Poços de Caldas Plateau, state of Minas Gerais, occupying an area of about 15 km<sup>2</sup>. It lies within the watershed boundaries of the most important hydrographic basins of the region, the Antas and Verde rivers.

Obtention of DUA involves mining and milling operations that consist of crushing, grinding, chemical processing, drying and final product packaging. The chemical process starts with leaching of ground ore pulp with addition of pirolusite for uranium oxidation, apatite for zirconium elimination, organic solvent extraction, aqueous sodium chloride re-extraction and alkaline precipitation.

The tailings disposal pond with 0.25 km<sup>2</sup> of surface area is supported by a dam of 435 m extent and 45 m maximum height.<sup>1</sup> It receives the waste from chemical processing plant after lime/limestone treatment and the solid phase originated at lime treatment station of drainage waters from waste rock piles and mine pit. Soluble material contents of CIPC's ore is about 2.5% and the major soluble elements in the acid liquor are precipitated at high pH; the solid phase from drainage water treatment area contains, among other elements such as calcium sulfate, manganese, aluminium, iron, manganese, fluoride, the uranium as calcium diuranate. At the tailings pond, the solid phase is

separated by settling from the liquid phase that overflows to the barium chloride treatment area; after elimination of radium–barium sulfate crystals in two settling ponds, the effluent is released to the Verde basin.

Although radionuclide contents of the waste from uranium mining and milling process is small compared with that generated at other stages of the nuclear fuel cycle, in the absence of proper management, it may become potential sources of low level radiation exposure to local and more distant populations over very long periods of time.<sup>2</sup> CIPC's Environment Management has been directing great efforts for waste retention concerning the natural radionuclide contents in the liquid effluent, maintaining at levels lower than limits established by governmental agency.<sup>3</sup> In 1992, CIPC's Tailings Management carried out a sampling within its programme aiming at the evaluation of stable and radioactive elements contents in the tailings pond and the mobilization of uranium series radionuclides. The present work intends to assess the performance of methodology applied for analyzing the collected materials comparing the results with those achieved by neutron activation analysis.

### Experimental

Four cores were collected with manual auger, two in west site (cores 1 and 2) and two in northeast site (cores 3 and 4) at non-submersed area of the tailings pond, in July 1992. A sample of each core was leached with water of pre-defined pH in four stages successively. Besides liquor sampling, leaching remaining materials were collected at the end of each stage, resulting five solid samples per core. Each sample has been designated by a couple of figures, being the first the core number and the second the stage of leaching number. Seven samples from leaching tests, two samples from sieve tests of tailings material (02 > 200 and

Table 1. Conventional methodology for determination of elements

Element	Dissolution	Detection
Fe	Fusion of 0.5 g of sample with 1-2 g LiBO <sub>2</sub> , pre-heat at Meker burner, melting at 900 °C for 10 min, dissolution with HCl (1 + 1), drying out on steam bath, redissolution with 20 ml HCl (1 + 1) per 100 ml of volume	EDTA titrimetry with sulfosalicylic acid as indicator <sup>4,5</sup>
K		Flame emission spectrophotometry
Th	Fusion of 0.4-0.5 g of sample with: (1) 4-5 g Na <sub>2</sub> CO <sub>3</sub> at 1000 °C for 20 min, (2) 4-5 g Na <sub>2</sub> CO <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> /Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (1:1:1) at 900 °C for 10 min Dissolution of melted material with HNO <sub>3</sub> (1 + 1); drying out at steam bath; redissolution with 15 ml HNO <sub>3</sub> (1 + 1)/100 ml	Extraction with 0.1M TOPO/cyclohexane re-extraction with aqueous oxalic acid 5%; spectrophotometry with Arsenazo III <sup>6-8</sup>
U	2 g sample, successive drying out on sand bath with 15 ml HNO <sub>3</sub> , 10 ml HClO <sub>4</sub> , 5 ml HF; 5 ml HNO <sub>3</sub> , 5 ml HF; 5 ml HNO <sub>3</sub> . Redissolution with HNO <sub>3</sub> (1 + 1), water, H <sub>2</sub> O <sub>2</sub> 3%; after boiling and cooling final solution 0.5M acidity	Extraction with 10% TBP/isooctane, re-extraction with aqueous buffer sodium acetate 0.5M/acetic acid pH 3 with 0.006% Arsenazo III <sup>6,7</sup>

02 > 300) and one of ore (PN) were selected for comparison study. To evaluate uranium determinations, three ore reference materials were also analyzed. All the samples were dried at 105 °C and ground to a granulometric size below 200 mesh. A summary of methodology applied for conventional chemical determination of Fe, K, Th and U is presented in Table 1.

Subsamples of about 150 mg of the powdered material were inserted into special polyethylene vials surrounded by a flux monitor wire and irradiated for eight hours at a thermal neutron flux of  $5 \cdot 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ , in the research nuclear reactor IEA-R1 of the Instituto de Pesquisas Energéticas Nucleares (IPEN/CNEN/SP). After suitable cooling times, the induced radioactivity was measured by using a hyperpure

germanium semiconductor detector (GMX 20190P, EG & ORTEC, 20% relative efficiency and 1.85 keV resolution at the <sup>60</sup>Co photopeak of 1332 keV) connected to a computerized multichannel buffer. Standard reference materials IAEA SL-1, Soil 7, and IAEA uranium ore materials (S-7, S-8 and S-13) were co-irradiated with the samples.

## Results and discussion

Iron, potassium, thorium, and uranium contents of tailings material determined by different techniques are presented in Table 2. It can be seen that almost all the elements demonstrated a coherent behavior, i.e., the metal

Table 2. Concentration of Fe, K, Th and U measured by conventional techniques (CT) and INAA

Sample	Fe, %		K, %		Th, µg · g <sup>-1</sup>			U, µg · g <sup>-1</sup>	
	CT	INAA	CT	INAA	CT-1*	CT-2**	INAA	CT	INAA
02 > 200	***	2.06	***	11.7	57	67	80	155	152
03 > 200	***	6.14	***	7.02	66	72	64	158	117
PN	***	2.46	***	10.1	113	108	153	530	516
01/01	1.69	1.55	11.9	11.1	62	63	68	134	129
01/05	1.53	1.58	11.5	11.0	47	60	68	136	135
02/01	1.85	1.77	11.8	11.8	47	45	53	125	129
02/03	1.61	1.53	11.7	11.9	41	50	50	123	126
03/03	6.06	6.00	9.80	9.74	74	91	105	174	185
04/04	1.88	1.59	11.6	11.9	49	49	53	146	146
04/05	1.62	1.52	11.6	11.5	39	46	49	135	140

\*Na<sub>2</sub>CO<sub>3</sub> fusion.

\*\*Na<sub>2</sub>CO<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub>/Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> fusion.

\*\*\*Not determined.

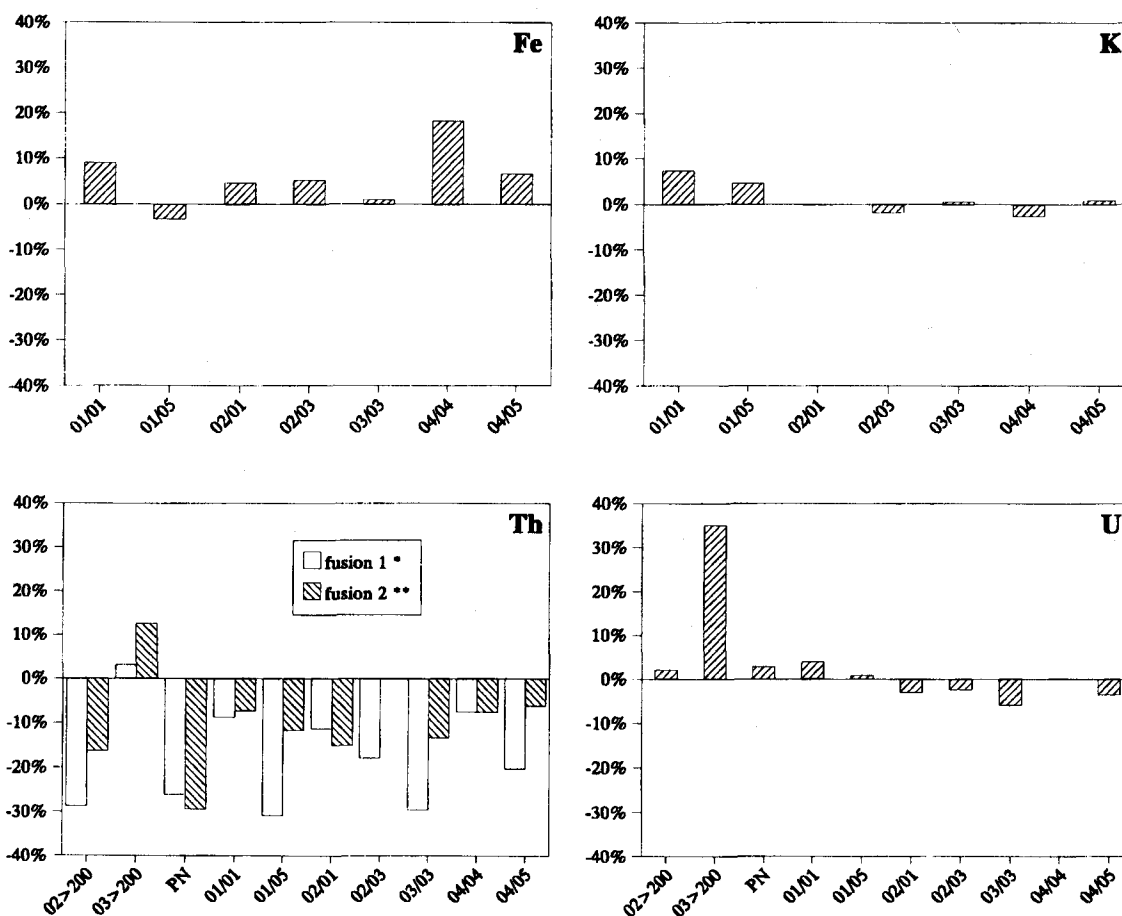


Fig. 1. Percent deviation of conventional techniques results from INAA. Positive values indicate conventional techniques results greater than INAA; \*with  $\text{Na}_2\text{CO}_3$ , \*\*with  $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{Na}_2\text{B}_4\text{O}_7$

contents decrease as leaching stage increases, indicating their dissolution in some extent.

The relative deviation of conventional results from those of INAA, taken as reference values (Fig. 1), demonstrates a good agreement for Fe, K, U, and Th, assuring the validity of such methodologies for dissolution and determination of elements in high silicate grade material, as is the present case (average contents of  $\text{SiO}_2 = 54\%$ ,  $\text{Al}_2\text{O}_3 = 23\%$ ).<sup>9</sup> The percentual standard deviations (C.V.) determined for Fe and K analysis were 0.2–5 and 0–1.9% respectively; for thorium, the Arsenazo III method recovery from spiked sample was 90% with C.V. value of 6%.

The uranium results (Fig. 1) are from the method that has shown the better performance in relation to INAA technique (Table 1). Uranium contents were calculated taking into account the average recovery value of 4.4  $\mu\text{g}$  (C.V. 19%) for ten sample solutions spiked with 5  $\mu\text{g}$  of U. For the seven samples from leaching tests, the uranium contents were also determined by other decomposition/determination procedures and related to INAA method (Table 3).

As commented above, the procedure (e) presents the best results taking INAA method as reference, followed by (c) and (a), with (b) and (d) showing the greatest deviations. Results of analysis of IAEA reference samples S-7, S-8 and S-13 by triacid mixture decomposition followed by Arsenazo III and dibenzolmetane methods, and INAA technique can be seen in Table 4. Except the result for S-13 by DBM, good agreement with certified values was achieved. These results have indicated that once the Arsenazo III method has sensibility about ten times higher than DBM's, deviations could be introduced because of Arsenazo's greater dilution factor. The suitability of DBM method for high uranium grade solid samples analysis should be investigated further more.

At CIPC, spectrophotometry by Arsenazo III and fluorimetry are both applied for environmental grade water analysis. Such techniques have been validated through the participation in EPA's intercomparison program co-ordinated by Instituto de Radioproteção e Dosimetria of Comissão Nacional de Energia Nuclear (IRD/CNEN). The spectrophotometry by DBM has been used for chemical

Table 3. Dissolution/determination procedures for uranium determination, contents achieved, in  $\mu\text{g} \cdot \text{g}^{-1}$  of U, and average concentration ratios related to INAA method, with standard deviation

Procedure	Samples							Ratio
	01/01	01/05	02/01	02/03	03/03	04/04	04/05	
(a) $\text{Na}_2\text{CO}_3$ fusion TOPO extraction, fluorimetry	147	187	125	147	138	156	184	$1.11 \pm 0.21$
(b) $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{Na}_2\text{B}_4\text{O}_7$ fusion TBP extraction Arsenazo III spectrophotometry	104	107	96	96	148	117	107	$0.78 \pm 0.03$
(c) $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3/\text{Na}_2\text{B}_4\text{O}_7$ fusion TOPO extraction, fluorimetry	154	144	143	125	188	152	165	$1.08 \pm 0.08$
(d) $\text{HNO}_3/\text{HClO}_4/\text{HF}$ -ethyl acetate extraction DBM spectrophotometry	145	166	148	186	234	156	165	$1.21 \pm 0.13$
(e) $\text{HNO}_3/\text{HClO}_4/\text{HF}$ -TBP extraction Arsenazo III spectrophotometry	134	136	125	123	174	146	135	$0.99 \pm 0.03$
(f) INAA	129	135	129	126	185	146	140	

Table 4. Uranium concentration ( $\mu\text{g} \cdot \text{g}^{-1}$ ) found for reference materials

Material	Certified value	Method		
		triac/Arsenazo	triac/DBM	INAA
S-7	$4466 \pm 38$	4872	4542	4504
S-8	$1203 \pm 17$	1364	1218	1054
S-13	$330 \pm 17$	317	274	282

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plant process control, together with ICP emission spectrometry, since most of the samples from processing come in liquid form and are analyzed through 24 hours per day. On the other hand, solid samples for mining and milling process control are analyzed by X-ray fluorescence spectrometry.

The conventional methods have been shown suitability for liquid samples analysis, performing accurate determination of uranium either in low interference media (environmental water) or in high concentration media (samples from chemical processing plant). Nevertheless, when dealing with solid matrix materials, a significant interference can be generated during the uranium solubilization process. Then, raising the interfering/uranium ratio the accuracy and sensitivity of the method will be diminished, becoming necessary a survey of the dissolution/determination methods, to improve similar material analysis.

As a final remark, this comparative study of conventional analytical methods with INAA, a technique independent on matrix composition, provided useful information about the applicability of controlling methods on a routine basis to samples from CIPC's tailings material analysis.

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