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THE USE OF DIFFERENT ANALYTICAL TECHNIQUES
AS A BACKUP TO MINERAL RESOURCES ASSESSMENT

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ABSTRACT

In order to assure suitable capabilities in the analytical chemistry field, the Empresas Nucleares Brasileiras S. A. - NUCLEBRÁS implemented and improved, since their foundation, in 1974, several laboratories in the Centro de Desenvolvimento da Tecnologia Nuclear - CDTN, in Belo Horizonte. In this area, skillful personnel, using a large spectrum of equipments and procedures, is able to determine fast and accurately almost any chemical element in any matrix.

About 340 000 analytical determinations have been performed during the last seven years, concerning primarily with chemical elements which are of most importance in the mineral technology programs. This considerable amount of results has been used, specially, as a backup to assess Brazilian uranium resources, a successful task.

1. INTRODUCTION

It is commonly agreed that any industrial complexes and, specially, those devoted to the research and development in sensitive areas such as the nuclear energy one, with a broad range of activities, must have very good capabilities in analytical chemistry. This has been taken into account by the Empresas Nucleares Brasileiras S.A. through the implementation and maintenance of suitable analytical laboratories in the Centro de Desenvolvimento da Tecnologia Nuclear, CDTN, in Belo Horizonte. Brief information about its historical background is given by TÓFANI et alii [1].

In the CDTN, the main analytical laboratories are managed by the Departamento de Apoio Técnico and, more precisely, concentrated in its Divisão de Química - DIQUI, recently improved according to guidelines proposed by ALVARENGA [2]. As far as mineral technology programs are concerned, these laboratories deal with problems on different ways and stages, from mineral prospection up to processing. Related aspects, such as environmental impact, material engineering and quality control have to be considered.

In this context, the laboratories have to consider many parameters, such as matrixes, chemical elements and compounds, procedures and techniques, content level,

required accuracy, time consumption and personnel, equipment and material availability, in order to provide a reliable backup to mineral and aforementioned areas.

A team of well trained chemists, with these techniques on hands, has been able of doing a continual research work and analysing all sorts of samples, under high confidence levels of accuracy, so endeavoring to support the NUCLEBRÁS in its task of assessing the Brazilian uranium resources. Besides, technical services in analytical chemistry, mostly comprising unusual problem solution and method development have been offered to private and public institutions.

2. ANALYTICAL CHEMISTRY CAPABILITIES

2.1. Available services

Generally speaking, analytical chemistry comprehends the methods and techniques used to obtain information about composition, identity, purity and constitution of all sorts of chemical species, as far as natural and artificial products. It is quite a broad field, including raw materials, process control and analyses of the partially or totally finished products.

To choose the analytical methods, the sample size, relative amounts of the constituents (macro, micro), nature of the material (ore, mineral, soil, sediment, alloy, etc.), degree of complexity of the matrix, wanted accuracy and many other factors must be criteriously weighed. The time spent in analysis depends very much on the analysed elements and on the matrixes, being from a few seconds to many weeks.

Clearly, the use of the results should be the main guide on the decision and better is when this decision comes out of a personal contact between analyst and user of the analyses.

- In the fuel cycle, many materials have to meet the nuclear specifications that are, in general, highly stringent as compared with the normal industrial quality.

2.2. Brief appraisal of the analytical methods

Most methods require sample pretreatment, like dissolution and separation of interferences. Some commercial equipments are able to make, directly, the quantitative determination v. g. gas chromatograph, evolograph.

The most important techniques, now available in DIQUI, are fully described, for example, by KOLTHOFF et alii [3].

Figure 1 shows the matrixes where each element is analysed

Figure 2 indicates the most used techniques according to the concentration ranges of the elements, i.e., 10 to 100% for major, 0.001 to 10% for minor and less than 0.001% for trace constituents.

2.2.1. Nuclear and radiochemical methods

These methods represent a very powerful tool, mainly because nuclear properties have nothing to do with the atomic (electronic) or molecular properties.

In neutron activation analysis, the samples are irradiated by neutrons in the reactor, the gamma activity detected in Ge (Li) detectors, the pulses brought to analysers. Characteristic peaks formed are compared with standards used in the same conditions.

In delayed neutron activation analysis, the uranium or thorium bearing samples are analogously irradiated and the delayed neutron activity is compared with standards of the same elements.

Radiometric methods include analyses of trace natural radionuclides by total alpha, beta and gamma activities.

2.2.2. Spectroanalytical methods

The spectroanalytical methods encompass a broad field of techniques in which one property of the substance is measured at the same time that the agent helping measure the property has some characteristic slowly changing. This produces the spectrum that is compared to a standard.

If use is made of the partial absorption of a light beam, when passing through a cell containing the sample, the method is called spectrophotometry. The source is not monochromatic, so calling for a monochromator before detection of the signal.

In the atomic absorption spectrophotometry, the light coming from a special lamp (that produces the pure spectrum of the element being analysed) is absorbed, very selectively, by the atomized sample in a flame or a graphite furnace. To get rid of the flame light, a monochromator is needed.

When the light emitted by a solution incorporated in a flame is filtered and measured, one has the flame photometry.

If the absorbed light leads to an outer molecular or atomic electronic excited state having such a half-life that the re-emitted radiation can be measured after the excitation is off, the method is called fluorimetry.

Turbidimetry is a procedure very similar to spectrophotometry and uses the same equipment, but here the scattered and unscattered light passing through the medium with

dispersed particles of different refractive index from the medium is measured.

In mass spectrometry, ionized molecules and atoms having the same m/e ratio are accelerated by electric and magnetic fields, focussed and the current measured. This permits to determine isotopic abundance.

2.2.3. Electroanalytical methods

Almost all electroanalytical methods are based on a very few principles, besides the classical stoichiometry, namely, Faraday's law, Ohm's law, Nernst equation and that the conduction of electricity by a solution is made partly by free electrons and partly by mass carrying anions or cations. In titrations, one uses an indicator electrode that sees some electrical property of the solution, so allowing inference about the end point, when plotted against the added titrant, time, applied voltage, etc.

Applying an external potential to the solution, the mass transferred to the electrodes is proportional to the charge that can be measured with high precision: coulometry.

Controlled potential electrogravimetry seeks an adhering quantitative pure deposit on an electrode, in a form suitable for weighing.

In amperometric titrations, the indicator electrode measures the current flowing through the solution.

One can, also, measure the potential appearing at zero current or with a constant current: potentiometry and potentiometric titrations. The indicator electrode may show electronic or ion transfer on its surface and may be specific or non-specific, but sensitive only to some ions.

In conductometric titrations, use is made of the conduction behaviour of the solution during addition of titrant.

Finally, the method is called voltametry if a constant potential produces a current in a special electrode that removes the electroactive material from its surface layer (diffusion layer), so limiting the current.

2.2.4. Titrimetry

Titrimetry is based on laws of stoichiometry by measuring the volume of a standard solution that reacts quantitatively with a solution of the substance under determination.

2.2.5. Gravimetry

In gravimetry, the pure element or compound is isolated and weighed under a known definite composition.

2.2.6. Gasometry

The gasometry comprehends many methods for the determination of constituents in gaseous mixture. The constituents are separated, whenever needed, and volume, pressure, thermal conductivity, magnetic susceptibility, or heat of combustion is measured.

2.3. Quality Control

Quality control of the analyses is obtained by several measures, depending very much on the matrixes and on the analysed element or compound.

A rigid procedure of separating samples according to the complexity of the associated analytical problem, together with duplicating, checking against other internally available methods and training personnel, is used. Besides, all reagents, measuring glasses, even though being of good makes, are routinely checked.

In order to keep as many as possible methods on a routine basis, standard samples from National Bureau of Standards (NBS), International Atomic Energy Agency (IAEA) and United States Geological Survey (USGS) are frequently analysed.

An international cross-checking with other laboratories is in effect for many years, through IAEA, in many matrixes and almost all elements, the DIQUI's results being excellent. A parallel program has been initiated in 1978 with the USGS, specially on rocks and soils. Other have been established with COMURHEX (France) and with KFA- Jülich (Germany).

3. ANALYTICAL RESULTS PRODUCTION

Presently, the most important demand for analytical services is connected to NUCLEBRÁS' uranium prospection and estimation of Brazilian reserves. This represents about 85% of the total number of analyses.

In prospection and measuring, attention is mostly paid to total U, soluble U, Fe(II), Fe(III), Mn, Ti, Na, K, Rb, Hg, C, S, F and Cl. In geochemistry, U, Mo, V, Fe, Hg, Li, Na, K, Rb, Ba, Au, As, F and Cl.

In concentrates, they are humidity, U_3O_8 , SO_3 , P_2O_5 , SiO_2 , CO_2 , V_2O_5 , As, Mo, B, halogens and isotopic concentration. In high purity nuclear materials, about 40 trace elements are determined.

Plastics, like PVA, polyethylene, polystyrene, Tygon and polycarbonate, have been characterized; many organic solvents and diluents have been determined, like TBP, TOPO, D2HEPA, decanol, DBP, kerosene and Varsol, and pure helium has been

frequently analysed for water, H, N, O, and total hydrocarbons.

In environmental control, the commonest determinations are U, As, Ba, Cd, Ca, Cr, Cu, Mg, Hg, Zn, Se, Pb, K, Mo, V, B, Mn, Ra-226, H-3, pH, COD, conductance, hardness, residues, turbidity, alkalinity, Cl^- , F^- , I^- , NH_3 , NO_3^- , $\text{PO}_4^{=}$, $\text{SO}_4^{=}$ and SiO_2 .

Other important demands are on metallurgical industry quality control, in both main line and raw materials.

4. CONCLUSIONS

Figure 3 shows the growth of the total Brazilian uranium reserves, according to IAEA's criteria. The initial value corresponds to the known reserves in 1974. Further data correspond to mineral prospection programs conducted by NUCLEBRÁS [4,5] .

In the same plot, the cumulative number of analytical determinations is shown. The number of determinations related to uranium prospection, considered as the most important in the mineral technology program under way, is about 15% lower.

It can be seen the interrelationship between the curves, so certifying the strong reliance of the uranium reserve assessment case on discussed analytical results.

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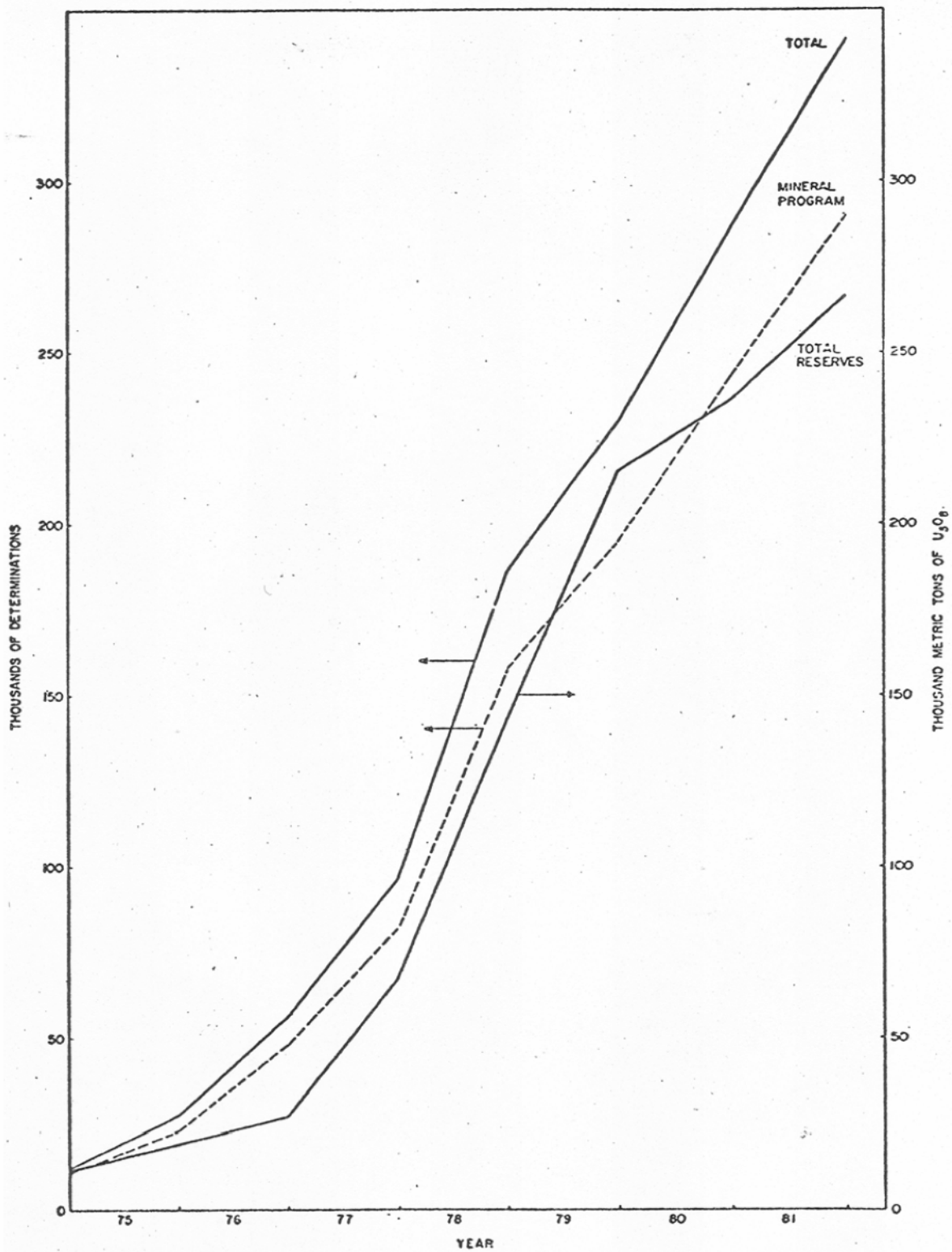


FIGURE 3 - EXPANSION OF BRAZILIAN URANIUM RESERVES AND TOTAL NUMBER OF DETERMINATIONS.