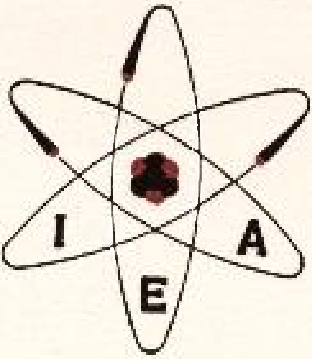

ISOTOPE PRODUCTION AND ACTIVATION ANALYSIS USING RESEARCH REACTORS

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* Presented at a Study Group Meeting on Research Reactor Utilisation, held from 11-15 December 1967 in Bogotá, Colombia. Promoted by the International Atomic Energy Agency.

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SUMMARY

Two main topics of utilization of research reactors, namely isotope production and activation analysis, are discussed. Special conditions inherent to new nuclear centers, specifically in developing countries, are emphasized. Types of problems that had to be solved for a routine production and distribution of isotopes are presented.

INTRODUCTION

I do not think an exageration to repeat once more the words of Wayne Meinke in connection with utilization of research reactors in developing countries (reference 1): "Research and development programs in chemistry as well as chemical service to research and development programs in physics, reactor engineering, agriculture etc, make sense only if they contribute something to the overall scientific effort of the developing country! The amount scientific manpower available in such countries is severely limited and cannot be squandered on projects which are of no consequence to the country or the area".

No doubt that research in certain fields of knowledge, such as Physics, is bound to be more "pure" than in other fields such as Agriculture or even Medicine where applications are more immediately apparent. However, again quoting Meinke (1), "I believe it is axiomatic that at a reactor center in a developing country even the pure research must have a slight vector towards some overall value to that country. If the research has absolutely no relationship to the welfare of the country in terms of possible

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training opportunities for future scientists, possible relationship to the country's future plans in the nuclear field, or short terms gains in applications, then the group has no business undertaking the research".

The possibilities for use of research reactors by chemists and the chemical engineers is extremely large. These possibilities are so large that no single center of research can hope to cover the whole spectrum of research potentialities in chemistry or chemical engineering. Groups in new research reactors centers should very soon decide which fields of work can contribute significantly to the overall progress and development of the country and, of these fields, the ones they can give the best of their contribution. Specially in south american countries this is really very important. Shortage of manpower is an ever present problem. If a leader of a group does not make a judicious choice of two or three fields of research or development, from the very beginning, the group is bound to end up with a load of work per man that is above any possibility of success.

Of the possible areas of utilization of research reactors, in chemistry, isotope production and activation analysis are the one most liable to give practical results and short term gains in applications and a real feeling of realization to the men engaged in work around a research reactor. Even those two fields are indeed too large for a small group and some choice of problems must be made in order to carry on the work successfully in compliance with available manpower, equipment, type of reactor and even with operating schedules of the reactor. In this paper the experience gained at the "Instituto de Energia Atômica" by using its swimming pool reactor for isotope production and activation analysis will be described.

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ISOTOPE PRODUCTION

The reactor mostly used for isotope production in Brasil is a 5 Mw swimming pool type, operating, for that aim , generally at 2 Mw power and giving thermal neutron fluxes, in the irradiation facilities, from 10^{12} to 10^{13} n/sec.cm^2. The operating schedules is of 8 hours per operation, three times a week (tuesday, wednesday and thursday). With some ingenuity in designing processing equipment and in choosing masses for irradiation it is possible to comply with that operation schedule and produce the necessary amounts of the main isotopes required for medical applications, meaning, iodine-131, phosphorus-32, sulfur-35 , colloidal gold-198, chromium-51, sodium-24, potassium-42 , bromine-82 and others under special order. The brazilian demand , and even of some other south american countries for those radioisotopes, has been completely attended. Some long lived fission products radioisotopes are now under production; these are used to make small radiation sources and for calibration of counting equipment for metrology of radioisotopes. In this way millicuries amounts of the following isotopes are made: strontium-89-90 , cesium-137, cerium-141-144, europium-155, yttrium-90-91 , zirconium-95, niobium-95, ruthenium-103, ruthenium-106 , praseodymium-144.

Description of production conditions for each radioisotope will be made, giving neutron flux, target used, irradiation time, amount of target, a brief description of the chemical process and activity obtained. In this way a prospect of production possibilities of those radioisotopes in small or medium size research reactors can be made. Detailed description of producing process can be obtained by contacting the Radiochemistry Division of the "Instituto de Energia Atômica", São Paulo, Brasil.

Iodine-131

Target: elementary tellurium.

Nuclear reaction: $^{130}\text{Te}\ (n,\gamma)\ ^{131}\text{Te} \xrightarrow{\beta} {}^{131}\text{I}$

Irradiation time: 72 hours (three periods of 8 hours each per week, for three weeks).

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: 50 grams

Chemical processing: dissolution of irradiated sample in NaOH and H_2O_2, the solution is made acid with H_2SO_4 and iodine is distillate.

Product for distribution: ^{131}NaI carrier-free dissolved in carbonate-bicarbonate buffer with or without reductor $Na_2S_2O_3$. Use via oral.

Total activity produced: 1,000 mCi.

Radioactive concentration: 20 mCi/ml.

Phosphorus-32

Target: elementary sulfur.

Nuclear reaction: $^{32}\text{S}\ (n,p)\ ^{32}\text{P}$

Irradiation time: 48 hours (three periods of 8 hours each, for two weeks).

Fast neutron flux: 10^{12} n/sec.cm^2.

Mass of target: 25 grams

Chemical processing: Irradiated sulfur is heated in reflux with HCl and octanol. The octanol is then distilled and the chloridric solution with ^{32}P is percolated throught a cationic ion-exchanger, the efluent contan̲ing ^{32}P is evaporated and organic matter eliminated with H_2O_2.

Product for distribution: $H_3{}^{32}PO_4$ or $Na_2H^{32}PO_4$ carrier-free. Use via oral.

Total activity produced: 100 mCi.

Radioactive concentration: 5 mCi/ml.

Sulfur-35

Target: KCl

Nuclear reaction: $^{35}Cl\ (n,\ p)\ ^{35}S$

Irradiation time: 24 hours (three periods of 8 hours each).

Fast neutron flux: 10^{12} n/sec.cm^2.

Mass of target: 10 grams

Chemical processing: Dissolution of irradiated sample in HCl 0.1 N and percolation of solution through Al_2O_3. Elution of ^{35}S with NH_4OH. The resulting solution is percolated through a cationic ion-exchanger and the efluent evaporated with H_2O_2.

Product for distribution: $Na_2{}^{35}SO_4$ carrier free. Use via oral.

Total activity produced: 15 mCi.

Radioactive concentration: 3 mCi/ml.

Colloidal gold-198

Target: metallic gold (laminated).

Nuclear reaction: $^{197}Au\ (n,\gamma)\ ^{198}Au$.

Irradiation time: function of desired activity (from 3 to 24 hours).

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: 300 milligrams

Chemical processing: Dissolution in "acqua-regia". Excess of "acqua-regia" is evaporated up to formation of crystals of chloroauric acid which are dissolved in water. Solution is neutralised with NaOH. The resulting solution of sodium chloroaurate is added drop by drop to the reduction solution made up of gelatin and a germ (gelatin-glicose-gold)

Reduction is completed by adding sodium ascorbate.

Product for distribution: colloidal gold with particles of 300 Å; sterilized.

Radiochemical purity: less than 2% of soluble gold.

Radioactive concentration: From 1 mCi/ml to 30 mCi/ml (function of irradiation time).

Chromium-51

Target: K_2CrO_4.

Nuclear reaction: $^{50}(n,\gamma)$ ^{51}Cr (Szilard-Chalmers process).

Irradiation time: 48 hours (three periods of 8 hours each, for two weeks).

Thermal neutron flux: 10^{13} n/sec. cm^2.

Mass of target: 30 grams

Chemical processing: The irradiated target is dissolved in a solution of KCl at 10% and the resulting solution is passed throught sintered glass G-4. Cr $(OH)_3$ is adsorbed in the sintered glass which is washed with water and chromium taken by dissolution with NaOH and H_2O_2, boiled and neutralised with HCl. The resulting solution is filtered in sintered glass G-4 to eliminate any hidroxide.

Product for distribution: $Na_2{}^{25}CrO_4$ isotonic solution and sterilized.

Radiochemical purity: less than 5% in Cr^{+++}.

Specifi activity: 10-20 mCi/ml.

Sodium-24

Target: Na_2CO_3.

Nuclear reaction: $^{23}Na(n,\gamma)\ ^{24}Na$.

Irradiation time: function of desired activity (from 1 to 8 hours).

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: 250 milligrams

Chemical processing: Dissolution of irradiated target in HCl to obtain a isotonic solution (0.9% in NaCl).

Product for distribution: $^{24}NaCl$ in isotonic solution and sterilized.

Radioactive concentration: 0.6 mCi/ml (function of irradiation time).

Specific activity: 100-150 mCi/g Na.

Potassium-42

Target: K_2CO_3.

Nuclear reaction: $^{41}K\ (n,\gamma)\ ^{42}K$.

Irradiation time: 8 hours.

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: 150 milligrams

Chemical processing: Dissolution of irradiated target in HCl to obtain a isotonic solution (12 o/oo in KCl).

Product for distribution: ^{42}KCl in isotonic solution and sterilized.

Radioactive concentration: 0.35 mCi/ml.

Specific activity: 40 mCi/g K.

Bromine-82

Target: NH_4Br.

Irradiation time: three hours.

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: 250 milligrams

Chemical processing: Dissolution of irradiated target in NaOH, elimination of ammonia by boiling. pH ascertained to 6-7 with HCl.

Product for distribution: $Na^{82}Br$ solution and sterilized.

Radioactive concentration: 0.25 mCi/ml.

Specific activity: 6 mCi/g Br.

Fission Products

Target: U_3O_8.

Nuclear reaction: ^{235}U (n, f) fission products.

Irradiation time: Function of desired activities and isotopes; from 10 to 200 hours.

Cooling time: Function of desired isotopes; from one to eight months.

Thermal neutron flux: 10^{13} n/sec.cm^2.

Mass of target: Pellets of 5 grams each.

Chemical processing: The irradiated target is dissolved in nitric acid and uranium is extracted with TBP-CCl_4. Oxalic acid is added to the rafinate and the solution concentrated to 5 milliliters. The residue is dissolved in HCl 0.1 M and the solution is made to 0.4 M in oxalic acid. The solution is percolated through a cationic ion-exchanger resin in hydrogen form retaining Cs-137, Sr-89, Sr-90, rare earths (Ce-141-144, Pr-144, Y-90-91 and rare earths are eluted with HCl of molarity 1.0, 1.5 and 6.0, respectively. The effluent from the saturation step on the cationic ion-exchanger contains Zr-95, Nb-95 and Ru-103-106. This effluent is percolated through an anionic ion-exchanger conditioned with oxalic acid. Zirconium-95, followed by niobium-95, is eluted with HCl 1.0 M-oxalic acid 0.01 M, and ruthenium-103-106 with HNO_3 3.0 M.

Product for distribution: Chlorides of Cs, Sr and rare earths, carrier free. Oxalic complexes for Zr and Nb.

Radioactive concentration: Function of irradiation time (see reference 2).

Most of the listed radioisotopes are used for medical applications such as determination of extracellular fluid and peripheryc blood flow (^{24}Na), extracellular space (^{82}Br), blood liver flow and liver scanning (^{198}Au), intracellular space (^{42}K), thyroidean diagnosis and treatment (^{131}I), labelling of red blood cells and plasmatic proteins (^{51}Cr). For agriculture and biochemical research, use is made of ^{32}P and ^{35}S. Iodine has also been used for labelling molecules by the Division of Radiobiology, such as hippuran, rose bengal, soroalbumin, denatureted albumin, oleic acid, triolein and lipids.

With exception of fission radioisotopes, whose production is not large since no enriched uranium in the 235 isotope is available, importation of the other listed isotopes has stoped with a considerable saving of foreign currency. An idea of the increase of production and use of those radioisotopes can be made through Tables I to VIII.

Tables I to VIII

Number of Shipments of Various Radioisotopes

TABLE I

^{131}I

	mCi					
YEAR	0,1 to 5	5 to 10	10 to 20	20 to 50	50 to 100	100
1959	20	-	-	-	-	-
1960	94	5	-	-	-	-
1961*	261	101	46	7	-	-
1962	147	179	299	179	10	-
1963	52	159	183	101	34	35
1964	90	132	183	164	57	35
1965	240	134	117	118	62	32
1966	375	139	218	138	77	33
1967**	356	136	248	136	62	34

* From 1961 on, first column is 1 to 5 mCi.

** Extrapolated to December

TABLE II

^{32}P

	mCi			
YEAR	0,1 to 5	5 to 10	10 to 20	20 to 50
1959	1	-	-	-
1960	2	-	-	-
1961*	20	27	4	-
1962	19	44	58	1
1963	36	32	5	1
1964	83	24	-	1
1965	61	19	1	-
1966	53	20	1	-
1967**	56	10	8	1

* From 1961 on, first column is 1 to 5 mCi.

** Extrapolated to December.

TABLE III

^{24}Na

	mCi		
YEAR	0,1 to 5	5 to 10	10 to 20
1963	14	-	-
1964*	21	3	4
1965	12	6	1
1966	10	8	-
1967**	6	4	1

* From 1964 on, first column is 1 to 5 mCi.

** Extrapolated to December.

TABLE IV

^{35}S

	mCi		
YEAR	1 to 5	5 to 10	10 to 20
1965	-	2	-
1966	-	1	1
1967*	-	3	2

* Extrapolated to December.

TABLE V

^{82}Br

	mCi	
YEAR	1 to 5	5 to 10
1966	25	-
1967*	46	2

* Extrapolated to December.

TABLE VI

^{42}K

	mCi	
YEAR	1 to 5	5 to 10
1966	3	3
1967*	32	4

* Extrapolated to December.

TABLE VII

^{51}Cr

	mCi		
YEAR	1 to 5	5 to 10	10 to 20
1965	1	-	-
1966	14	8	1
1967*			

* Extrapolated to December

TABLE VIII

^{198}Au Coloidal

	mCi					
YEAR	1 to 5	5 to 10	10 to 20	20 to 50	50 to 100	100
1964	5	8	-	-	-	1
1965	5	16	5	-	-	4
1966	23	85	10	4	-	8
1967*	22	68	40	4	1	2

* Extrapolated to December

SOME CONSIDERATIONS ON THE PROBLEM OF ISOTOPE PRODUCTION IN DEVELOPING COUNTRIES

A phylosophy of isotope production in research reactors has been put in the excellent "Manual of Radioisotopes Production" published by the International Atomic Energy Agency (3). It seems to us that the general ideas of the Manual are simpathetic to local production of radioisotopes for local requirements, otherwise no Manual would be written since, in accordance with its Introduction, "it has been compiled primarily to help small reactor establishments which need a modest programme of radioisotope production for local requirements".

Even so, on the "pros and cons" considerations in regarding small nuclear centers starting their activities on the lines of isotope production it may seems that the "cons" are a bit severe.

It is considered that from the economic point of view, local production will cost more than importation from large suppliers. Less strong arguments go along the lines that a research reactor will never produce all the isotopes needed, such as cobalt-60 for cobalt therapy, carbon 14 and tritium. Also, labelled coumpounds required in research are so varied that it is impossible to make reasonable provision for the production of all that may be needed in a particular country. It is mentioned that the speed of air transportation is such that only isotopes with half-life of about 30 hours or less should have their production considered.

The points of economy and price has already been raised and largely ventilated during another Study Group Meeting with special view to Latin America countries, meaning, the one that took place in December 1965 in Caracas, Venezuela (see reference 4). Examples were given of university reactors in the United States in which the production of radioisotopes might interfere with research programmes. It was admited that in cases as the one mentioned, i.e., a large and developed country with many and diversified activities on the field of nuclear energy, it would be more rational to buy isotopes from a large central place, such as Oak Ridge.

However, the discussion led to the general viewpoint that in developing countries which already have research reactors of reasonable size and power the production of radioisotopes is convenient for various reasons, among them being the impracticability of importation of short-lived isotopes for reasons of heavy shielding and too much activity in one shipment; also, radioisotope production, in general, does not interfere with the operation and other uses of the reactor, although irregular operation schedules will interfere with isotope production; saving of foreign currency is a top priority argument when considering the advantage of local isotope production over importation. Favourable arguments in connection with local production of radioisotopes, and listed also in the Agency's Manual, are, among other, that local production stimulates a more rapid growth in the use of radioisotopes , provides good training ground for scientists who can give advice to new customers and assist them in their projects. Other research activities are also stimulated by radioisotopes production. Independence from foreign supply is no small matter to consider when continuity of research or work must be taken into account, since a better programming of delivering schedules can be made when only local arrangements have to be considered. No doubt that the speed of modern aircraft is such that would allow use of a short-lived isotope within hours of production time, even when production centers are at thousands of kilometers from utilization centers. However, the amount of red-tape and paper work that goes together with importation is such that even radioisotopes such as iodine-131 becomes a "short-lived" isotope requiring the importation of larger amounts than the actual needed in order to compensate for radioactive decay. In Brasil, importation of a medium half-life isotope such as iodine-131, for distribution from a centralizes place, makes the conversion rate of NCr$ 2,71 per dollar raise to NCr$ 4,50 per dollar after all taxes, handling and transportations charges, shielding etc are paid; if distribution is not made from a centralized distributing place the conversion rate goes to NCr$ 6,00 per dollar.

All facts considered it still seems reasonable to use research reactors that have available neutron fluxes from 10^{12} to 10^{13} n/sec.cm^2, in developing countries, also for isotope production. The amounts of benefice that results in terms of training , independence from foreign supply, saving of foreign currency, simplicity on ordering, largely compensate for the extra amount of work and money in construction and maintenance of processing laboratories.

ACTIVATION ANALYSIS

Other important field of utilization of research reactors and one that can be explored from the start of the activities of new reactor centers, is activation analysis, whatever is the viewpoint under which it is considered, i.e., service function or research.

Thermal neutron fluxes of the order of 10^{11} to 10^{12} n/sec.cm^2 are sufficient for solving a good number of analytical problems. Standard counting equipments such as Geiger tubes and scalers and single channel gamma spectrometers, used together with radiochemical techniques, are all that are needed to face a very large spectrum of problems in chemical analysis. No doubt that more elaborate and expensive equipment such as multichannel analyzers would facilitate the solution of some special cases and in fact activation analysis carried out by means of short--lived isotopes (from seconds to minutes) will require the use of multichannel analyzers and pneumatic systems to carry sample to and from the reactor. Good progress has been made along the lines of non-destructive activation analysis by using multichannel analyzers and computing techniques. However it does not seem that non-destructive techniques are to be routinely applied in a near future. This means that new and small nuclear centers are in a position where work of good level can be carried out with the more simple counting equipment described above, together with radiochemical separation methods, specially the ones that involve fast radiochemistry.

Activation analysis development at the "Instituto de Energia Atômica" started in the same year the reactor was put in operation in 1957. By that time only Geiger tubes and ordinary scalers were available; in 1958 a home made gama spectrometer , provided with manual scanning systems, was added to the equipment. Various problems were tackled and solved with this simple equipment and using thermal neutrons fluxes of 10^{12} n/sec.cm^2.

In order to show the possibilities of research or service function in the field of activation analysis using rather simple equipment and techniques some of the work which was carried out with that equipment will be described.

Analysis of uranium in various materials and of gold and uranium associated in some minerals (ref. 5-6)

Samples of minerals containing 0.1% of uranium and 20 ppm of gold were analysed by irradiating 0.1 to 0.5 grams of sample in a thermal neutron flux of 10^{12} n/sec.cm^2 for two hours. After irradiation a cooling period of 24 hours was observed and the sample dissolved in "acqua-regia". Separation of gold-198 and neptunium-239 is based on the fact that the anionic chloroauric complex is held by an anionic ion-exchanger in the chloride form while neptunium is eluted with diluted hidrochloric acid. Neptunium, in the effluent, is separated from other radioactive species by a rare earth separation procedure adding lanthanum as carrier. Counting was done in a single-channel gamma analyzer at the energies of 0.41 Mev and 0.275 Mev for gold-198 and neptunium-239, respectively.

By the same general technique uranium was determined in the ion-exchanger resins from the water treatment system and in smearing taken from the external parts of the aluminum cladding of fuel elements.

Hafnium in Zirconium (ref. 7)

The determination of hafnium in zirconium is an example of analysis that can be made non-destructively using multichannel analyzer and pneumatic rabbit system to transport samples in a rapid way to and from the reactor. In this method samples of 1-2 milligrams of zirconium oxide are irradiated for 5 seconds in a thermal neutron flux of 10^{12} n/sec.cm^2; counting is started 1.5 minutes after irradiation using the multichannel analyzer as a multiscaler. In this way the decay curve for the isotope hafnium-179 of 19 seconds of half-life is automatically obtained for samples and standards of known content in hafnium. The amount of hafnium in the samples is determined stablishing the proportion of counting at the same point of the decay curves for sample and standard.

This same analysis can be carried out using simpler equipment such as single-channel analyzer. Samples of 0.5 grams of zirconyl chloride are irradiated for about five hours in the same neutron flux mentioned. After irradiation the samples are dissolved in water and the volume made up to 25 milliliters from which aliquots of one milliliter are taken for counting. Scanning was carried out manually in a home made single-channel analyzer and the area under the peak corresponding to 0.133 Mev, for hafnium-181 with 46 days of half-life, is calculated and compared with the same area for standards of zirconyl chloride of known content in hafnium. To avoid interference from other radioactive species present in the zirconyl chloride samples a cooling period of about one week can be observed. Samples of zirconium with a hafnium content from 0.1 up to 5% were analysed by this procedure.

Sodium in water and graphite (ref. 8)

Sodium in the reactor pool water was analysed by evaporation of 250 milliliters of water in platinum crucibles and and irradiating the residue for a time from half an hour to four hours. A cooling time of two hours was observed and the irradiated sample was counted in a single-channel analyzer with manual scanning using the peak at 1.37 Mev for calculation. Comparison of samples and standards allows analysis, without chemical separation, of sodium in water of high purity in concentration as low as 0.01 ppm. Sodium in graphite at a proportion of one part per million can also be analysed, without chemical separation, and an irradiation time of two to four hours in a flux of 10^{11} to 10^{12} n/sec.cm^2.

Internal standard methods was adopted for the analysis of sodium in water. Three irradiation capsules were prepared: one containing the evaporation residue from the water to be analysed; another with the same residue plus an added mass of sodium (internal standard) of the same order of magnitude as the one to analysed ; and a third one with the same mass of sodium as used for the internal standard.

Chromiun in water (ref. 9)

Chromiun in water, at a level of parts per billion, can be analysed by oxidizing the chromiun to chromate ion, with hydrogen peroxide, and percolation of the water through an anion--exchanger resin in the OH-form. The amount of anion-exchanger required is very small and the whole of the resin is irradiated for a period of eight hours in a thermal neutron flux of about 10^{12} n/sec.cm^2. Resin blanks are treated and irradiated in the same way as the resin used for actual analysis. A cooling period of about 72 hours is observed and the resins are scanned in a multi-channel analyzer. The area under the peak corresponding to 0.32 Mev for the resin-sample minus the same area for the resin blank and comparison of this value with the ones obtained for standards, allows calculation of the chromiun content in the water matrix.

Chlorine and copper in water matrix (ref. 10)

Chlorine and copper, at the level of parts per billion, in water can be analysed by irradiation of about 100 milliliters of water, placed in polyethylene bottles, in thermal neutron flux of 10^{13} n/sec.cm^2 for half an hour. After a 10 minutes cooling time, carriers for copper, chlorine and iron are added, the hydroxides are precipitated with sodium hydroxide and filtered. Chloride ion passes into the filtrate and is precipitated with silver nitrate. The iron and copper precipitates are dissolved in hydrochloric acid and the iron is again precipitated with ammonium hydroxide leaving the copper complex in solution. The filtrated from this last precipitation is acidified and copper precipitated as sulfide. Chlorine is determined by counting the beta particules (4.8 Mev) of the chlorine-38 isotope of 37.3 minutes of half-life using an aluminum absorber to cut any beta contamination. Copper is determined by counting the sulfide precipitate in single-channel gamma spectrometer at the peak corresponding to 0.51 Mev. The same procedure used for the samples is adopted for standards of copper and chlorine.

<u>Some other analysis</u> (ref. 11, 12)

Analysis of various material are part of the general program of activities of the Division of Radiochemistry, at the "Instituto de Energia Atômica". Since they involve a more sophysticated equipment, such as multichannel analyzer and pneumatic rabbit transfer system, only a brief mention will be made regarding these problems, since the principal aim of this review is to show actual examples of activation analysis problems which can be solved with rather simple equipment.

By using short-lived radioisotopes some rare earth elements can be analysed without chemical separations. In this way dysprosium was analysed in erbium oxide of high purity by irradiating the erbium samples for five seconds in a thermal neutron flux of 10^{12} n/sec.cm^2; after a cooling time of 30 seconds counting is started using the multichannel analyzers as multiscaler and obtain-ing the decay curve for the isotope dysprosium-165 ($t_{1/2}$ = 1.3 minutes) automatically. Comparison of decay curve for sample and for standards allows the calculation of dysprosium in erbium. A complet analysis takes about 20 minutes. Samples used for the mentioned analysis had a dysprosium content of about 30 parts per million. The same type of analysis was carried out for the dysprosium content in holmium (0.3%). In the same general way ytterbium was determined in thullium samples using the isotope ytterbium-117 ($t_{1/2}$ = 6.5 seconds); irradiation and cooling times were 15 seconds and 20 seconds, respectively. Amounts analysed were of the order of 6% of ytterbium in thullium.

Silver in lead was analysed by irradiating lead samples for 5 seconds and observing a cooling time of about 30 seconds. Decay curve is automatically obtained for the isotope silver-110 ($t_{1/2}$ = 24 seconds) and compared with the same curve for standards. Samples with about one part per million were analysed. Each analysis may take about 15 minutes.

A more elaborate method of analysis is being developed for all elements of the rare earth family present in the same sample. A previous separation in ion-exchanger resins in made using the double column technique: one loaded with the rare earth mixture followed by another one loaded with a cation whose stability constant with EDTA is larger than the stability constant for a certain rare earth and smaller for the next rare earth . Cations used in the second column are zinc, or copper, or manganese. Since the various rare earth elements separated are contaminated in the head and tail of elution curves by the adjacents elements in the separation, isotope dilution technique is applied in such a way that a pure fraction of each element is obtained. The amount of each element recovered in that pure fraction is determined by activation analysis. Yttrium oxide of high purity has been analysed by this method with the following lower detection limit: Lu-0.001%; Yb-0.003%; Tm-0.015%; Er-0.050%; Ho-0.005%; Sm-0.005%; Pr-0.050%;

Nd-0.010%; Ce-0.010%; La-0.010%. Work is being developed in such a way as to increase the sensitivity of the method.

An important aspect of activation analysis is that the method has shown to be of possible applicability in forensic sciences. Although this possible application is still in its first stage of development it deserves some detailed coments for two main reasons: one, because the method is really promising and, as consequence, may have an important social meaning in scientific crime investigation; two, misapplication of the method in an actual problem may lead to nefarious results.

Forensic Applications of Activation Analysis (ref. 13)

A very common problem in scientific crime investigation is to stablish the identity of two pieces of evidence, for instance a piece of cloth found at the scene of a crime and a piece of cloth pertaining to a possible suspect.

One of various means to stablish identity of two materials, i.e., to verify if they come from the same source , provided this source is homogeneous, is through an analysis for the inorganic elements present in the source. Usually the amount available for analysis in actual criminal cases is very small: one single hair, a small piece of an automobile glass windowshield, a flake of paint left on the cloth of a hit-and-run victim. For these small samples activation analysis is the method "par excellence".

The problem of stablishing a common origin for samples is exemplified in the case of hair individualization, i.e., to be able to say if two hairs come from the same individual or not. As it is known, inorganic elements coming from the metabolic processes are eliminated through the hair. There are very good indications that the elements present in hair, as well as their proportion, are the same for a individual but it varies from individual to individual. In this way an analysis of two single hairs from the same head should give the same qualitative and quantitative results. Classical chemical analysis, for various elements present in a single hair, is absolutely impractical if not impossible. Activation analysis is, perhaps, the only practical method that allows analysis of, for instance, ten elements present in a single hair.

Actual application of the method to scientific crime investigation by means of individualization of hair is made when hair is found at the scene of a crime, in the hands of the victims, in weapons of agression, etc. Neutron activation analysis is performed in that hair and in the hair of a suspect. Gama spectrometry of the activated hair samples will give information concerning the inorganic elements present in each hair. Usually three types of irradiations are made: one short (seconds), one medium (minutes to hours) and one long (from hours to days). The three types or irradiation, concerning the lenght of time that the irradiation takes place, will give information about elements of short, medium and long half-life.

This type of investigation is still in its early stages of research and various points remain to be verified. For instance, the work carried out by Colleman (14) from the Atomic Weapon Research Establishment, in England, has shown that a mere visual comparison of the spectra of two irradiated hairs, one of the suspect and the orther found at the scene of crime, is not sufficient to inform about the possible common origin of the two samples and that a statistical interpretation of the data is necessary before one can say that the two hairs come from the same person. Also, the information available up to now show that the concentration of trace elements in the hair may very in a period of months. Movement of some elements along the hair lenght has also been verified (15), (16), (17), (18), (19). These points still need research in order to be correctly interpreted. The method of hair individualization is promising and it seems that large application in actual court cases can be made in a near future once all those points have been made clear.

Application of neutron activation analysis has also been made in connection with the determination of high concentration of arsenic in hair, nails and visceras in cases of criminal poisoning. Also in these cases the amount of sample available for analysis is very small and a high sensitive method is required. Activation analysis is a powerfull method for analysis of that kind of material, giving results of much higher sensitivity and precision than the classical Gutzeit method for arsenic.

Other applications on the field of forensic science are the determination of gunshot residues left on the hands of people who have fired a gun recently; barium and antimony are elements present in gunpowder and analysis of residues on the hand of a suspect will indicate the presence of those two elements. The distance from which a gun has been fired can also be determined by analysing those same elements around the hole made by the bullet.

A word of precaution must be said in connection with the general application of the method of neutron activation analysis in actual cases, at least at the present stage of development. Specially true is the case of individualization of hair for which some questions are still not definitely answered. Does the inorganic composition of the hair from the same individual remains unchanged for months and months? A change of feeding habits, an occurrence of a pathological state, the ingestion of medicine, movement of the person from a living place to another, industrial exposures and work in particular plants, do not alter the hair composition?

Questions as such, and others, that has made application of the method to actual cases still not accepted in all courts, were the reason why during the First International Conference on Forensic Activation Analysis* it was decided to form a informal "Forensic Activation Analysis Coordinating Group" with representants from the main geographical areas in the world. The objectives of such a group is to encourage the sound development of the field of forensic activation analysis but also to discourage the premature use of only partially developed applications in actual case work and in court. In connection with the group activities a list of United States court cases involving activation analysis testimony has been prepared**. This list register 27 cases in which activation analysis was used and the results accepted for presentation in U.S. courts.

So far, the use of neutron activation analysis in forensic problems has not been very large. It is a promising field to exploit and a close co-operation between the nuclear scientist and the forensic scientist will certainly bring fruitful results in a no remote future.

Education, liaison with industry and university relations

On the lines of education and university relations, courses in Activation Analysis have been given by the Division of Radiochemistry of the "Instituto de Energia Atômica". The course follows the general outline of Lyon's book (21). The course is given in thirty lectures and five laboratory demonstrations.

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* First International Conference on Forensic Activation Analysis, promoted by General Atomic Division of General Dynamics and California Association of Criminalist and held in São Diego, Calif., September, 1966.

** Copies of this list and other informations concerning the activities of the Informal Forensic Activation Analysis Coordinating Group can be obtained by writing to

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Following the lectures facilities for work are provided for some of the students to make actual analysis of interest to their own work.

Liaison with industry has been made by performing analysis on various materials. By now a nominal price is charged but in the future, when the method of activation analysis has shown to be of wide acceptance in São Paulo, the idea is to charge actual prices. Examples of problems proposed are analysis of magnesium metal of high purity to be used in alloys for motor blocks in the automobile industry. Analysis of silver in scraps of lead have also been made in order to evaluate the possibilities of economic recovery of the silver in the scraps. Arsenic was analysed in hair of cattle accidentally exposed to ingestion of pesticides containing arsenic. Hafnium was analysed in zirconium oxide for plants that process zirconites. Mercury in vegetables that had been treated with pesticides containing that element. Other analysis on the line of isotope dilution have also been performed; in this way labelling of BHC (hexachlorocyclohexane , benzenehexachloride) with chlorine-36 was made and the labelled compound used for analysis of the biologically active gamma isomer.

RÉSUME

Deux utilisations principales d'une pile de recherches, c'est-à-dire l'analyse par activation et la production de radioéléments, sont examinées. Les conditions particulières des nouveaux centre nucléaires sont discutées surtout celles existantes dans les pays en développement. Les problèmes qui se présentent pour une production routinière de radioéléments sont aussi discutés.

SUMÁRIO

Faz-se uma revisão relativamente a dois tópicos de utilização de um reator de pesquisas, isto é, análise por ativação e produção de radioisótopos. Em especial são examinados

os problemas típicos de centros nucleares novos, particularmente quando os mesmos se localizam em países denominados em desenvolvimento. Os problemas enfrentados para se poder atingir um nível de produção de distribuição de radioisótopos, rotineiramente, são também apresentados.

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