NUCLEAR METHODS IN TRACE AND ULTRA-TRACE ANALYSIS: PAST EXPERIENCES AND FUTURE POSSIBILITIES

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Abstract - A description of the successive developments of different nuclear analytical methods is made. The salient features of the developments and the specific advantages of each method are discussed. Some examples of intercomparisons between analysis by different nuclear methods and others are given, to show the actual necessity to continue these studies to point out the true limits of all analytical methods.

INTRODUCTION

In this conference we wish to show the main evolutions of some nuclear analytical methods. It is impossible to cover all the facts even of a certain importance in one conference. It is for this reason that we have made the choice to show mainly the trends of this evolution of nuclear analytical methods through the work of our research groups in activation analysis and some others with whom we have had some research programme in cooperation, as in the B. C. R. [*] multidisciplinary community project of analysis for the production of reference materials for the determination of non metals, in metals (O, C, N, B .. .. in Al, Cu, Mo, Zr, Ti, W .....) and in semiconductors (Si, GaAs, Ge ....) or B. N. M. [**] project for the certification of pure iron reference material.

1. EARLY STUDIES

First experiments concerning neutron activation analysis were made by Von Hevesy and Levi (1) in 1936 and those concerning charged particles by Seaborg and Livingood (2) in 1938 and by King and Henderson (3) in 1939. The first 10 years of activation analysis yielded less than two dozen contributions to the Scientific bibliography. The neutron activation analysis research began to grow with the easy accessibility of the nuclear reactors. Let us mention particularly the groups headed by, Leddicotte (Oak Ridge), Smales (Harwell) and Leveque (Fontenay aux Roses). We began to work in 1950 with irradiations in "ZOE" Reactor (Fontenay aux Roses). Until the Symposium on Radioactivation analysis in June 1959 (4), organized by the International Atomic Energy Agency (I. A. E. A.) and the Joint Commission on Applied Radioactivity (I. C. S. U.) in Vienna, the researchers working on activation analysis have had only a few opportunities to meet in International Conference on uses of Radio-isotopes in Scientific and Technical Research. As example we mention : Radioisotope Conferences, Oxford July 1951 and 1954, sponsored by AERE, Harwell, International Conference on Peaceful uses of Atomic Energy Geneva, 1955-1958, sponsored by United Nations organization and International Conference on the Radio-isotopes in Scientific Research, 1957, Paris, organized by UNESCO. In June 1959 the annual accretion of articles on activation analysis was about a hundred and the cumulative total number of publications was about a thousand. Only twelve communications were presented in the symposium (4). They were :

Leddicotte, on applications of activation analysis in different analytical problems;

Cook, on a general survey on developments in activation analysis;

Herr, on neutron activation applied to geochemistry;

Lenihan, on radioactivation analysis in biochemistry and medicine

Hoste, on activation analysis of minor constituents in high alloy steels with improved accuracy and precision by a method of internal standard;

Albert, on systematic analysis of pure aluminium and iron after neutron activation;

Ljunggren, on new progress in NaI γ-spectrometry by fast Coincidence Circuit;

Leveoue, on some examples of analysis using properties of nuclear radiations: n-absorption, β-diffusion, X-ray emission induced by β-radiation;

Communications from Leliaert, Ljunggren and Westerma rk, Gibbons and Simpson, Ascoli and Germagnoli, concerned with activation analysis of specific interest.

Significant Contributions to the discussions were by Meinke, Reed, Muller and Kellershohn.

1.1.   At the time of this Symposium [4] the status of activation analysis
            techniques was:

1.1.1   Neutron activation is applicable for a wide variety of elements ($\sim$ seventy
            elements have been investigated and a useful bibliography is available [5]);
            the sensitivity is high and is amenable to simple calculation (a comparison
            of the sensitivities of other methods of trace analysis with radioactivation has
            also been made [5]);

1.1.2.   The specificity is high, since a chemical process can be devised which is
            unique for the element in question, and the success of the operation can be
            checked by measurements of the half-life and β - and γ -ray energies of the
            radioisotope concerned. The recently developed technique of gamma-scintilla-
            tion spectrometry can be used in conjunction with radioactivation analysis to
            determine many of the isolated radionuclides. The principles of this method
            have been described elsewhere [7, 8]. Typical spectral data obtained by this
            method are given in several reports [9-11].

1.1.3.   The method is free from reagent blank corrections, as only the constituents
            of the irradiated sample will be radioactive and only the radioactive content is
            determined.

1.1.4.   There is, in general, little interference from the matrix with no stringent
            requirements for special standards.

1.1.5.   Subject to adequate chemical exchange, the chemical procedure need not be
            quantitative.

1.1.6.   The chemical manipulations are carried out with semi-micro amounts of
            carrier (e. g. 10-50 mg), rather than with micro and submicrogram amounts.

1.1.7.   The method can be "non destructive". The most suitable technique is γ - ray
            analysis using the γ -ray scintillation spectrometer. With this instrument, the
            characteristic γ -energies (and their abundances) of a given nuclide can be
            recognized and quantitative estima te made of the amount of radiation detected,
            either from the photoelectric peak height or its area on the pen-recorder
            tracing and using the standard to normalize the intensities to obtain the
            elemental abundances. However, since a γ -ray energy is not a unique
            identification of a nuclide, some further assurances of identity may be
            necessary. These can be provided by the detection of other γ -rays known to
            be emitted by the nuclide, if its decay scheme is complex, and from half-life

determinations,
when using the single-channel pulse height analyser, the sensitivity of detection using the γ-scintillation spectrometer is less by a factor of at least 20, than that of methods involving determination of β-particles. Some gain in sensitivity is obtained by using a multichannel pulse height analyser, particularly when applied to short-lived isotopes, as these decay appreciably during the time of a scan by the single-channel instrument. The attractions of this approach to activation analysis are so obvious that further improvements both in reliability and cost of instruments, are to be expected. (7, 9 — 13).

1.1.8.   Any nuclear reaction producing a radionuclide can be used in radioactivation analysis. In the United States, alpha particles, protons, deuterons, photons and fast and thermal neutrons have been used as the projectile particles. American work on charged particle radioactivation analysis (2-3, 14-21) has been somewhat more limited than on the Continent (22-31). This is probably caused by the fact that more nuclear reactors have been available and much work has gone into these efforts, while charged particle accelerators have been used in basic research programmes.

1.2   On the debit side of the ledger we have the following facts :

1.2.1.   Few laboratories have suitable irradiation facilities within immediate reach such as a reactor or an accelerator, a fact which restricts the use of the method, when shortlived isotopes only are formed.

1.2.2.   Certain samples cannot be accepted as they might endanger the safety of the reactor, e. g. volatile organic liquids which might decompose under the action of the intense gamma and neutron bombardment, building up dangerous pressures in the sealed sample containers.

1.2.3.   Certain matrices become highly radioactive, particularly in slow neutron activation, emitting penetrating radiation, so that the laboratory facilities suitable for handling relatively high levels of radioactive materials are required.
It can be seen that the objections to the method are not very restrictive. However, it is unfortunate that several important elements such as oxygen, carbon nitrogen, and fluorine cannot be analysed adequately by slow neutron activation.
At this time (1959) it began to be seen that activation by γ-photons, charged particles and fast neutrons (14 Mev) could be complementary methods for the determination of many elements, for which detection is difficult or impossible by slow neutron activation.

2.   DEVELOPMENTS IN THE PAST TWO DECADES

2.1.   Neutron Activation Analysis :

We will describe now, with some selected examples, the trends in the evolution of the nuclear methods between 1960 and 1980 and the outlook for the future of these methods in relation to some chemical and physical methods of analysis.
It is not possible, in a conference of this kind, to mention all the work made in nuclear analytical methods. There are very good books and articles to locate any selected reference:
NBS Technical Notes give bibliography from the beginning of radioactivation analysis until 1971 (32) and also articles by Lyon, Ricci, and Ross, which appear every two years from 1966 until 1980 (33, 34). We mention also a review article by Bujdoso and Toth (35).

2.1.1.   Reactor Neutron Activation Analysis :

As early as 1950-1959 some research groups (our C. N. R. S. - CECM VITRY; General Electric Laboratory - Schenectady; Cosgrove and Morrison at Sylvania Electric Product, Bayside; Kant and Cali, Cambridge Research

Center, Bedford; Smales at Harwell..... (32), were looking for the system-
atic analysis of materials.
Hence we discuss only the evolution of systematic multielement analysis of a
sample after irradiation.   This kind of analysis is made mainly after thermal
neutron irradiation in a convenient reactor (heavy water, graphite, BeO mode-
rator/reflector).   It is possible to have positions of high
flux, allowing high sensitivities for about 70 elements, as is required in the
studies of properties of very high purity materials (Semi conductors, metals).
Even with the help of NaI(Tl) γ-spectrometry it was necessary to make many
chemical separations of radioisotopes and often β- counting was made for
better sensitivity.
In this domain the development has been made step by step.   During 1964-1969
many separation schemes involved complex operations.   The trends have been
to make more ion exchange separations, more selective extractions, and use
of ion exchange or selective retention of ions on some inorganic compounds
(alumina, tin dioxide, hydrated antimony pentoxide, zirconium phosphate,
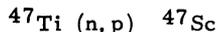silcon   dioxide, hafnium dioxide, ... etc.).

The work of Korkisch (36) particularly called our attention to the
possibilities of mixed media as HCl - H_2O - acetone in ion exchange separ-
ations.   Studies by Deschamps and Cleyrergue and the results of Korkisch,
have given us the possibility to use, in the analysis of pure iron, a new scheme
for radiochemical separations (37).

The work of Girardi (38 - 40) has given rise to a wide development
of the studies on ion retention on inorganic compounds.   The work of C.N.R.S. -
VITRY and C. N. R. S. P. SUE-SACLAY have given new schemes of radio-
chemical separations for analysis of iron with tin dioxide (41) and of chromium
and silver with nickel ferrocyanide, hydrated antimony pentoxide and Dowex
1 x 8. (42, 43).   The main advantage of these new schemes is the shortest
duration of radiochemical separations with very good separation factors for the
matrix elimination.   The automatization of these separation systems is parti-
ally possible.

2. 1. 1. 1. Influence of the choice of irradiation conditions - epithermal and fast neutrons:

We mention by two examples the importance of the "quality of neutron flux".
Blondiaux and Vialatte have shown that 22 elements can be determined non-
destructively in titanium by γ-spectrometry after a long (72 hours) and a
short (30 seconds) irradiation in a good thermal neutron flux (5. 10^{12} n. cm^{-2}.
s^{-1}, heavy water reflector of the EL$_3$ Seclay Reactor) (44). Neirinck x, Adams
and Hoste found it necessary to make chemical separations because their
irradiation was made in a light water reactor (45).
The second example concerns the use of fast neutron reactions for analysis
of aluminium and iron, where titanium is determined by (n, p) reaction ·

$$^{47}Ti \ (n, p) \quad ^{47}Sc$$

With a 72 hour irradiation - 1, 4 x 10^{13} fast n. cm^{-2}. s^{-1} in the light water
reactor "Osiris" (Saclay), the activities are 1, 2 x 10^6 imp/min for 1 mg of
titanium and 13 imp/min for 1 mg of vanadium by the reaction $^{50}V(n, \alpha) \ ^{47}Sc$.
The irradiations are made in a cadmium container.   The lowest titanium
contents are 0, 01 ppm in pure aluminium and iron (46).
We mention the great advantage of activation analysis of rocks, with a cad-
mium shield to have an epithermal and fast neutron irradiation.   In these
conditions, the ^{46}Sc activity is lowered and better detection of some elements
is obtained (Tb, Ni particularly) (47).

2. 1. 1. 2. High resolution γ -spectrometry

Let us recall, the most important milestone in neutron activation analysis is
the semiconductor detectors and their utilization has been progressively
increasing between 1968-1975.

It gives the possibility to develop direct γ-spectrometry after irradiation without chemical separation for materials of the highest purities; a good example is nondestructive analysis of high purity aluminium by Revel's group (42-48).
With a 53 cm^3 Ge(Li) detector, 2,35 keV resolution for 1332 keV of ^{60}Co, they are able to determine 25 to 30 elements, after irradiation with thermal neutrons, 3 x 10^{12} n. cm^{-2}. s^{-1} for 7 days, in a suitable position.
These detectors give also the possibility to reduce the chemical separation schemes to only a few group separations; at times, only the extraction of the matrix element (42); for e. g. we will mention the analysis of rocks and semiconductors (49).
These γ-spectra from Ge(Li) detectors are complex and the data treatment must be made by computers. The instrumentation for γ-spectrometry has seen significant developments. A recent International Conference has been wholly devoted to computers and their programs (51).

2.1.2. 14 MeV Neutron Activation Analysis :

We have already discussed in detail in June 1980 at the Berlin Conference, the developments of 14 MeV neutron activation analysis. It was mainly for problems of oxygen determination in metals (52). Here, we will recall only a summary of our conclusions about the role of B. C. R. programme on the development of oxygen activation analysis with 14 MeV neutron generators. The technique was already very good in 1969 for steels and studies on non-ferrous metals was already in progress (53).
For the low oxygen content of some metal samples, the sensitivity was not enough. The increase in sensitivity has been obtained by studying very precisely critical conditions for irradiation and detection.

2.1.2.1. Selection of optimal energy region for ^{16}N counting :

Oxygen analysis is done using the reaction, ^{16}O (n, p)^{16}N; ^{16}N emits γ rays of energies 6.13 MeV (69%), 7.11 MeV (5%); 2,75 MeV (1%), with a $T_{1/2}$ = 7.14 sec.
i. It was experimentally found that background values are drastically reduced by using an upper and a lower energy threshold for counting. For e. g. Vandecasteele (54) used : 4.5 $\angle$ E_γ $\angle$ 6.5 MeV; and Beurton (55) used : 4.9 $\angle$ E_γ $\angle$ 6.3 MeV.
ii. For reduction of pile up effect of the low energy -rays, which give a background in the counting region, the use of special "fast" electronic circuits is needed.
iii. Dimensions of the detector crystals and the intensity of neutron beam must be carefully defined.
It has been shown that the background has a minimal value for a certain value of the product $\varnothing$ (n. cm^{-2}. s^{-1}) x t and it is not good to use larger values of $\varnothing$(n. cm^{-2}. s^{-1}) x t, where 't' is the duration of irradiation.
iv. Evaluation of Interferences : The interferences have been evaluated according to the following relationship.

$$\Delta\,(O) = 4.10^{-1}(F) + 5.10^{-2}(B) + 3.10^{-4}(N) + 3.10^{-5}\,(Si),$$

where Δ (O) is the correction for apparent content in oxygen produced by contents in F, B, N and Si.
In many instances this correction is negligible.
v. Chemical etching for about 12 seconds was found necessary if the oxygen content is less than 20 µg/g.
vi. Particular attention should be paid, for the standardisation of the methods, and monitoring, including the correction factors needed thereof. For example Beurton (55) reported a limit of detection of 6 micrograms of oxygen for a sample volume of 4.5 cm^3 (about 10 to 90 g sample), with the following experimental conditions : 1 milliampere deuteron - 10 seconds irradiation, 12 seconds waiting time (etching) - 14 seconds measure time at 4.9 $<$ E_γ $<$ 6.3 MeV.
For 10 repetitions of the determination the limits of detection are of the

order of:

       0, 5 ppm in aluminium
       0, 2 ppm in ziroconium
       0, 1 ppm in tungsten

This analysis is nondestructive, short and near-impossible on uranium, fluorine boron, silicon and nitrogen and compounds of these elements (55, 56).
Many other elements can be determined by 14 MeV neutron activation. ^{14}N $(n, 2n)^{13}$N gives nitrogen at the level of 10 micrograms, under the Beurton conditions, with 30 minutes for a chemical separation. With 10 g sample, the detection limit is about 1 ppm (with 3σ). ^{19}F$(n, 2n)^{18}$F gives fluorine at the level of about 1 microgram under Beurton conditions with 30 minutes chemical separation. With 10 g sample, the detection limit is 0. 1 ppm (with 3σ).
Looking at the bibliography (32, 33, 57-60) we can see that many elements can be determined by 14 MeV neutron activation. After oxygen, the elements most studied are silicon, aluminium, phosphourous, chlorine, nitrogen, fluorine, iron, sodium, magnesium, sulfur and calcium. Weinerdi et al (61) have discussed the analytical possibilities with high flux neutron generators.

2. 1. 3.   Cyclotron Neutron Activation Analysis :

The most commonly used reactions for neutron production with a cyclotron are ^{9}Be$(d, n)^{10}$B, ^{9}Be $(^{3}$He, n$)^{11}$C, ^{9}Be$(p, n)^{9}$B. Only very few reports have been made on cyclotron neutron activation analysis (62 - 66).
Melki, with the Orleans cyclotron has made a systematic study on the possibilities of activation analysis with cyclotron neutrons for (d, n) and $(^{3}$He, n) on beryllium target upto maximal energies of 25 MeV deuterons and 53 MeV ^{3}He (66). Forty three elements have been irradiated and 131 radioisotopes studied.
Krivan has studied the theoretical calculation of (n, α), (n, p) and (n, 2n) reaction sensitivities for cyclotron neutron activation at deuteron energies of 16, 23, 33 and 53 MeV. Melki's work provides us very important data; they show the great interest of cyclotron neutron activation analysis as one method that can compliment the possibilities of trace analysis with other kinds of particles such as reactor neutrons, 14 ^{M}eV neutrons, charged particles and gamma photons.
Melki has shown that experimental sensitivities can be much better than theoretically calculated values, because two or three nuclear reactions can contribute to produce the same radioisotope for the determination of an element with a better reaction as an option for e. g. ; (n, n') or (n, γ); as an example we mention iron :

       ^{54}Fe$(n, \alpha)^{51}$cr
  + ^{56}Fe$(n, \alpha$ n n$)^{51}$cr   230

       ^{54}Fe$(n, p)^{54}$Mn
  + ^{56}Fe$(n, t)^{54}$Mn   25

       ^{56}Fe$(n, p)^{56}$Mn
  + ^{57}Fe$(n, d)^{56}$Mn   0. 017

       ^{54}Fe$(n, 2n)^{53}$Fe   4. 47

where the quantities given are the experimental detection limits, in micrograms.
The theoretical detection values, in micrograms with the same condition are:

    (n, α) = 50 ; (n, p) = 15 and (n, 2n) = 4

The experimental sensitivities can be 10 to 1000 times better than pure (n, p), (n, α) or (n, 2n) reaction sensitivities.
Until now (γ , n) reaction was considered the best for fluorine determination in any material. Vandecasteele, Kieffer, and Hoste have already, shown

that (n, 2n) reaction, with 20-25 MeV deuterons, gives the same results as (γ, n) for fluorine content in aluminium (67).

Melki gives the comparison of the detection limits for activation by cyclotron neutrons, 14 MeV neutrons and γ-photons :

i. for nitrogen and fluorine, cyclotron activation is more sensitive than that by 14 MeV neutrons and γ-photons;

ii. for carbon, intrinsic sensitivity is comparable for cyclotron activation and for γ-photon, but more amount of sample can be irradiated with cyclotron than with γ-photon.

iii. for oxygen, intrinsic sensitivity is comparable for cyclotron activation and for γ-photon, with possibility of heavier samples with cyclotron. Even though intrinsic sensitivity is lower with 14 MeV neutrons, the main interest of this last activation is its being nondestructive, quickest, cheaper and easier to use, because 14 MeV generators can be installed in every laboratory in comparison to cyclotron.

iv. for elements $Z > 10$

-39 elements have been studied for detection limits, 21 of them can be detected without any nuclear interference with detection limits from 10^{-1} ppm to 10^{-4} ppm on 30 g samples (1 hour irradiation, 50 micro amperes, 25 MeV deuterons).

- also, cyclotron neutron activation is complementary to reactor activation.
- heavier sample can be irradiated,
- lower flux attenuation in some samples,
- different reactions can be used with advantage; for example : higher sensitivities for iron, nickel, zirconium, thallium and lead - γ-emitting radioisotopes for strontium, yttrium, niobium-longer half-life for rhodium.

2.1.4.   Activation Analysis with Isotopic Neutron Sources :

The first experiments in activation analysis have been made with neutrons produced by (α, n) or (γ, n) reactions on beryllium (1). Since then progress has been to make more precise analysis related to industrial problems of production control.

The most important milestone in this domain has been the use of 252_{Cf}, as a fission neutron source.

From a survey report by Hoste for CCE Bruxelles (Commission European Communities), we can have some general informations on ISOTOPIC NEUTRON SOURCES and their main characteristics. (Table 1.)

Table 1. Isotopic Neutron Sources

Source	Type	Half-life	Average neutron energy	Yield n/s/Curie	Yield n/s/gram	Gamma dose rate r/h at 1m (10^{10}n)	Volume cm^3 for 10^{10} n/s
124Sb-Be	γ,n	60 d	24 keV	1.6×10^6		0.9×10^4	40
239Pu-Be	α,n	24360 y	4.5 MeV	2.0×10^6	1.2×10^5		
241Am-Be	α,n	433 y	4 MeV	2.0×10^6	6.5×10^6	(10)	4400
210Po-Be	α,n	138 d	4.3 MeV	2.5×10^6	1.1×10^{10}		40
238Pu-Be	α,n	89 y	4 MeV	2.8×10^6	4.5×10^7	0.08	70
244Cm-Be	α,n	18.1 y	4 MeV	3×10^6	2.5×10^8	0.04	15
242Cm-Be	α,n	163 d	4 MeV	4×10^6	10^{10}	0.06	2
226Ra-Be	α,n	1620 y	3.6 MeV	1.5×10^7	1.5×10^7	600	
227Ac-Be	α,n	21.8 y	4 MeV	2.4×10^7	1.7×10^9	80	
228Th-Be	α,n	1.9 y	4 MeV	2.8×10^7	2.3×10^{10}	300	
252Cf	spont. fiss.	2.646y	2.35 MeV	4.4×10^8	2.34×10^{12}	1.6	1

Dugain (Aluminium-Pechiney-Voreppe Laboratory), based on his use of activation analysis for fluorine, aluminium and silicon respectively in salts, bauxites and Al-Si hypereutic alloys (56), concludes, that an isotopic source provides accurate and rapid control determinations at lower cost.

2. 2.   Gamma Photon Activation Analysis :

Engelmann has made, in 1973, a review of photon activation from the beginning with 93 references (68).
The first experiments by Basile, Hure, Leveque and Schuhl in 1954 (26) have shown that it was possible to use photons to determine O, C and N by (γ, n) reactions. At that time, the bremsstrahlung of 30 MeV electrons from a betatron was used and the best sensitivity obtained was about 0.1%.
But the first determinations for oxygen, carbon at the ppm level sensitivities in beryllium have been the work from Beard, Johnson, Bradshaw (21, 69) in 1957-1959. In 1960 we had a collaboration with Engelmann to investigate whether it was actually possible to determine very low concentrations of O, C and N by means of (γ, n) reactions, in high purity metals (70).
Our own goal at the C. N. R. S. (Centre d' Etudes de Chimie Metallurgique-Vitry) was to compare the results obtained on the one hand by photon activation and on the other hand by classical methods, such as, oxidizing or reducing fusion followed by volumetric, chromatographic or colorimetric measurements. This was our goal because our opinion was that the results given by the so-called "classical methods" were totally wrong, when they were of the order of several ppm for high purity Al, Fe, Ni or Cr prepared in our laboratory. Tracer studies and several preliminary activation experiments performed by us from 1950 to 1954 had given us this certitude (22, 23).

The first experiments performed with Engelmann (70) have shown that, using a linear accelerator, it was possible to reach sensitivities, of the order of 0.1 to 0.5 ppm for C, N and 0 in high purity metals.
Our group at the C. N. R. S. has been interested mostly in the determination of carbon and oxygen; carbon only being determined by photon activation and oxygen being determined by charged particle activation.
We will show in our text that large differences have been observed for the carbon content of high purity iron, when measured by photon activation and by classical methods. As an example, we can mention that activation gives 0.1-0.2 ppm when classical methods give 2.5 and even 10 ppm (71). The same remark applies to other high purity metals and to the determination of oxygen, as several researchers in our group and in other groups have shown.
Because the (γ, n) reactions give generally β^+ radioactivities, the radiochemical separations are needed to have a good and absolutely sure identification of the radioisotope used for the determination of an element.
Hence the evolution of analytical techniques has been mainly concerned with the quality of identification of radioisotopes, the reproducibility of determinations and measurements of possible nuclear interferences.

2. 2. 1.   Studies of radiochemical separation :

At the beginning, carbon, oxygen and nitrogen have been isolated by the simplest methods used in classical analysis: oxygen, by carbon reduction in high temperature furnace; carbon, by combustion in oxygen and nitrogen, by Kjeldahl method (70, 71).

2. 2. 1. 1. ^{11}C separation :

For the different materials analysed, the researchers have used many specific conditions: addition of flux products to help fusion and extraction of CO or CO_2 from the molten bath, treatment to purify gases CO, CO_2, N_2; different getters to trap gases in a container for γ-counting in the most reproducible conditions. (72 - 76).

Recently, Fedoroff et al (77) have begun a new study on the best extraction conditions for carbon in many materials. They have studied six new molten salt baths for carbon determination. We can see from Table 2, the actual results on the efficiency of these baths for different materials; sign '+' indicates that the dissolution seems to be adequate, but further studies are needed for carbon determination; 'yes' indicates a good dissolution.

Table-2. Performance of Molten Salt Baths

[Possibility of dissolution of various materials in molten salts for carbon determination. The sign + indicates that the dissolution seems to be adequate, but further studies are needed for carbon determination]

Sample	Pb_3O_4 B_2O_3	H_2SO_4 KIO_4	H_2SO_4 KIO_4 H_3PO_4	H_2SO_4 KIO_4 NaF	NaOH $NaNO_3$	NaOH $NaNO_3$ NaF
Ag	+	Yes			No	No
Al	No	No	+	No	No	Yes
Graphite	No	Yes	Yes	Yes	Yes	Yes
Cr	No	No			Yes	
Cu	No	No	+	No	No	No
Fe	Yes	No	+	No	No	No
Mg	No	No	Yes	No	No	No
Mo	Yes	No	+	No	Yes	
Ni	Yes	No			No	No
Si	Yes				+	
Ta	No	No		No	+	
Ti	No	No		No	Yes	
W		No		No	Yes	
Zn	No				No	Yes
Zr	No	No	No	Yes	No	No
AlMg	No	No			No	Yes
AgZn	+	Yes				
ZnMgTe					No	Yes

With all these studies we have now, and we will have later, an increasing number of very definite methods to make radiochemical separation of ^{11}C, which is produced by (γ, n) reaction on carbon and also by many other reactions with charged particles, used for the determination of boron, nitrogen, beryllium and carbon.

2.2.1.2. ^{18}F separation :

This radioisotope is used for fluorine determination by (γ, n) or $(n, 2n)$ reactions and for oxygen with charged particles. Many studies have been made for solvent extraction of fluorine, for separation by selective retention on ion exchange resins and inorganic compounds and to improve H_2SiF_6 steam carrier distillation. We mention the work of Chermette et al (78) on triphenyl antimony, of Faure et al (79) on diphenyl dichlorosilane for oxygen determination in molybdenum and lead alloys. Many studies have been made in our group (C.N.R.S., Lab. P. Sue, Saclay) by Vialatte et al. (80), Blondiaux (81), Kohn et al. (82) and developed by Jaffrezic-Renault (83) on the retention of fluorine on ionrganic compounds such as hydrated antimony pentoxide, alumina, hafnium dioxide and tin dioxide. New possibilities have been found for good separations for fluorine from iron, cobalt, manganese, copper and silver. Vialatte (84) and Vandecasteele et al. (85) have established the quantitative H_2SiF_6 steam carrier distillation for the analysis of aluminium and its alloys and germanium. Recently Minoru Yoshida et al (86) have found a new distillation method for fluorine. The sample solution is treated with hexamethyl disiloxane and sulfuric acid, and the volatile trimethylfluorosilane, thus formed, is expelled with a nitrogen carrier gas without external heating and collected in an alkaline absorbing solution. Fluoride can be recovered quantitatively within 30 minutes without the serious dilution that accompanies the classical steam distillation. The interference of aluminium can be eliminated by the addition of phosphoric acid. Concentration

of fluoride in 12 cm^3 is possible.
This new distillation method is a conclusive progress.

2.2.1.3. ^{15}O separation :

This radioisotope is used for the determination of oxygen by (γ, n) reaction, of nitrogen and carbon by charged particles. During the past 10 years many studies have been made to obtain the best conditions of extraction of ^{15}O by reducing fusion (vacuum or inert gas carrier (72, 75, 87-89) in copper (90, 91), aluminium (67), lead (92, 93), zirconium (94, 95), molybdenum (96), and nickel (97).
Engelmann et al. (98), have improved a wet chemistry method for the analysis of sodium sample and Hislop et al have shown that it was possible to obtain a better sensitivity by increasing the energy of the γ-photons to 36-39 MeV without nuclear interference from sodium.
Analysis of selenium has been made by Engelmann et al. (99) by sulfur reduction at 400°C for 5 minutes.

2.2.1.4. ^{13}N Separation :

This radioisotope is used for the determination of nitrogen by the (γ, n) reaction, and of carbon, oxygen and boron by charged particles.
During the last ten years, many improvements have been made in the utilization of reducing fusion and Kjeldahl methods (75, 89, 100-102).
On the other hand, Engelmann et al. have developed a simultaneous separation method for ^{11}C and ^{13}N by oxidizing fusion (103) which is good only for metals (77).
This method has been adapted for sodium analysis. (104).

2.2.2. Activation analysis of elements Z $\rangle$ 10 :

Many other elements give highly radioactive isotopes by (γ, n) reactions and multielement analysis is possible. We mention here only work from Debrun (105) and a review article of Engelmann (106) where he gives as examples, the experiences of Chattopadhyay, Segebade, Hislop and Kato. Particularly Chattopadhyay et al. irradiate at different energies for production of (γ, n) reactions for instrumental analysis of about 30 elements.

2.2.3. Nuclear interferences :

Engelmann's measurements give the importance of nuclear interferences, following γ-photon activation (Tables 3 and 4).

Table-3 Interferences from competing reactions

		Thresh. MeV	Interfering reactions	Threshold MeV
C	^{12}C(γ, n)^{11}C	18.7	^{14}N(γ, t)^{11}C	22.7
			^{16}O(γ, αn)^{11}C	26
N	^{14}N(γ, n)^{13}N	10.5	^{16}O(γ, t)^{13}N	25
			^{19}F(γ, α2n)^{13}N	25.4
O	^{16}O(γ, n)^{15}O	15.7	^{19}F(γ, tn)^{15}O	27.4
			^{20}Ne(γ, αn)^{15}O	20.4
F	^{19}F(γ, n)^{18}F	10.5	^{20}Ne(γ, d)^{18}F	21.1
			^{23}Na(γ, αn)^{18}F	21

Table-4   Evaluation of the Interferences

Eγ maximal	1 μg de C ou		1 μg de N ou μg de O	1 μg de F ou μg de Na
	μg de N	μg de O		
26				>11000
27		>12500	>3700	5600
30	56	1000	800	145
32	50	800	300	105
34	41	520	200	85
36	36	370	150	70
38	35	275	110	58
40	32	210	85	52
42	31	160	70	45

By comparing the relevant concentration ratio for C, N, O and F, we can see that, it can be more 'safe' to irradiate below 30 or even 25 MeV ɣ-energy, but at a little lower sensitivity for carbon and nitrogen determinations.

2. 3.   Charged Particle Activation Analysis (CPA)

2. 3. 1.   Developments :

To point out the development in the field of charged particle activation, we can recall the following stages in the standardization of methods :
Internal Standard, used by Ph. Albert et al. in 1953 (22).
The procedure followed by Markowitz in 1962 (107), it is a calculation from data.
Equivalent thickness, proposed by Engelmann (108), in 1964.
Average cross section approach, proposed by Ricci and Hahn (109) in 1967.
Stopping power methods. There have been different formulations :
DECONNINCK in 1972 (110), Chaudhri in 1976. (111), Vandecasteele and Strijckmans in 1980.   They make the complete numerical integration of the exact activity calculation.   Finally there is the "average stopping power method", proposed by Ishii, Valladon and Debrun (113) in 1978.
  We can also recall the successive developments in the determination of elements and the problems studied :
During 1953-1956, Albert et al (22, 23) looked for the determination of carbon in pure iron.   A better knowledge of its overall purity and of the correlation of the impurities with the properties of purest metal has been the motivation since 1972.   A lot of work has therefore been devoted to the systematic analysis using 10-11 MeV proton activation which is similar to the systematic thermal neutron activation and we can see the complementary nature of the two approaches (114).
In 1962, Markowitz and Mahony introduced the ^{3}He ion for activation analysis (107).
In 1961, Nozaki et al (115) gave the first analysis for pure silicon.
In 1968, Barrandon and Albert made the first valuable determination of oxygen on a metal surface by triton activation under vacuum.
In 1976-1977, Valladon and Debrun determined oxygen in semi conductors by $^{16}O(t, n)$ ^{18}F reaction at the level of 6 ppb in GaAs and at 25ppb in germanium.   It is the beginning of a long cooperation with people doing research in the properties of semi conductors.   Metals also could be analysed for very low contents of oxygen and carbon (116).
In 1976-1977, Borderie, Barrandon and Debrun, showed the possibilities of determination of many elements in materials by triton activation at low energy (3. 5 MeV) (117).   The sensitivities for the determination of 25 elements from Z=4 to Z=33 are calculated from experimentally measured yields for 50 radioisotopes obtained.   For 1 hour irradiation with maximum of 1 micro ampere, only 9 elements give detection limits of better than 100 ppb.

In 1977, McGinley et al (118) showed the possibilities of determination of hydrogen and deuterium by activation with heavy ions (Table 5).

<p align="center">Table 5. Interference free detection limits for a few reactions</p>

Reaction	T		$E_{\beta max}$, MeV	E_γ, keV	Thick target yield, cps/μg[a]	Interference-free detection limit, ppm
$^1H(^7Li, n)^7Be$	53	d	–	480	0.051	0.1[b]
$^2H(^7Li, p)^8Li$	0.85	s	13.0	–	$5.79 \cdot 10^3$	0.1[c]
$^1H(^{10}B, n)^{10}C$	19	s	1.9	720	–	
$^1H(^{10}B, \alpha)^7Be$	53	d	–	480	0.0261	0.5[b]
$^1H(^{11}B, n)^{11}C$	20	m	0.96	511 (β^+)	–	
$^2H(^{11}B, p)^{12}B$	0.02	s	13.0	4400	$6.9 \cdot 10^4$	0.1[c]
$^1H(^{16}O, \alpha)^{13}N$	10	m	1.19	511 (β^+)	–	
$^1H(^{19}F, n)^{19}Ne$	18	s	2.23	511 (β^+)	–	
$^2H(^{19}F, p)^{20}F$	11	s	5.4	1630	$1.24 \cdot 10^2$	1.2[c]
$^2H(^{22}Ne, p)^{23}Ne$	38	s	4.4	440	–	

[a] Irradiated at 1 μA for 1 hr or 1 half-life, whichever is shorter.

[b] Irradiated at 3 μA for 3 hrs, counted for 12 hrs following a 1 week delay. $E(^7Li) = 74$ MeV, $E(^{10}B) = 64$ MeV.

[c] 20 repetitive irradiations at 1 μA, count time equal to the half-life. $E(^{11}B) = 60$ MeV, $E(^{19}F) = 109$ MeV.

2.3.2. Comparison with other activation methods :

Charged particle activation analysis is very different from neutron and γ -photon activations.

i. Activation is not uniform in the sample since $\sigma = f(E_p) = f(X_p)$ where E is the energy of particle which varies rapidly with x, the distance to the surface; as an example, 3.5 MeV tritons, lose all the energy after traversing 25 microns in the sample.

ii. Particle beam can be easily focussed on a definite area of irradiated sample.

iii. Total energy of the particles being dissipated in a small volume producing heating of the sample; hence cooling is needed.

iv. A minimum energy is needed to produce a nuclear reaction between a charged particle and an atomic nucleus, hence light elements can be determined by activation with no nuclear reaction on matrix element of high Z. Many analysis can be nondestructive for this reason.

v. Etching after irradiation is very critical because of the rapid variation of activity. The accuracy and precision of the analysis depends on the surface roughness after etching and on an accurate measure of the etching depth. A lot of work has been made in our groups and a very good method has been developed. (119).

vi. Many reactions can be used for the determination of an element. As example we mention the work by Krivan (120) for molybdenum. Molybdenum can be determined with high sensitivity via five proton-induced principal reactions. One of the important features of this multi-reaction activation technique is the possibility of checking the accuracy of the analysis with regard to nuclear and instrumental interferences as well as with regard to the depth distribution pf the indicator radionuclide activity which differs with depth for the individual principal reactions. The results of analysis of VP -purity cobalt for molybdenum obtained by various proton-induced reactions are given in Table 6.

Table 6. Molybdenum in High Purity Cobalt

Reaction	Concentration (ppm)	Detection Limit (ppm)
$^{92}Mo(p,n)^{92}Tc$	87.6 ± 7.1	9.2
Mo + p ^{94g}Tc	87,0 ± 4.2	1.1
Mo + p ^{95m}Tc	85.1 ± 6.9	5.2
Mo + p ^{95g}Tc	93.4 ± 3.8	0.09
Mo + p ^{96g}Tc	89.1 ± 3.9	0.1
$^{100}Mo(p,2n)^{99m}Tc$	91.1 ± 5.2	1.2

As another example we mention the work of Vandecasteele for BCR on the determination of boron in aluminium-magnesium alloys. The results are obtained by two reactions :

Reaction	Concentration ppm
$^{10}_{5}B(p,\alpha)\ ^{7}_{4}Be$	65,6 ± 2,3
$^{10}_{5}B(\alpha,n)\ ^{13}_{7}N$	67,4 ± 4,5

2.2.3.   Non-destructive multielemental trace analysis :

Another interesting aspect of charged particle activation is that it can be "non-destructive" and at the same time be able to determine many elements simultaneously; it is then similar to SSMS, except that it does not require reference samples.   This possibility of non-destructive multielemental analysis exists mainly in the case of proton activation, although it can also be exploited with less success in the case of other particles - for instance ^{3}He (121). Proton activation at 10-12 MeV can be used to determine selectively 50 elements at trace level, and this can be done non-destructively in ∿ 25 matrices (114) and in a number of minerals (122).   This is possible because by limiting the energy to 10-12 MeV, most (p, np) or (p, d) reactions are avoided, and this eliminates unwanted matrix activities or interferring reactions. In this type of analysis, one uses the (p, n) reactions, sometimes the (p, 2n) reactions; the cross-sections are rather uniform compared to the (n, γ) reactions and this is quite often an advantage because no impurity is going to mask all others, as happens in neutron activation.   An interesting point is that nondestructive multielemental proton activation is quite complementary to nondestructive thermal neutron activation.   Generally speaking, one can say that elements which are highly and/or durably activated by thermal neutrons, are not activated by protons or yield short-lived radioisotopes. The contrary could be identified in the subsequent tables (Table 7, 8 & 9).

Table 7.   Thermal neutron and proton activation: examples of "sensitive" and "Insensitive" elements, using γ -ray spectrometry

	"Sensitive"	"Insensitive"
Thermal neutrons	Na, Co, Mn, Ga, Ge, Br, Sc, Rh, I, In, R. earths, Hf, W, Re, Ta, Hg, Ag, Au, Ir, ...	Ca, Ni, Y, Zr, Sn, S, Si, P, Pb, ...
10 MeV protons	Cu, Ga, Br, Se, Pd, Ru, Ti, Ca, Fe, Ni, Y, Zr, Sn, S	Si, P, Pb, Na, Mn, Co, Rh, In, Hf, W, Re, Ta, Ir, Au, Hg, R. earths.

Table 8. Non-destructive analysis by direct γ-ray spectrometry

	Analysis is feasible	Analysis is $\sim$ impossible
Thermal neutrons	Be, C, Mg, Al, Si, S, Ti, V, Nb, Pb, Ni, Cu, Li, ...	Sc, Co, Ta, Ir, Tb, Ag, ...
10 MeV protons	Be, C, Mg, Si, Al, Mn, Co, Ta, Ir, Tb, Sc, Ag, ...	B, Li, Ti, V, Cu...

This means that non destructive analysis is feasible in some matrixes using thermal neutron activation and is feasible in other different matrixes using proton activation. Also, when a given matrix can be analyzed by both methods, the detected elements are usually different.

Table 9.   Elements detected non-destructively

Matrix	Thermal neutron activation	10 MeV proton activation
Au	Ag	Ag, Cr, Fe, Ni, Cu, Zn, Ru
Rh	Br, Ir, Pt, Na, Cl, Co, Au	Br, Ir, Pt, Ca, Ti Cr, Fe, Cu, Zn, Ru, Cd, Sn, Sb, Os
Sanidine Na_xK_{1-x} $AlSi_3O_8$	Fe, Cs, Sc, Cr, Co, Rb, Ba, Eu, Ta, Na	Fe, Cs, Li, Ca, Ti, V, Ga, As, Br, Sr, Zr, Y.

2.2.4.   Accuracy of charged particle activation :

During the early years of charged particle activation, one was usually satisfied to obtain by this method the correct order of magnitude for the concentration of the impurities sought; actually, to obtain the correct order of magnitude is still a success, even now, in some instances.

Later very reproducible results were obtained using CPA, but there were still the problems of accuracy: indeed, there was no method for the calculation of the accurate concentrations.

Very accurate results can, in practice, be obtained now, either by the average stopping power method or by the "two reactions method"; this is possible, by simply using a series of standards whose stopping power is close to the stopping power of the target to be analyzed (113).   This is shown by many results at BCR. Those on the titanium alloy (TA6V), for oxygen, are particularly demonstrative. (Table 10).

Table 10.   Oxygen in titanium alloy

Method	mean value (ppm)	s[a]	Sample weight (g)
14 MeV neutron activation (6 labs)	1741	46	$\sim$ 20
Reducing fusion (10 labs)	1751	68	0.2
CPA (1 lab)	1775	31	0.0007

a) Estimate of the standard deviation.

3. FUTURE POSSIBILITIES FOR ACTIVATION ANALYSIS

The modern analytical chemistry and particularly the physical spectrometric methods have made prominent progress during the last 20 years and one could believe that there will be no more interest for the utilization of the nuclear methods.

But there is enough information to make intercomparison between some determinations made by the different analytical methods and the nuclear methods of analysis to point out the true limits of these analytical methods.
Examples :

1. Figures 1 and 2 show the dispersion of the first results in the round robin organized by the B. C. R. on oxygen determination in aluminium and copper (91, 67).
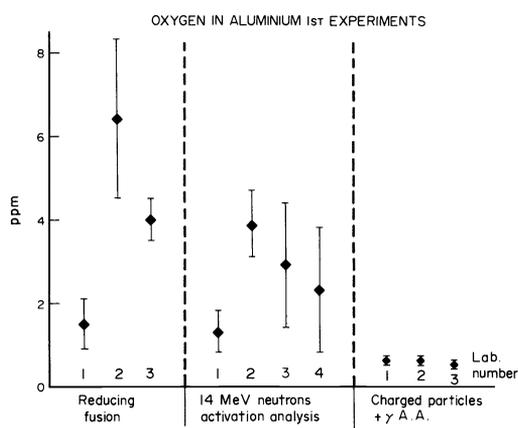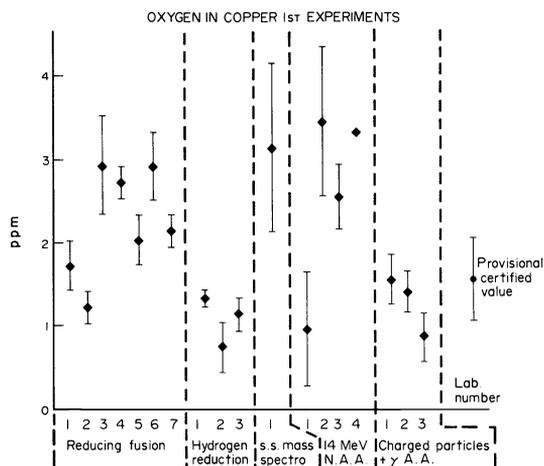

Fig. 1. Oxygen in aluminium

Fig. 2. Oxygen in copper

Ten years ago the oxygen content in aluminium was estimated to be about 10 ppm, as indicated by several techniques including 14 MeV neutron activation. Since then, photon and charged particle activation have been invited to participate in these studies and these methods have demonstrated that the actual oxygen concentration is much lower. In fact, the higher values were obtained either because of the presence of alumina at the sample surface, or because of the implantation of recoiling radioactive atoms (14 MeV neutrons). This last phenomenon was clearly demonstrated by etching the sample after irradiation. Today, the maximum oxygen concentration in the same aluminium is certified by the BCR to be less than 0. 1 ppm. This limit was derived from 66 accepted individual measurements obtained with three different methods by five laboratories (67).

For oxygen in copper, the first round robin included methods such as macro hydrogen reduction, activation with ^{3}He and with photons, and also included methods considered as less reliable like reducing fusion, micro hydrogen reduction and 14 MeV neutron activation (fig. 3). The results led to a weighted average of 1. 5 ppm and with uncertainty of 0. 5 ppm estimated on the basis of the precision of the methods used and on the difference between the reuslts which may be due to heterogeneity or to systematic errors.

A special effort on charged particle and photon activation, in relation to sample treatments before and after irradiation, led to the following new

certification results : 1. 2 ppm and uncertainty of 0. 3 ppm corresponding to the unweighted mean of 92 accepted individual measurements obtained by five independent methods by seven laboratories (91).

Fig. 3. Oxygen in copper-final certification

2- In another round robin, we had observed the same kind of dispersion for the analysis of Cu and Ge :

-Spark source mass spectrometry and neutron activation are the only techniques that gave results for a large number of elements, detected or undetected.

The results obtained by mass spectrometry present a very high dispersion (20 laboratories participated for Cu and 7 for Ge) and it is not possible to ascertain the probable mean values for the detected elements ; indeed there are 2 and even 3 orders of magnitude differences between results obtained by the different laboratories, especially for Cu. In Germanium, mass spectrometry could give results for only 24 elements.

For quite a few elements there was a great discrepancy between activation and mass spectrometry, the results being much higher using the latter technique:

    for Oxygen   :   2 to 500 times higher
    for Chromium : 100 to 2000 times higher
    for Nickel   : 80 to 180 times higher
    for Zinc   : 200 to 2000 times higher
    for Silver   : 100000 to 200000 times higher

The interesting point is that except for oxygen all activation results were obtained by direct γ-ray spectrometry, without chemistry, and these results may then be really trusted.

3- The results of the B. N. M. project on high purity iron were no better

- Emission spectrometry gave limits of detection for 13 undetected elements and these limits ranged from 1 to 15 ppm. Copper, Chromium, Molybdenum, Manganese, Nickel were detected and determined at concentrations ranging from 0. 2 to 8 ppm.

-Spark source mass spectrometry detected 20 elements and for others gave limit of detection from 50 ppb up to 1 ppm.

- Neutron activation detected 9 elements and for others gave limit of detection from 1 to 100 ppb.

-Charged particle and photon activation detected 4 elements.

It is worth noting that activation is more sensitive for some of the elements than spark source mass spectrometry and vice-versa; Table 11 shows some elements for which neutron activation was much better than SSMS:

Table 11. Limits of detection by SSMS and neutron activation

	Sc	Ga	Sb	Hf	W	Au	Zn	Mo	Zr	Total
Limits by NAA (ppb)	1	20	20	6	30	0.1	30	30	10	147.1
Limits by SSMS (ppb)	25 à 80	150 à 350	60 à 80	200	200	350	500	100	50 à 600	1635 à 2460

We believe in the necessity to develop these comparisons. It is indeed necessary that many laboratories participate in these programs in order to clearly establish the practical fields of application of activation analysis. We think activation analysis has at least three domains of work:

i)   - Standardization of a good method though non independant and/or not completely safe; a good example is our work concerning an ion beam analyzer (123, 124).

ii)   - Participation in Scientific Studies : as an example two important industrial companies in France have their own activation analysis laboratory; and two others work in cooperation with AEC and CNRS activation analysis laboratories.

iii)   - Routine work; which can be performed with 14 MeV neutrons and with isotopic neutron sources (56). In some cases, other activation methods are the best. For instance, routine analysis is best achieved by 10 MeV proton activation (Barrandon, (125)). .

4.   FINAL REMARKS

4. 1   Desiderata of Methodology for Trace Analysis of High Purity Materials :

4. 1. 1.   The most important quality of a method for trace analysis is the accuracy. A good precision may be the result of very reproducible inaccurate measurements. To try to obtain an accurate analysis one can compare the reuslts of several independant methods, used by specialists working independantly.

4. 1. 2.   We must be aware of the fact that by coincidence it is quite possible to encounter occassions where the value obtained by a single method may be the "true value", even if other independant methods all obtain an identical result, different from the value found by the single method.

4. 1. 3.   If a method is subject to contamination, it must be permanently checked by a reference method.

4. 1. 4.   Purity can only be defined when the analysis is complete.

4. 1. 5.   A complete analysis necessitates the use of multielemental methods.

4. 1. 6.   The methods for trace multielemental analysis that must be used complementarily are in our opinion and at the present time, spark and ion source mass spectrometry, ICP spectrometry (which needs dissolution of sample with the possible contamination), emission spectrometry, and the different methods of activation (thermal, epithermal, fast neutrons, charged particles, photons).

1. 2.   Domains of Analytical Methods :

1. 2. 1.   Example 1: A good example of the domains of different analytical methods is
given by our common work with Thomson-CSF on the determination of oxygen
in GaAs (123, 124).
The presence of oxygen in gallium arsenide is a serious obstacle when we
wish to obtain a high quality material. The effects of this element on the
electrical properties are under careful study (123). Moreover, in the majority
of applications in the field of electronics, GaAs is used in the form of thin
epitaxial layers varying in thickness from 0.1 to a few microns. It is
therefore important to have at our disposal means of measuring the oxygen
content in these epitaxial layers.

The most suitable method of measuring very low concentrations of impurities
in epitaxial layer is secondary ion mass spectrometry (SIMS). This method
can give the concentration of elements, with a high degree of sensitivity, in
some cases as great as 0,005 ppm (atomic). The minimum analyzable thick-
ness is $\sim$ 0.05 micron.
In order to carry out a quantitative analysis in GaAs, it was necessary to
constitute standard samples and to check the effect of residual oxygen in the
apparatus. In this work, the SIMS instrument is the CAMECA 300. The
residual pressure in the chamber is $\sim 10^{-7}$ torr.
This was studied by introducing a specifically determined pressure of oxygen
into the instrument during analysis in order to observe its effect on the
signal from secondary oxygen ions from the matrix.
As a basis for comparison, we show first the variation of the oxygen signal
with the oxygen pressure in the case of a silicon matrix. (Fig. 4). This
signal increases drastically with pressure as a result of the high degree of
reactivity of the silicon with oxygen; thus the quantitative analysis of this
element in silicon is not possible under these vacuum conditions. Fig. 5 shows
variation in oxygen signal in the case of GaAs. The intensity of the secondary
ion current due to oxygen from GaAs remains constant with pressure, up
to 5.10^{-5} torr, then increases with pressure. The reference ion current
$^{75}As^{-}$ remains constant up to 5.10^{-5} torr and then starts decreasing.
This result shows that the residual oxygen pressure in the instrument
($\sim 10^{-7}$ torr), does not affect the analysis.
The xygen concentration of the standard sample is determined by activation
with tritons through the reaction $^{16}O(t, n)^{18}F$; the limit of detection of oxygen
by this method is about 10 ppba (10^{-8} in atoms) by pure instrumental analysis
as shown in figure 6 where we can see the comparison of the radioactivities
produced by the irradiation of the matrix atoms and of oxygen (123); a very
good correlation has been obtained between the values of the ratio 0^{-} As^{-}
for the SIMS and the values of the oxygen content determined by activation,
for seven determinations ranging between $0.9.10^{15}$ and 6.10^{15} atoms cm^{-3}.
With SIMS, measurements carefully made, give the profile of oxygen concent-
ration in an epitaxial layer as shown in figure 7. The minimum thickness
needed for analysis is 0.05 micron, the resolution is about 100 A° (depth) and
the sensitivity 0.01-0.02 ppma. The figure shows the difference between the
profiles for silicon and chromium doped GaAs substrates.

4. 2. 2.   Example 2 :

Another study has concerned the possible correlation between oxygen and the
electronic deep-energy-level, E_c - 0.75 eV. Oxygen belongs to the sixth
group of the periodic table and as such, it is basically expected to behave
as a donor impurity in III-V compound semiconductors, provided that it
substitutionally occupies a group 5 atom site. This has been shown for GaP
with O_p. (Oxygen in place of phosphorus).
In GaAs, from theoretical calculations for O_{As}, the idea that the E_c - 0.75 eV
donor level is due to oxygen, has gained acceptance and a recognized place
in overviews, and even in textbooks. But some experimental results were
reported which either did not directly support it, or were indeed difficult to
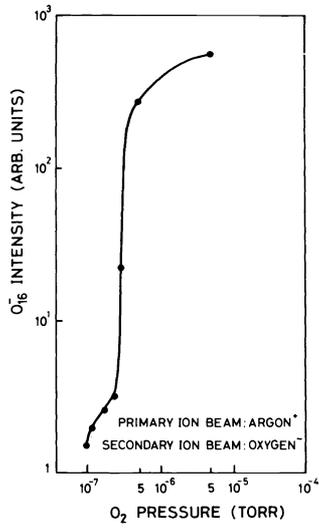reconcile with it. Thanks to activation analysis, a cooperative work with
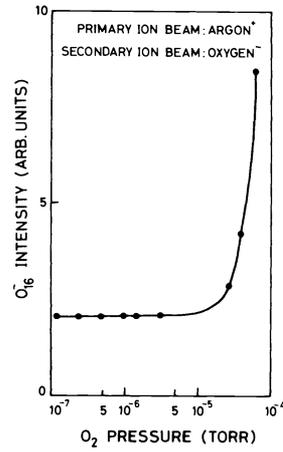
Fig. 4. O⁻ ion intensity in silicon vs O_2 pressure

Fig. 5. O⁻ ion intensity in GaAs vs O_2 pressure

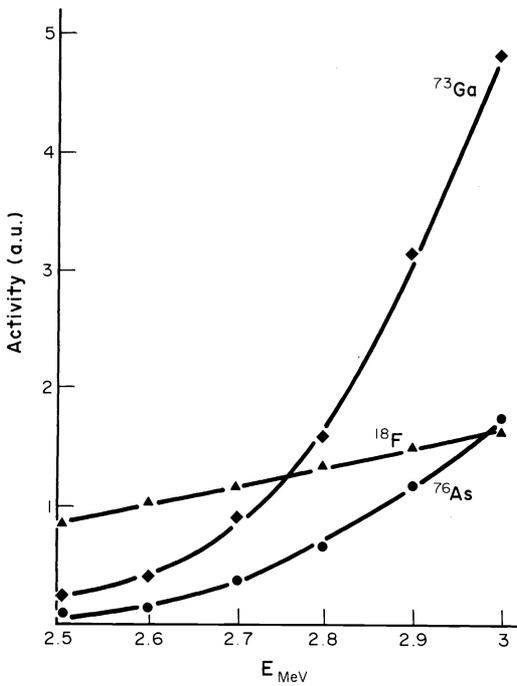Fig. 7. SIMS profiles. Oxygen in GaAs epitaxial layers. Vapor phase epitaxy (V.P.E.)

Fig. 6. The comparison of specific activities of radioisotopes produced on GaAs matrix and on 0.1 ppm (10^{-7}) in weight of oxygen shows the possibility to measure ^{18}F radioactivity directly by non-destructive γ spectrometry
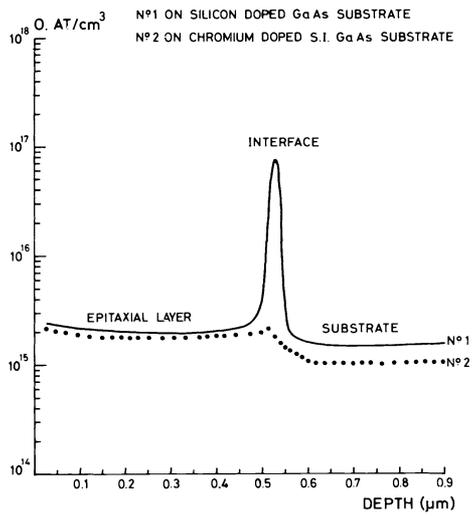
LEP and Thomson-CSF laboratories has shown, by the direct comparison
between quantitative atomic oxygen concentration and electronic deep-energy-
level concentration in GaAs, that oxygen is not involved, either directly or
as part of a complex defect, in the origin of the main electron trap at E_c -
0.75 eV (123).

4.2.3.   Example 3 :

Electrical measurements are often used for the evaluation of the purity of
metals and semi-conductors. For a full understanding of the electrical pro-
perties of the impurities, we believe that elemental analysis (as complete as
possible), is a necessity. Indeed, the influence of these impurities on the
properties (resistance, recrystallization) of the materials is quite variable
and often unpredictable . As an example, figure 8 shows that oxygen has a
much lower influence on the recrystallization temperature of zirconium when
this metal is very pure; without a complete knowledge of the purity of the
zirconium sample, it would not have been possible to determine the influence
of oxygen on recrystallization (126). Numerous other examples can be given
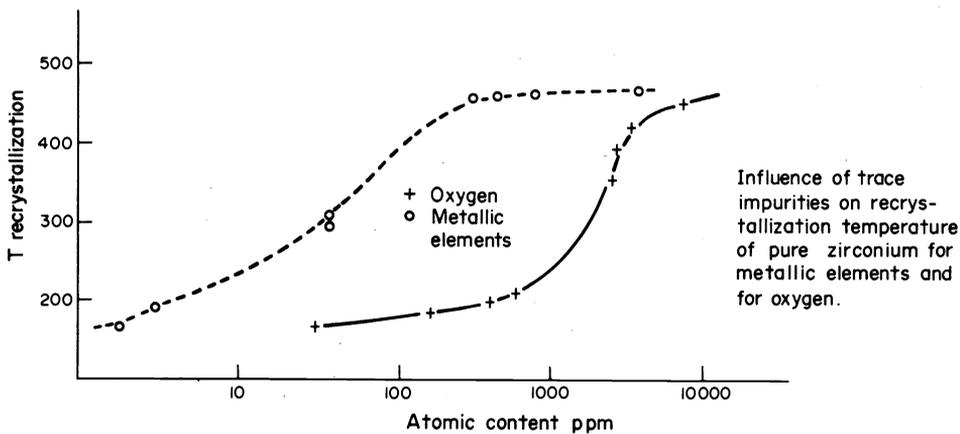(127).

Fig. 8. Influence of trace impurities on recrystallisation temperature

In conclusion, we have at our disposal a number of powerful methods and
it is now very important to develop programs of intercomparison of these
methods. This is the only manner in which we will be able to increase our
knowledge on the actual possibilities of these methods. Then, it will be
possible to place these techniques into the hands of a greater number of
laboratories, for the best benefit of Science.

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