ACTIVATION ANALYSIS WITH PARTICLES FROM A CYCLOTRON : DETERMINATION OF TRACE OXYGEN IN METALS

BY ³₂He ACTIVATION, MULTIELEMENTAL TRACE ANALYSIS BY PROTON ACTIVATION

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Abstract

It is shown that when using charged particle activation, not only sensitivity but also accuracy and precision imply the use of relatively high energy beams. Examples of application of $\frac{3}{2}$ He activation to the analysis of oxygen in metals, and of proton activation to multielemental non-destructive analysis, are given.

1. Need for relatively high energy beams

Sensitivity : It is well-known that the higher the energy, the higher the sensitivity. Indeed, the sensitivity is proportional to the total radioactivity obtained through a given nuclear reaction and this radioactivity itself is proportional to the integrated cross-section curve.

 $\frac{\text{Precision and accuracy}}{\text{is set-up to deliver a given energy E, there} \\ \text{can be an uncertainty of } \pm \Delta E \text{ because there is an} \\ \text{uncertainty of } \pm 1 \text{ on the number of revolutions} \\ \text{accomplished by the particles. This is a source of} \\ \text{inaccuracy when samples and standards are not} \\ \text{irradiated in the same beam, as is often the case.} \\ \text{This also affects the precision of a serie of experiments performed over a number of weeks or months}^{\texttt{u}}$

Figure 1 shows the error introduced by the ΔE corresponding to \pm 1 revolution, using protons and harmonic 2 at the Orléans cyclotron, in the case of the determination of nickel by means of three different nuclear reactions. It can be seen that the higher the energy, the smaller the error ; indeed, at high energy the variation in the integrated activation curve becomes relatively small. Also, it is worth noting that the error is quite different for different nuclear reactions : this is due to different thresholds and different shapes for the activation curves. For this reason, it is necessary to possess a good knowledge of the activation curves and to carefully select the nuclear reactions the available particle energies.

In order to eliminate surface contaminants, etching of the samples is always performed after irradiation (sometimes also before irradiation). Any error in the measurement of the etching is reflected in the final result of the analysis.



Fig. 1 - Error on the determination of nickel, introduced by a ΔE corresponding to ± 1 revolution.

Figure 2 shows the error introduced in the measurement of the oxygen concentration of Al and Cu samples, by an error of 1 micron on the etching [reaction used ${}^{16}O({}^4_2\text{He,pn}){}^{18}\text{F}$].

Again of course, the higher the energy, the smaller the error. In conclusion, it can be said that high sensitivity, accuracy and precision imply the use of relatively high energy beams, from a cyclotron or from a Tandem Van de Graaff. Higher precision and accuracy can be reached with a Tandem Van de Graaff because of the well defined and well reproducible energy; on another hand, the intensities delivered by these machines are limited.

Proc. 7th Int. Conf. on Cyclotrons and their Applications (Birkhäuser, Basel, 1975), p. 507-510



Fig. 2 - Determination of oxygen by ¹⁶O(⁴₂He,pn)¹⁸F. Error introduced by an error of 1 micron in the measurement of the etching - Al and Cu matrixes.

2. <u>Application of charged particle activation</u> analysis to the determination of oxygen in metals

- Surface oxygen : Several experiments 2 , 3) have shown that the oxygen adsorbed on the surface of the samples (or the oxides formed on the surface), cannot be completely removed by etching the samples. This creates a very difficult problem when determining low oxygen concentrations by non-radioactive methods, because of the blanks introduced.

In the case of activation methods, this problem is usually solved by etching the samples after irradiation.

On figures 3 and 4 are presented the results for the analysis of oxygen in Al and Ta samples, obtained in the frame of a program sponsored by the Bureau Eurisotop of The Commission of the European Communities.

Several methods were used, reducing fusion, 14 Mev neutron activation analysis, photon and charged particle activation.

It can be seen that at the 0.5 - 2 ppm level, the agreement between charged particle activation (several laboratories) and photon activation is good, while there is great dispersion in the case of other methods. Also, the values obtained by other methods are generally higher, due to the blank problems. Below the ppm level, charged particle activation is the only method that can be used ; the other methods lack in sensitivity.







Fig. 4 - Analysis of oxygen in tantalum. Comparison of results obtained by different methods.

Table I gives some results obtained in our laboratory for the analysis of oxygen in Cu, CuZn, Ta and W, using the well-known nuclear reaction : $^{16}O(_2^{3}\mathrm{He,p})^{18}\mathrm{F}.$

 $\frac{\text{TABLE I}}{\text{RESULTS OF OXYGEN ANALYSIS BY }^{16}\text{O}(_{2}^{3}\text{He},p)^{18}\text{F}}$

metal	mean value (ppm) 12 determinations	от at 95 % confidence level (ppm)
Cu ASARCO	0.31	0.04
Cu OFHC	1.32	0.16
Cu Zn	2.56	0.26
Ta*	2.20	0.26
W*	2.25	0.27

* non destructive analysis

3. <u>Multielemental and non-destructive</u> proton activation analysis

In the past, charged particle activation analysis was mostly used for the determination of light elements like 0, C, N, B, F, that could not be determined by neutron activation.

Recently however, it was shown that charged particle activation and especially proton activation could be used to determine about 50 elements, at trace level $\frac{4}{5}$ $\frac{5}{6}$ $\frac{7}{7}$ $\frac{8}{8}$.

Moreover, it was shown that non-destructive activation could be achieved in a number of matrixes provided that the proton energy was kept around 10-12 Mev in order to avoid matrix activation by (p,pn) + (p,d) reactions and activation with secondary neutrons.

Table II shows the sensitivities for \sim 50 elements under the following standard conditions :

- Irradiation : 1 hour, 10 Mev protons, 1 microampere.

- <u>Counting</u>: The sample is supposed to be counted at the end of the irradiation during 1.8 x T or 60 hours maximum on a Ge(Li) with 20 % efficiency relative to a 3 x 3 inches INa. The sample is supposed to be an aluminum sample.

- <u>Calculation</u> : The detection limits were calculated from the activities obtained for the different elements, assuming that the minimum detectable activity was equal to 3 times the square root of the background within the energy window considered.

TABLE II

SENSITIVITIES FOR 10 MEV PROTON ACTIVATION UNDER STANDARD CONDITIONS*

10 ⁻³	-	10 ⁻² ppm	10 ⁻²	- 10	-1 ppm	10 ⁻¹	-	lppm	1-30	ppm
Ca	Ti	Cr	Li	۷	Fe	В	S	Re	In	Ba
Ni	Cu	Zn	As	Sr	Nb	Ir	Au	T1	W	Eu
Ga	Ge	Se	Ag	Sb	Ι	Рb	La	Pr	Rh	Tb
Br	Rb	Y	Pt	Hg	Nd	Sm	Gd	Dy		
Zr	Мо	Ru	Er			Yb				
Pd	Cd	Sn								
Te										

Table III shows the matrixes in wich nondestructive analysis with 10 Mev protons is feasible.

TABLE III

MATRIXES IN WICH NON DESTRUCTIVE ANALYSIS IS POSSIBLE, USING 10 MEV PROTONS

\sim Immediately	Waiting period : 1-15 days		
Be, C*, Na, Mg, Al*,	Ca, Sc, Ni, Ag*, Nb*,		
Si*, Mn, Co*, Tb*, Ho*,	Ba, Ce, Pr*, Dy*, Ir*,		
Ta*, Bi, Rh*	Au*, Tl		

*Analysis already achieved in our laboratory.

Table IV shows the results for the nondestructive analysis of samples of Si, Au, Rh and Tb. Other matrixes like Al, Ag, Co, Nb, Ho, Pr, Dy, Ta, Ir, and various geological samples were also analyzed non-destructively, but results cannot be given here because of lack of space.

Conclusion

In this short communication we intended to show that charged particle activation needs relatively high energy beams in order to achieve accuracy and precision as well as sensitivity, and some examples of application were given.

The results shown here were obtained with beams of rather poor quality ; considering the characteristics of a new machine like the Orléans Cyclotron, it is felt that soon, much better work will be achieved.

TABLE IV

NON-DESTRUCTIVE ANALYSIS OF Si, Rh, Tb, Au BY ACTIVATION WITH 10 MEV PROTONS

	Si	Rh	ТЬ	Au
Li B	< 0.01 < 0.1	-	< 0.25 < 2.5	< 0.01 < 0.1
S CTI V CFEIU CTI V CFEIU CTA CTI V CFEIU CTA CTI STEI CTI STEI CT	<pre>< 0.03 < 0.003 < 0.003 < 0.02 < 0.003 < 0.025 < 0.02 < 0.002 < 0.005 < 0.003 < 0.003 < 0.003 < 0.003 < 0.003 < 0.003 < 0.003 < 0.0003 < 0.0004 < 0.0002 < 0.002 < 0.002 < 0.005 < 0.0005 < 0.0002 < 0.002 < 0.0005 < 0.0005 <</pre>	9.4 \pm 2.7 0.5 \pm 0.2 < 0.5 50 \pm 4.5 81 \pm 4 < 5 7.8 \pm 0.5 1.3 \pm 0.1 < 0.07 < 0.08 < 0.08 < 0.2 7.1 \pm 0.35 < 0.2 < 0.9 < 0.15 63 \pm 3 - < 1.7 < 5 2.2 \pm 0.3 1.9 \pm 0.1 1.25 \pm 0.6 < 0.2 < 0.5 < 72 < 0.5 < 72 < 0.5 < 74 360 \pm 74 340 \pm 23 < 6 < 2.7 < 3 < 5 < 5 < 2.7 < 3 < 5 < 5 < 2.7 < 3 < 5 < 2.7 < 5 < 2.7 < 3 < 5 < 3 < 5 < 2.7 < 7 < 5 < 2.7 < 5 < 2.7 < 5 < 2.7 < 5 < 2.7 < 5 < 3 < 5 < 3 < 5 < 3 < 5 < 5 < 3 < 5 < 3 < 5 < 3 < 5 < 5 < 5 < 5 < 7 < 5 < 5 < 5 < 5 < 5 < 5 < 5 < 5	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<pre>< 0.35 < 0.006 < 0.1 0.04\pm0.01 1.55\pm0.08 0.22\pm0.03 0.7 \pm0.04 0.4 \pm0.02 < 0.01 < 0.02 < 0.02 < 0.02 < 0.02 - < 0.025 - < 0.02 0.26\pm0.06 < 0.15 2.6 \pm 3 < 0.25 - < 0.15 < 0.25 - < 0.15 < 0.26 \pm 3 < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.25 - < 0.26 \pm 3 < 0.25 - < 0.55 - < 0.55 - - < 0.55 - - - - - - - - - - - - - - - - - -</pre>

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DISCUSSION

M.A. CHAUDHRI: Did you use "thick" or thin targets for these activations?

P. ALBERT: Yes, sample thickness is of the order of the range of 11 MeV protons -- and if possible not much more -- for good cooling conditions during irradiation.

M.A. CHAUDHRI: Are the detection limits which you have shown in various studies calculated or actually measured?

P. ALBERT: Limits of detection are derivated from measurements after irradiation of the element. It is $3\times\sqrt{N_B}$, where N_B is the background in the energy domain of the γ peak used for determination of the element. Intrinsic sensitivity is determined for the shielded counter background (\approx 5 cm lead). For multi-elemental analysis examples, the limit of detection are measured on the background of the γ spectra from the samples studied.

M.A. CHAUDHRI: While comparing the irradiated samples and standards, what sort of theories did you use for matrix differences between the two and how much inaccuracy on your measurements is due to the limitations of this theory?

P. ALBERT: For an answer, I should like to refer you to the thesis by P. Benabeu and C. Rouxel, which will be available shortly.