

DETERMINATION OF OXYGEN IN METALS AND SEMICONDUCTORS BY MEANS OF THE $^{16}\text{O}(\text{T}, \text{n})^{18}\text{F}$ REACTION

M. VALLADON, J. L. DEBRUN

*Centre National de la Recherche Scientifique, Groupe d'Applications des Reactions
Nucleaires à l'Analyse Chimique, Service du Cyclotron,
45045 Orleans-Cedex (France)*

(Received November 15, 1976)

Tritons accelerated up to 3.5 MeV by a Van de Graaff, were used to study the $^{16}\text{O}(\text{T}, \text{n})^{18}\text{F}$ reaction, which was then applied to the analysis of oxygen in metals and semiconductors. The calculated sensitivity for the determination of oxygen is 0.5 ppb at 3.5 MeV. Si, Ti and Mo were analyzed non-destructively at 3.5 MeV and the results agreed with results obtained by other methods. Pure Ge and AsGa were analyzed non-destructively at 3 MeV and the detection limits were respectively 25 and 6 ppb.

Introduction

Activation analysis is often used for the determination of oxygen in metals and semiconductors. This method is especially useful at low concentration, where blank problems and oxygen from the surface of the sample, lead to incorrect results when other methods are used.^{1,2} Many particles may be used: helium-3, helium-4, protons, deuterons, photons and 14 MeV neutrons. Tritons are not currently used in activation analysis because they are rarely accelerated in a Van de Graaff or in a cyclotron. In the past, however, 2 MeV tritons were used for the determination of surface oxygen.^{3,4} Tritons are of great interest because of the characteristics of the $^{16}\text{O}(\text{T}, \text{n})^{18}\text{F}$ reaction:

- Positive Q-value;
- High cross-section at low energy;
- No nuclear interference below 4 MeV.

Thus, it was felt that by irradiating at low energy, a sensitive and often non-destructive determination of oxygen in the bulk of samples could be achieved. In this work, we studied the $^{16}\text{O}(\text{T}, \text{n})^{18}\text{F}$ reaction from 1 MeV up to 3.5 MeV, and we achieved the non-destructive analysis of oxygen in Si, Ti, Ge, AsGa, and Mo. Our results are compared with results from other laboratories, obtained on identical samples in the course of a research project launched by the European Bureau for Reference Materials (BCR, Brussels).

Experimental

Irradiations

The 3.5 MeV Van de Graaff of the CNRS at Strasbourg–Cronenbourg was used for the irradiations. The experimental set-up is shown in Fig. 1. The targets are placed at the end of a Faraday cup and cooled with air from the back. The ana-

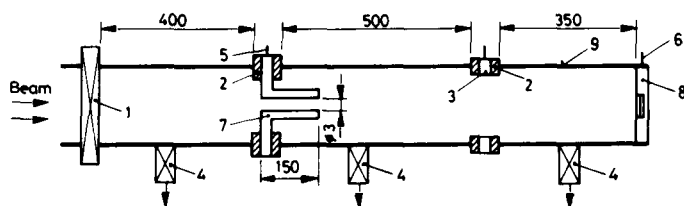


Fig. 1. Experimental set-up

- 1 - Valve;
 - 2 - Insulators;
 - 3 - Negative ring voltage (-200 V);
 - 4 - To the pump unit;
 - 5 - Collimator current measurement;
 - 6 - Target current measurement;
 - 7 - Collimator;
 - 8 - Sample holder;
 - 9 - Faraday cup;
- (Dimensions in mm)

lyzed beam is collimated by a long (150 mm) and thin ($\varnothing = 3$ mm) collimator. The actual irradiated area is of the order of 10 mm^2 .

For the determination of the activation curve and for quantitation, thick Al_2O_3 standards were irradiated during ≈ 30 sec at ≈ 50 nA. The samples, in which oxygen was determined, were irradiated up to 3 hours and up to $0.5 \mu\text{A}$. In all experiments, beam monitoring was achieved by current integration.

γ -ray spectrometry

A Ge(Li) detector with an energy resolution of 2.4 keV FWHM for the 1332.5 keV γ -ray of ^{60}Co , a photopeak efficiency of 19.8% relative to a $3'' \times 3''$ NaI(Tl) detector, and a peak to Compton ratio of 33 was used. We also used a $4'' \times 3''$ NaI(Tl) detector. Ge(Li) detector was preferred for the Ge and AsGa samples, while both detectors were suitable for Si, Ti, and Mo.

Samples

The samples were distributed by the BCR, in the frame of a program for the intercomparison of methods and for the elaboration of standards; they were industrial samples:

Si	(V.M.)	$\varnothing = 20 \text{ mm} - e = 1 \text{ mm}$
Ti	(U)	$\varnothing = 17 \text{ mm} - e = 1 \text{ mm}$
Ge	(H)	$10 \times 10 \times 1 \text{ mm}$
AsGa	(RTC)	$10 \times 10 \times 1 \text{ mm}$
Mo	(P)	$\varnothing = 17 \text{ mm} - e = 1 \text{ mm}$

Preparation of samples before irradiation

All samples were polished before irradiation; in addition, Ge was etched chemically just before irradiation. For Si, Ti, Ge and Mo, polishing was started with SiC and terminated with a diamant paste (granulometry = $0.2 \mu\text{m}$). AsGa was especially prepared at the Thomson CSF laboratories (Corbeville), by etching and polishing at the same time, by means of a felt disk impregnated with Br_2 (15%) + CH_3OH .

Etching after irradiation

It is well-known that surface oxygen is not eliminated even after careful etching.^{1,3} Table 1 gives the conditions for which the amount of oxygen after etching is minimum, and indicates the amount of bulk oxygen equivalent to this residual oxygen.

Clearly in charged particle activation analysis, the ratio (surface/volume) of the samples is so high that the contribution of the residual surface oxygen is important. Etching, after irradiation to eliminate ^{18}F created from surface oxygen, is therefore extremely important. The range of 3.5 MeV or 3 MeV tritons is short: 25 to 60 microns for the studied materials. It is then necessary to control perfectly the etching. In our experimental conditions, the analyzed weight is, after etching, about 1.5 mg. It is to be noted that due to chemical and/or physical transformation of the sample during irradiation, an etching bath may become inefficient or too active for an irradiated sample, while it worked perfectly on an unirradiated sample. To overcome this problem, we suggest to use first a SiC paper or a diamant paste, and then, to use alternative periods of chemical etching and grinding. Table 2 shows for each material, the energy of irradiation, the range of particles, the usual etching depth and the etching technique (after irradiation).

The measurement of the etching is also very important, since it strongly influences the accuracy and the precision of the analysis. The system that we have developed to measure the etching is shown in Fig. 2.

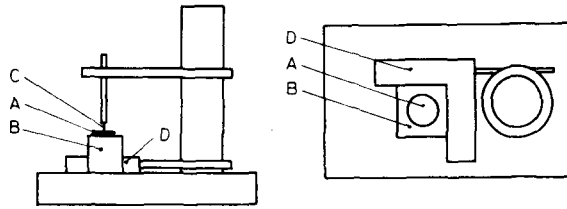


Fig. 2. Measurement of the etching

Table 1
Residual surface oxygen after etching

Sample	Etching*	Residual surface oxygen,* $\mu\text{g}/\text{cm}^2$	Equivalent bulk oxygen concentration for 3.5 MeV tritons, ppm/weight
Si	5 HNO_3 + 3 HF + 3 CH_3COOH 20 °C 75 sec	0.035	2
Ti	4 HNO_3 + 1 HF 20 °C 60 sec	0.5	25
Ge	5 HNO_3 + 3 HF + 3 CH_3COOH 20 °C 45 sec	0.04	1.5
AsGa	5 HF + 95 H_2O 20 °C 3 min	0.08	3
Mo	(1) 4 HF + 1 HNO_3 20 °C, 10 sec (2) HCl 20 °C, 20 sec	0.27	9

* Ref.⁵

After irradiation, the sample (A) is glued with a special glue* on a well machined graphite block (B) covered by a thin film of PTFE to avoid any interaction of the etching bath. The graphite block is then placed under the end (C) of an electronic measuring system,** in such a way that this end (C) touches the irradiated zone of the sample. The electronic system is then adjusted to $e = 0$, the graphite block is taken away and the sample is etched while still glued. After etching, the graphite

**"Colle elephant" – Ultrasons, 74103 Annemasse (France).

**TESA 38 rue du Bugnon – Chiozo-Renens (Switzerland).

Table 2
Etching after irradiation

Sample	Energy of irradiation, MeV	Range of tritons, μm	Usual etching depth, μm	Etching
Si	3.5	63.7	10	1 HF+10 HNO ₃ +3 H ₃ PO ₄ +6 CH ₃ COOH speed $\sim 2 \mu\text{m}/\text{min}$ SiC paper "1000" ($\sim 5 \mu\text{m}$)
Ti	3.5	46.8	5	1 HF+1 H ₃ PO ₄ +20 H ₂ O speed $\sim 2.5 \mu\text{m}/\text{min}$ SiC paper "1000" ($\sim 3 \mu\text{m}$)
Ge	3	39.3	10	3 HF+5 HNO ₃ +3 CH ₃ COOH speed $\sim 14 \mu\text{m}/\text{min}$ SiC paper "1000" ($\sim 5 \mu\text{m}$)
AsGa	3	39.3	5	Br ₂ 1.5% in CH ₃ OH speed $\sim 2 \mu\text{m}/\text{min}$ SiC paper "1000" ($\sim 2 \mu\text{m}$)
Mo	3.5	29.8	5	(1) 1 HF+4 HNO ₃ +2 H ₃ PO ₄ +5 H ₂ O -30 s (2) -20 s $1.5 \mu\text{m}$ SiC paper "1000" ($\sim 3 \mu\text{m}$)

block is replaced exactly in the same position under (C), (C) is lowered again and the etching depth is read directly. The glue we use is not degraded in the etching baths, except if sulfuric solutions are used for long time. The electronic measuring system is accurate to $0.05 \mu\text{m}$, but in practice, the final accuracy is not nearly as good and is evaluated to be 0.3 to $1 \mu\text{m}$ according to the depth of the etching and the nature of the sample. The system represented in Fig. 2 insures a measurement of the etching within the irradiated zone. As mentioned above, this is very important since the etching speed, inside the irradiated zone, is often not the same as outside.

Quantitation

For quantitation, the method of the average cross-section was used.⁶ Oxygen concentrations were calculated according to Eq. (1):

$$x \text{ ppm/weight} = \frac{A_x}{A_s} \cdot \frac{R_s}{R_x} \cdot 10^6 \cdot 0.47$$

where A_x, A_s – the activities of ^{18}F for the sample and for the standard respectively under the same conditions;
 R_x, R_s – the ranges of tritons in the sample and in the standard, respectively;⁷
0.47 – the oxygen concentration in the Al_2O_3 standard.

Limits (for Ge and AsGa) were calculated assuming that the minimum detectable activity was equal to 3 times the square root of the background in the 511 keV region.

Results and discussion

Activation curve, sensitivity

Fig. 3 represents the variation with energy of the ^{18}F activity, obtained by irradiation of a thick target, e.g. the variation of the ^{18}F yield. (normalized to 3.5 MeV).

The experimental points, in Fig. 3, are known to $\pm 2\%$ when 6 measurements are performed at a given energy and under given operating conditions for the Van de Graaff. Fig. 3 gives the shape of the activation/calibration curve, and it is recommended to measure some points at different energies each time an analysis is to be made, in order to standardize with the highest accuracy. The sensitivity at

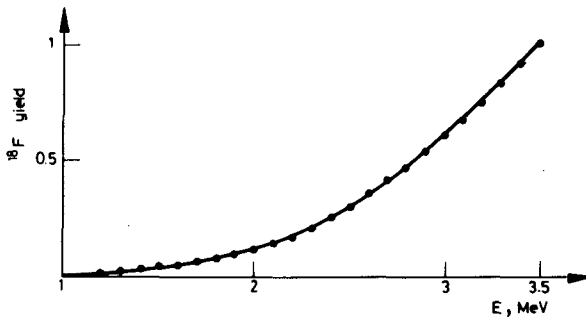


Fig. 3. ^{18}F yield versus energy of irradiation

3.5 MeV was determined to be 0.5 ppb in an iron matrix for an irradiation of 1 hour at $1 \mu\text{A}$, for a counting period equal to $1.8 \times T$ (T = half life of ^{18}F) assuming that the minimum detectable activity is 3 times the square root of the background. With the help of Fig. 3, it is possible to obtain the sensitivity at any energy comprised between 1 MeV and 3.5 MeV.

Interferences

Nuclear interferences do not exist at 3.5 MeV, as shown below:

$^{20}\text{Ne}(\text{T}, \alpha\text{n})^{18}\text{F}$	Threshold = 4.01 MeV
$^{19}\text{F}(\text{T}, \text{Tn})^{18}\text{F}$	Threshold = 12.08 MeV
$^{24}\text{Mg}(\text{T}, 2\alpha\text{n})^{18}\text{F}$	Threshold = 14.36 MeV
$^{23}\text{Na}(\text{T}, \alpha\text{Tn})^{18}\text{F}$	Threshold = 23.54 MeV

Usually, in charged particle activation analysis for oxygen, fluorine is the most serious risk of interference and this risk exists at all energies. Here, there is absolutely no interference below 4 MeV, and the first interference to be encountered is that of neon. As neon is a noble gas (19 ppm in air), its concentration is probably extremely small in metals and semiconductors, and, in practice, the analysis of oxygen should be interference free even at 12 MeV.

Analysis of samples

Si, Ti, Ge, AsGa and Mo could be analyzed non-destructively. Our results are presented in Table 3 and compared with those obtained by other laboratories using different methods. The values in Table 3 are expressed in ppm/weight; the figure after the \pm represents the estimation of the standard deviation, for 12 determinations or for the number of determinations indicated in parenthesis. For Ti and Mo, we have also indicated the certified value x . All the results given in Table 3 were obtained in the frame of a research project supported by the "Bureau Communautaire de Reference" (BCR) in Brussels.*

Silicon

Irradiations of 15 min at 500 nA and 3.5 MeV were performed. The samples become very active because of the $^{28}\text{Si}(\text{T}, \text{n})^{30}\text{P}$ reaction, and are left to decay for 30 mn. After etching 5 to 15 μm (cf. Table 2), γ -ray spectrometry is performed. ^{31}Si , formed by $^{30}\text{Si}(\text{T}, \text{d})^{31}\text{Si} + ^{29}\text{Si}(\text{T}, \text{p})^{31}\text{Si}$, is detected but does not disturb the analysis, at least down to 20 ppb which was the oxygen concentration that we determined in the purest type of silicon analyzed by triton activation. As shown in Table 3, our results are comparable to those obtained by infrared absorption (except one laboratory), or obtained by ^4He and by the mean of ^3He . γ -activation gives some-

*Secretaries of the project: BCMN-B 2440 Geel-Steenweg Naar Retie (Belgium). Metals: Dr. J. PAUWELS. Semiconductors: Dr. WERZ.

Table 3
Comparative results for the analysis of oxygen in Si, Ti, AsCa and Mo (results expressed in ppm/weight)

Sample	14 MeV neutron activation	Inert gas reducing fusion	Vacuum reducing fusion	Activation with			Triton (this work)
				^3He	^4He	γ	
Ti x = 608 ± 23	588 ± 24(48)	604 ± 24	608 ± 14				591 ± 18
	596 ± 21(48)	606 ± 20					
	616 ± 19(48)	609 ± 14					
	621 ± 13(48)	612 ± 9					
Mo x = 14.7 ± 2.1	13.4 ± 1.4(24)	14.6 ± 2	14.7 ± 2.1	16.1 ± 0.7	16.7 ± 2.2	13 ± 0.5	15.9 ± 1.1
	14.5 ± 2.4(24)	14.9 ± 2.2	(10 labs)			15.1 ± 0.8	
	14.6 ± 2.8(36)	15.2 ± 1.5					
		15.3 ± 0.9					
Sample	Infrared absorption	SSMS	SIMS	Activation with			Triton (this work)
				^3He	^4He	γ	
Si	8.3 ± 0.9	19 ± 4	0.7-7	6 ± 1.3	8.5 ± 0.6	5.7 ± 1.2	8.35 ± 0.5(8)
	8.8 ± 0.2	19 ± 2.3		8.4 ± 1.9			
	9 ± 1			10.1 ± 0.14(2)			
	14.5 ± 1						
Ge	<0.13	0.017		0.066 ± 0.025 (proton activation)	<0.02		<0.025
AsCa	<0.1	0.1 ± 0.02 0.03 ± 0.01	0.14 ± 0.02		0.55 ± 0.05	0.04 ± 0.02	<0.006

what lower results (problems in the recovery of ^{15}O by heat extraction), SSMS* gives much higher results (problems in standardization) and SIMS** yields dispersed results (0.7 – 7 ppm).

Titanium

Irradiations of 5 mn at 500 nA and 3.5 MeV were performed. The samples are left to decay for 50 mn because of the activity induced by the following nuclear reactions:



$\approx 5 \mu\text{m}$ are then etched away and γ -ray spectrometry is performed. There is also formation of ^{47}Sc by $\text{Ti}(\text{T}, \alpha) ^{47}\text{Sc}$ and of ^{48}V by $^{46}\text{Ti}(\text{T}, \text{n})^{48}\text{V}$, but these two radioisotopes do not disturb the analysis, at least down to 20 ppm which was the oxygen concentration that we determined in the purest type of titanium analyzed by triton activation.

Our results are in agreement with the results of 14 MeV neutron activation, of inert gas and vacuum reducing fusion (cf. Table 3) and the precision is comparable.

Molybdenum

Irradiations of 15 min at 500 nA and 3.5 MeV are performed. The samples are etched (cf. Table 2) and γ -ray spectrometry is performed. Here again, our results are in agreement with those of 14 MeV neutron activation, inert gas and vacuum reducing fusion, but also with results of ^3He , ^4He and activation. Our mean value, though, is $\approx 8\%$ higher than the certified value which in turn is only known to $\pm 14\%$.

Germanium and gallium arsenide

Ge and AsGa were irradiated 90 to 180 min at 400 nA maximum and 3 MeV. The energy of 3 MeV was chosen because, after etching $\approx 5 \mu\text{m}$ for AsGa and $\approx 10 \mu\text{m}$ for Ge, these matrices are almost not activated and non-destructive analysis of oxygen is then feasible, even at trace level. Alternatively, it is possible to irradiate at 3.5 MeV and to etch away more microns, to reduce the incident energy. Another solution that we will not describe here in detail, but that we have used, is

*SSMS = Spark source mass spectrometry

**SIMS = Secondary ion mass spectrometry

to irradiate at 3.5 MeV, to etch away the same number of microns as at 3 MeV, and to perform a chemical separation of ^{18}F .

The main radioisotopes detected in AsGa and Ge, even at 2.7 MeV, are ^{73}Ga and ^{76}As for AsGa [$^{71}\text{Ga}(\text{T}, \text{p})^{73}\text{Ga}$ and $^{75}\text{As}(\text{T}, \text{d})^{76}\text{As}$], and ^{76}As for Ge coming from $^{74}\text{Ge}(\text{T}, \text{n})^{76}\text{As}$. These radioisotopes create a background and for this reason, the detection limit is 6 ppb for AsGa and 25 ppb for Ge. In the case of Ge, our results are in agreement with SSMS and one laboratory using activation. Infrared absorption has a relatively high detection limit. There is disagreement with proton activation [$^{16}\text{O}(\text{p}, \alpha)^{13}\text{N}$] and with the second laboratory using activation. It is felt that these two last laboratories may have had problems for the etching, either before irradiation or after irradiation. In the case of Ge, etching just before irradiation is of absolute necessity⁸ since it was noted that O and/or ^{18}F may diffuse strongly during irradiation, thus leading to erroneous results. In the case of AsGa, our results are compatible with those obtained by infrared absorption and activation, but these methods present here rather high detection limits (≤ 0.1 ppm). We disagree with SSMS, SIMS and photon activation. SIMS is in disagreement with all other methods, the 2 SSMS laboratories differ by a factor of 3 and photon activation agrees with one SSMS laboratory. At the present time, all these differences cannot be explained.

Conclusions

Low energy triton activation for the determination of oxygen in metals and semiconductors seems to be accurate and as precise as other valid methods, when a comparison can be made. It is to be noted that even at 3/3.5 MeV, RICCI's method⁶ yields accurate results; this is somewhat unexpected in view of the simplifications concerning the expression of the stopping power which are made in this method.

Low detection limits are obtained in high purity materials like Ge and AsGa. For these materials, it is not easy to make comparisons, because of the difficulties encountered by the other methods. It should be pointed out that triton activation is a very safe and simple method: irradiation, etching, counting. There are no lengthy and difficult chemical separations. If chemistry is to be performed, very simple separations may be used because of the activation of the matrixes:

- short half-lives for low Z (\rightarrow Ti);
- low activity levels for medium Z (Fe \rightarrow As);
- inexistant (above Zr).

The energy of 3.5 MeV, however, is a little too low for matrixes, like Mo (or Ni, W, Ta, etc), in which the range of tritons is only 25 to 30 microns. In this case, the precision is strongly limited by the accuracy of the control of the etching.

M. VALLADON, J. L. DEBRUN: DETERMINATION OF OXYGEN IN METALS

In our experiments, we have been limited by the maximum energy and intensity of the Van de Graaff (3.5 MeV and 500 nA); it is hoped to continue these experiments when tritons will be available on the tandem Van de Graaff. Also, to improve the accuracy and the precision, it is planned to etch the samples before irradiation and after irradiation in a clean and high vacuum cooled target assembly, with an ion-gun.

*

The authors are indebted to Mrs. D. MAGNAC-VALETTE and MM. GERARDIN, SELTZ for the use of the 3.5 MeV Van de Graaff at Strasbourg and for their kind reception in their department. The cooperation of the technical staff of the Van de Graaff is also very much appreciated.

References

1. J. N. BARRANDON, J. L. DEBRUN, M. CUYPERS, L. QUAGLIA, G. ROBAYE, C. R. Acad. Sci. Paris, 267 (1968) 1306.
2. J. PAUWELS, *Analisis*, 3 (1975) 434.
3. J. N. BARRANDON, Ph. ALBERT, *Rev. Phys. Appl.*, 3 (1968) 111.
4. J. N. BARRANDON, L. QUAGLIA, J. L. DEBRUN, M. CUYPERS, G. ROBAYE, *J. Radioanal. Chem.*, 4 (1970) 115.
5. L. QUAGLIA, G. WEBER, D. DAVID, J. VAN AUDENHOVE, J. PAUWELS, Bureau Eurisotop, Report ITE No. 90, 1976.
6. E. RICCI, R. L. HAHN, *Anal. Chem.*, 39 (1967) 794.
7. C. S. WILLIAMSON, J. P. BOUGEOT, J. PICARD, Report C. E. A., R 3042, 1966, France.
8. J. HOSTE, C. VANDECASTEELE (Private communication).