Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 158, No. 2 (1992) 463–470

DETERMINATION OF OXYGEN IMPURITY IN HIGH PURITY MATERIALS BY CHARGED PARTICLE ACTIVATION ANALYSIS USING ALPHA PROJECTILES

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(Received September 20, 1991)

40 MeV α-particles have been used to determine oxygen impurity at ppm levels in silicon, copper, and stainless steel, through the radiochemical separation of ^{18}F from the matrix. The separation of ^{18}F has been carried out by two techniques, viz.(1) distillation of H_2SiF_6 and (2) precipitation of KBF_4 and some modification has been applied in the separation, depending on the nature of interferences from the matrix. Instrumental approach was also carried out to determine the oxygen impurity at ≥ 100 ppm in Si matrix because this approach is not possible in Cu and stainless steel samples due to matrix activity.

Introduction

Charged particle activation analysis (CPAA) has become the most suitable and sensitive technique[1–5] for the determination of oxygen at ppm levels and below in high purity metals and semiconductors. The classical methods such as combustion, hydrogen fusion, reducing fusion, when compared with CPAA, suffer from poor sensitivity and reproducibility.[5,6]

The projectiles ^3He, t, d, p and α can be used to determine oxygen in CPAA and the radioisotope ^{18}F is the most suitable monitoring nuclide in the determination of oxygen. Among the projectiles listed above tritium is the most preferred one, because there is no interference up to 4 MeV triton beam; but the availability of triton beam is very limited. ^3He projectile is better than α with respect to the positive Q values but nuclear interferences from fluorine and sodium are severe for both projectiles. Since α-beam is readily available in most of the accelerator centers, we have standardized the method for the determination of oxygen, using α-beam by both instrumental and radiochemical approach.

Elsevier Sequoia S. A., Lausanne
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Experimental

Irradiation

The samples were irradiated with 40 MeV α-particles at the Variable Energy Cyclotron Centre, Calcutta. All the irradiations were carried out under vacuum ($1 \cdot 10^6$ torr), and water cooling was provided during irradiation to avoid decomposition and/or melting of the target. A sample holder was designed in such a way that samples of different sizes (5 to 20 mm diameter) could be fixed. A well collimated stable beam, with variation less than 5% as monitored, was used for irradiation and the intensity of α-particles was measured through a Faraday cup arrangement and also checked with a 10 μm copper monitoring foil (Goodfellow metals), placed just before the target.

Etching

All the samples were etched before chemical separation with appropriate solutions. The rates of etching for different samples are as follows: Si: 25 μm/min at 25 °C with CP4A solution ($HF:HNO_3:CH_3COOH = 3:5:3$ by volume); Cu: 15 μm/min at 25 °C with 1:1 nitric acid; stainless steel: 10 μm/min with 11M HCl at 60–70 °C.

Instrumental approach

The Si samples produced from rice husks for solar energy program were analyzed by instrumental approach as they were found to contain larger amounts of oxygen. The samples (10 mm diam., 1 mm thick) were irradiated at 500 nA beam current for about 20 minutes, etched by CP4A solution and after a cooling time of about 4 hours, counted using HPGe detector (15% efficiency to 3″ × 3″ NaI detector, 2 keV resolution at 1332 keV) coupled to a multichannel analyzer (Canberra Series 40). A quartz plate of similar size was irradiated for the standard.

Radiochemical approach

The radioactive product ^{18}F was separated from the matrix by two techniques: (1) distillation of H_2SiF_6 followed by precipitation of PbClF and (2) precipitation of KBF_4.

Distillation

Silicon. Silicon samples, after irradiation, were etched by CP4A solution and ground into a powder. The powder was dissolved in molten NaOH in a Ni crucible (Si:NaOH = 1:25, by weight), cooled and finally dissolved in water. Then steam distillation was carried out in an all-quartz set-up at 126–130 °C using 30 mg NaF as carrier, 1 g SiO_2, in perchloric-phosphoric acid medium (50 ml $HClO_4$ + 25 ml H_3PO_4). The distillate (about 175 ml), containing H_2SiF_6, was collected for 45 min in alkaline medium of NaOH.

The precipitation of PbClF from the above alkaline distillate was done in the following way:[7] 3 ml 10% NaCl solution was added to the distillate and the pH of the solution was made about 7 with dilute nitric acid (5M) and finally 1 ml concentrated HCl (11M) was added. The reaction mixture was then heated on a steam bath. About 5 g $PbNO_3$ was added with stirring and after its complete dissolution, 5 g CH_3COONa was poured immediately and the solution was stirred vigorously for 5 minutes under heating. The white precipitate of PbClF was filtered with a suction pump, dried and finally weighed. This precipitate was used for counting on the HPGe detector.

Copper. The copper samples, after irradiation, were etched by nitric acid (1:1) and transferred into the distillation flask. The sample was first dissolved in 10 ml concentrated HNO_3 (16M) with steam in a closed distillation system and the distillation was continued after addition of $HClO_4$ (40 ml) and H_3PO_4 (20 ml). The distillate, collected in alkaline medium of NaOH, contains a trace amount of Ga which was removed[8] completely by extraction twice with 0.01M solution of oxine in chloroform at pH 4–6, after addition of Ga carrier (about 100 μg). Finally the precipitation of PbClF was done as described above.

Stainless steel. Since stainless steel is dissolved in $HClO_4$, both the dissolution and distillation were carried out in the distillation flask using $HClO_4$ (50 ml) and H_3PO_4 (20 ml). Here the distillate was free from other radioactive contaminations. The precipitation of PbClF was carried out as described above.

KBF_4 precipitation

Radiochemical separation of fluorine was also done through KBF_4 precipitation as described by NOZAKI.[4] It has been found in the case of silicon sample that the KBF_4 precipitate obtained in the first step itself was free from radioactive contaminations; but with copper sample, even after two reprecipitations using $Zn(OH)_2$ as the scavenger, the precipitate contained radioactive contamination from Ga isotopes like ^{66}Ga (9.4 h) and ^{68}Ga (68 m), which were removed in the following way. The KBF_4

precipitate, first obtained with H_3BO_3, KCl and HF in strong acid was dissolved in a sufficient amount of water by warming and then extracted twice with 0.01M oxine solution in chloroform at pH 4–6, after addition of Ga carrier. The volume was reduced to 70–80 ml before proceeding for the precipitation of KBF_4. We have applied KBF_4 precipitation in some of the Si and Cu samples.

Chemical yield

The chemical yields of the two steps in the distillation method (1) distillation of H_2SiF_6 and (2) precipitation of PbClF, were measured separately, using inactive NaF. A known amount of NaF was taken and the fluorine obtained in each step was determined by fluoride ion selective electrode. Similarly, the chemical yield of KBF_4 was also determined. Typical chemical yields are: distillation method: distillation = 95%, precipitation = 90%, KBF_4 precipitation method: 80%.

During radiochemical work the actual chemical yield was determined for each sample gravimetrically by taking the weight of PbClF and KBF_4.

Results and discussion

All the computations were based on average cross-section method developed by RICCI and HAHN.[1] The range of 40 MeV α-particles in silicon, copper, stainless steel and quartz (used as standard) were obtained from a published reference[9] and are shown in Table 1.

It has been found that the instrumental approach is adequate if the oxygen impurity in Si is ≥ 100 ppm. In this case initially up to two half-lives of ^{18}F after irradiation, decay does not follow with respect to the half-life of ^{18}F due to the presence of some short-lived isotopes. Then the activity decays according to ^{18}F nuclide for another 3

Table 1
Range of α-particles in different matrices

Material	Range of 40 MeV α-particles, μm (A)	Range of 20.4 MeV* α-particles, μm (B)	Effective range, μm (A - B)
Silicon	718	231	487
Copper	198	84	114
Stainless steel	267	92	175
Silica	590	188	402

*Threshold energy of the reaction $^{16}O(\alpha, pn)^{18}F$.

to 4 half-lives, finally showing the presence of some long-lived isotopes (Fig. 1). During computations, corrections from the activity of long-lived isotopes and background were taken into consideration and the results are presented in Table 2.

At ppm levels of oxygen in high purity silicon, as well as for copper and stainless steel matrices, both at ppm levels and above radiochemical separation is necessary. The distillation technique gives a clean separation in most of the matrices. However, it is slightly tedious and careful attention is required. It has been found that in matrices like Cu some volatile products distill off along with steam and in such cases some modifications are required in the separation technique as described in the experimental section. The silicon matrix gives very pure radiochemical product ^{18}F, whereas in the copper sample some Ga-isotopes distill off along with steam during distillation. Gallium can be easily removed as described earlier. The removal of Ga is evidenced from the γ-spectra of the distillate, before and after the extraction, using HPGe detector

Table 2
Instrumental determination of oxygen in silicon by 40 MeV α-particles

Sample	Beam current, μA	Time irradiation, min	Cooling time, hour	Oxygen content, ppm
Silicon* 1	1.2	10	4	117±16
2	1.0	15	5	120±17
3	1.2	10	5	110±16

*From rice husk.

The KBF_4 precipitation method as described by NOZAKI is quite fast and easy to operate. However, it suffers from coprecipitation of other ions from the solution and this coprecipitation is dependent on the matrix. The KBF_4 precipitate from Si matrix is very pure radiochemically. In the case of Cu sample, it has been found that all the Ga isotopes produced from Cu like $^{63}Cu(\alpha, n)^{66}Ga$, $^{65}Cu(\alpha, n)^{68}Ga$, $^{65}Cu(\alpha, 2n)^{67}Ga$ coprecipitated along with KBF_4. Gallium could not be removed completely even after two reprecipitations and with the increase of steps of reprecipitation the overall chemical yield is reduced drastically. But before the precipitation of KBF_4, gallium can be successfully removed by extraction with oxine in chloroform as described in the experimental section.

The validation of analytical methodology using the distillation technique has been performed in matrices of silicon, copper and stainless steel. Standard samples of Si and stainless steel were analyzed by the present activation method. In the case of copper the same sample was analyzed by the present activation as well as by an established Inert Gas Fusion (IGF) technique. The analytical results are presented in Table 3.

Table 3
Validation of analytical methodology of activation analysis using α-particles*

Sample	Determination of oxygen by the present method			Recommended value of oxygen in standard samples, ppm	Oxygen content in Cu by inert gas fusion, ppm
	Beam current, μA	Time off irradiation, hour	Oxygen content, ppm		
Silicon (Standard)	1.1 1.2	2 2	9.8±0.7 10.1±0.6	10.4±0.5	–
Copper	0.9 0.8	2 2	1.8±0.2 1.5±0.2	–	1.6 ± 0.1
Stainless steel (Standard)	0.5 0.5	0.5 0.5	53±5 60±5	55.±3	–

*Distillation technique was used for radiochemical separation.

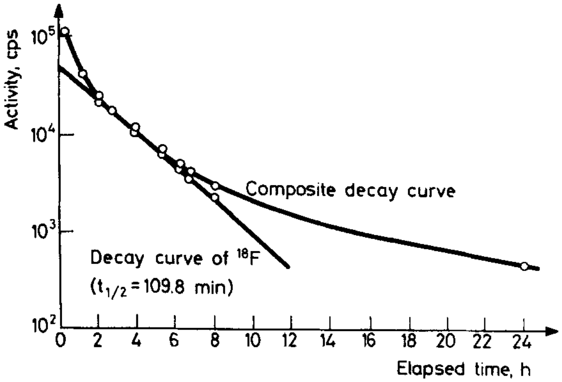

Fig. 1. Decay curve for a non-destructive determination of oxygen in silicon

Table 4
Determination of oxygen in Si and Cu using two independent radiochemical separations

Sample	H_2SiF_6 distillation technique			KBF_4 precipitation technique		
	Beam current, μA	Time of irradiation hour	Oxygen content, ppm	Beam current, μA	Time of irradiation, hour	Oxygen content, ppm
Si	1.1	1.5	22.4±3.1	1.0	1.5	25.1±4.6
Cu	1.0	1.2	12.9±2.1	0.9	1.2	10.2±1.8

Table 5

Determination of oxygen in different samples by α-particle activation analysis*

Sample		Beam current, μA	Time of irradiation, hour	Oxygen content, ppm
Silicon	A	0.8	2.0	16.7±2.8
	B	0.8	1.9	13.1±2.7
	C	0.9	2.0	22.6±1.9
Silicon (p-type)		1.2	2.5	2.3±0.3
		1.1	2.5	2.5±0.4
Silicon (n-type)		1.1	2.5	3.1±0.4
		1.1	2.5	2.8±0.3
Copper		1.0	2.0	2.3±0.3
		1.0	2.0	2.6±0.3
Copper		0.5	0.3	380±12
		0.5	0.3	370±15
Stainless steel		1.0	1.5	20.8±2.8
		1.1	1.5	23.4±2.6
Stainless steel		0.5	0.5	151±15
		0.5	0.5	162±12

*Distillation technique was used for radiochemical separation.

The same Si and Cu samples have been analyzed by distillation of H_2SiF_6 and precipitation of KBF_4. The analytical results are presented in Table 4, showing good agreement between the two radiochemical separation techniques.

The different Si, Cu and Stainless steel samples, containing varying amounts of oxygen impurity, have been analyzed using distillation technique. The results are shown in Table 5.

In all the above computations, the main errors arising from counting statistics and range of the α-particles, nave been considered. The errors were estimated on the basis of one σ-variation in the counting statistics and assuming a 10% error in the range. The presence of several other impurities like F, Na, Ne, N, Mg in the samples interfere in the estimation of oxygen. Ne and Mg are unlikely to be present, while F, Na and ^{15}N were present in very low concentration (less than a ppm). In Si samples, a serious interference can arise from the matrix itself through fission type reactions like $^{28}Si(\alpha, ^{14}N)^{18}F$, particularly at higher energies. It was pointed out[10] that the level of interference would be less than a ppm at the bombarding energy of 40 MeV and hence may be neglected at higher oxygen contents.

One interesting observation made during this work was that Si samples etched with

CP4A solution before irradiation yielded higher oxygen values even after post-irradiation etching. The sample with pre-irradiation etching gives higher values (sometimes even by a factor of 3) and this might have been due to the penetration of fluorine atoms deep into the matrix. In the light of this observation, pre-irradiation etching has been avoided in the present work.

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The authors are grateful to Dr. Bikash SINHA, Director, VECC, Calcutta and the staff of VECC for making it possible to carry out this experiment.

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