

DETERMINATION OF CARBON IN METALS BY PHOTON ACTIVATION

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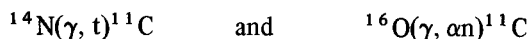
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Determination of carbon in metals was achieved by the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction in 35 MeV photons. We showed that usual methods of carbon separation such as fusion in an oxidizing bath heated by a high-frequency furnace are suitable only for a few metals. We developed two new separation methods: fusion in an alkaline bath followed by acidification and attack in a hot acid solution. The experimental conditions fitted for many metals and alloys (Ag, Al, Cr, Fe, Mo, Ni, Se, Ti, W, Zn, AlMg, ZnMgTe) were systematically studied. The analytical procedures were controlled using specially prepared standard alloys containing a known quantity of radioactive ^{11}C .

Introduction

Impurities and especially light elements like carbon disturb properties of metals even at low concentrations. Carbon must be determined in high purity metals at concentrations lower than 1 ppm. Activation in γ -photons is one of the most reliable and sensitive method for the determination of this element.¹ The determination is performed through the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction leading to ^{11}C , which is a β^+ emitter with a half-life of 20.4 min.

The irradiations were performed at the linear accelerator of Saclay. The maximum energy of the photons was 35 MeV. This energy was chosen in order to obtain enough sensitivity with minimum interferences. The main interferences are caused by the reactions:



According to ENGELMANN,² who used the same accelerator, the weights of nitrogen and oxygen leading to the same radioactivity as 1 μg of carbon are about 40 and 450 μg respectively at 35 MeV. According to the same author, the limit of detection is $5 \cdot 10^{-8}$ g with a 100 μA beam.

The main problem of this analysis is the chemical separation of carbon. Gamma spectrometry is not efficient in this case as the γ -annihilation peak of ^{11}C will be always covered by other β^+ -emitters, which are very often produced from the sample by photon irradiation. This separation is generally performed by volatilization of carbon as CO_2 . One of the methods used for that purpose is the oxidation in an oxidizing acid bath heated by a high frequency furnace.³⁻⁵ This method was successfully applied to metals such as iron and molybdenum. However experiments showed that this method could not be applied to all metals: in many cases either the sample is not attacked by the bath or the separation of carbon is not quantitative.⁶ The purpose of our work was to develop methods of carbon determination well fitted to each type of sample.

Three types of separation methods were studied:

- (1) Fusion in an acid oxidizing bath fused by a high frequency furnace.
- (2) Fusion in an alkaline bath, followed by acidification in order to release CO_2 .
- (3) Attack by an acid solution.

Methods of investigation

The study of new separation methods was performed in four stages:

(1) *Attack of inactive samples.* Only methods which perform complete dissolution of the sample in the tested bath are retained after these experiments.

(2) *Studies with a carbonate tracer.* The tracer was produced by irradiating a carbonate in 35 MeV photons. Few mg of this irradiated salt was put together with a piece of non-irradiated metal and submitted to the tested separation procedure. By this method we could reject procedures in which the separation of CO_2 is not quantitative. But the results of these experiments do not allow to conclude that carbon is really released from the sample.

(3) *Studies with samples doped with radio-carbon.* The best method of testing a separation procedure is to use samples whose carbon content is radioactive. For that purpose we irradiated pieces of some mg of graphite in 35 MeV photons. One of these pieces was incorporated into the metal sample. This operation was performed by fusion in a high frequency furnace. For most of these fusions we used the levitation technique, which avoided contact of the fused sample with a crucible.

We measured the concentration and homogeneity of the obtained alloys by γ -counting. Samples of these alloys were submitted to the tested separation procedures. As the other components of the alloy were inactive, it was easy to measure the rate of carbon separation and notice eventual carbon losses under conditions very close to a real sample.

(4) *Determination of carbon in samples.* The last check of the full analytical procedures was the measurement of determination reproducibility.

In a first series of determination, we used samples doped with a known quantity of carbon. These samples were obtained as described in 3. The concentration of carbon was deduced from the radioactivities of pieces of graphite irradiated at the same time. These standard samples could be used as soon as the radioactivity of ^{11}C completely decreased.

A second series of determination was performed on unknown samples.

Analytical procedures

General conditions

Samples up to 1 g were irradiated by photons emitted from a platinum target submitted to an electron beam of 35 MeV and 70–80 μA in the linear accelerator of Saclay. Two graphite foils were placed perpendicularly to the beam axis on each side of the sample. They were used as standards.

After irradiation the samples were etched in order to remove surface contamination. Carbon was then separated with procedures peculiar to each sample type. Carbon dioxide was absorbed in 12M KOH.

The radioactivity of absorbers and standards was measured on a NaI detector for the annihilation γ -ray. A correction was made in order to take into account the difference of geometry between the liquid absorbers and the graphite foils. The concentration was deduced from the radioactivity of the sample and from the mean radioactivity of the two standards.

Peculiar conditions

The methods and baths fitted for each sample type are given in Tables 1 and 2.

High temperature acid bath attack. The sample was put in an alumina crucible containing Pb_3O_4 87.5% – B_2O_3 12.5% and a piece of iron in order to start the fusion. The crucible was heated by a high frequency furnace of 1 kW at 10 MHz under an argon flow of $50\text{ cm}^3 \cdot \text{min}^{-1}$. The gas passed through a cotton filter, then I_2O_5 on silicagel (in order to oxidize CO to CO_2), and finally through a KOH (12M) absorber.

Alkaline attack. The sample was put in a nickel crucible containing a fused alkaline bath (Table 2) heated by a gas burner. After complete dissolution of the sample, the bath was cooled and put in the flask of the apparatus of the figure. The bath was then dissolved in 9M HNO_3 introduced by a peristaltic pump. The apparatus was swept by air, which bubbled in KOH (12M) absorbers at a flow rate of $50\text{ cm}^3 \cdot \text{min}^{-1}$.

Table 1
Usable methods for the attack of various samples
for carbon determination

Sample	Acid attack	Alkaline attack	Acid solution attack
Ag	+		+
Al		+	
AlMg		+	
Cr		+	
Fe	+		
Mo	+	+	
Ni	+		
Se		+	
Ti		+	
W		+	
Zn		+	
ZnMgTe		+	

Table 2
Quantity of each component in the bath for alkaline fusion of various samples
for carbon determination

Sample	NaOH, g	NaNO ₃ , g	NaF, g
Al	3	15	6
AlMg	2	10	2
Cr	1.5	5	0
Mo	1	5	0
Se	1	5	0
Ti	6	2	0
W	1	5	0
Zn	5	3	2
ZnMgTe	5	3	2

Some matrix elements such as Zn and Se gave rise to volatile species which were detected in the KOH absorbers. This effect was avoided by placing a 9M HNO₃ washer before the first KOH absorber.

Acid solution attack. The same apparatus was used in this case. The sample was put in the flask of the figure and directly attacked by an acid solution containing 10 cm³ of concentrated H₂SO₄ and 3 g of KIO₄ heated to boiling by a gas burner. The apparatus was swept by air at the same flow-rate.

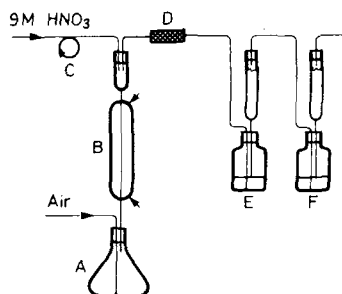


Fig. 1. Apparatus for the separation of carbon after alkaline fusion. A – flask for the dissolution of the alkaline residue, B – refrigerant, C – peristaltic pump, D – quartz-wool filter, E, F – 12M KOH absorbers

Results

The separation procedures chosen in Table 1 and applied to samples doped with carbon give a separation yield better than 99%. The extraction of carbon by acidification is performed in less than 10 min.

Determinations were performed on the standard samples obtained after decreasing of initially introduced ^{11}C . Results were in agreement with the expected values. However we observed a scatter in the results. The main cause of scatter seems to be the heterogeneity of γ -flux: it may be seen from the difference of radioactivities between the two graphite standards which achieves 20% in the worst cases.

The analytical procedures were applied to various metals and alloys (Table 3). For several metals (Ag, Al, AlMg, Fe, Mo, Ni, W, Zn) we found carbon concentrations about $1\text{ }\mu\text{g/g}$ or less. For some metals we noticed a variation from one sample to another. It is often the case for rather high concentrations in chromium and selenium. For ZnMgTe we observed a mean value of about $10\text{ }\mu\text{g/g}$ and localized heterogeneities from 1 to $100\text{ }\mu\text{g/g}$. Heterogeneity was also observed in zone-refined chromium and iron where the carbon concentration depends on the sampling location.

For the analysis of molybdenum we had the possibility to compare two methods: alkaline and acid attacks. We did not observe a significant discrepancy between the results obtained by these two methods.

The limit of detection calculated by the CURRIE's method⁷ was $0.02\text{ }\mu\text{g}$ of carbon in the following conditions: 20 min of irradiation in gamma photons produced from a $80\text{ }\mu\text{A}$ beam of 35 MeV electrons, 20 min of radioactivity measurement 30 min after irradiation on a $3'' \times 4''$ NaI(Tl) detector with a background of 60 pulses per min in the 511 keV range.

Table 3
Concentration of carbon in various samples and alloys

Samples		C, $\mu\text{g/g}$
Ag	high purity	0.21, 0.22, 0.5, 0.4
Al	99.7	0.1, 0.3, 0.2
AlMg		1.5, 1.9, 1.5
Cr	electrolytic	38 to 70
	A	13
	zone-refined B	1.7
	C	8.6
Fe	OH	100 to 120
	OH treated with H_2	0.25, 0.34
	zone-refined	0.18, 0.53
Mo	Climax	12, 13, 17, 18, 13
	Metalwerk	90, 93, 140
	Annealed under vacuum (10^{-7} torr 1 hr— 1800°C)	5.1, 6.8, 6.2
	Annealed under 2.10^{-5} torr O_2 2 hrs— 1650°C	0.27
Ni	carbonyl	33, 38, 42
	zone-refined	0.2, 0.5
Se	Prolabo	120 to 200
Ti	industrial	66, 59, 71, 67
	Van Arkel	12, 22
W	Prolabo	0.4, 0.8
Zn	Prolabo	≤ 0.02 , ≤ 0.06
ZnMgTe		1 to 100

Conclusions

We studied quantitative and selective separation methods for the determination of carbon by γ -activation in some usual metals. This study was made possible by use of samples doped with radioactive ^{11}C . It showed that separation of carbon by oxidation in an acid bath with H. F. heating can be applied to only a few metals. For other metals, we developed alkaline fusion and acid solution attack

methods. We defined the separation conditions fitted for each sample type of metal or alloy.

By these new analytical methods we were able to measure the concentration of carbon in metals where this determination has been not yet performed. The limit of detection is 0.02 μg .

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References

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