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EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

THE DETERMINATION OF OXYGEN IN METALS BY 14 MeV NEUTRON ACTIVATION ANALYSIS

by

J. HOSTE, D. De SOETE and A. SPEECKE
(University of Ghent)

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Report prepared by the
University of Ghent — Belgium

Euratom Contract No. 028-64-9 IRAB

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Summary

An automated oxygen analysis system for steel samples has been elaborated, where with 14 MeV neutrons from a neutron generator the reaction $^{16}O(n,p)^{16}N$ ($T_{1/2} = 7.4$ s) is used. A fast double pneumatic transport system for rectangular 18 g samples has been constructed, which allows the standard to be activated at the same time as and behind the sample. The ^{16}N γ-activities are measured above 4.5 MeV with two separated counting systems. Interferences from B and F are given. Sensitivity of the method is approx. 0.1 mg oxygen at maximum neutron output. Correlation between activation and reducing fusion results has been extensively studied on numerous samples of different origin, and is excellent.

The complete activation analysis apparatus for 38 g disk samples has been industrialised in a steel work.

As an extension to the steel analysis the oxygen determination in 11 different non-ferrous metals, Al, Bi, Cd, Co, Cu, Nb, Pb, Ta, Ti, Zn and Zr has been studied.

Possible matrix effects on the oxygen standards were investigated and found to be negligible. Whereas most matrices do not interfere with the ^{16}N measurement, Pb and Zr interfere seriously, Al and Cu to a lesser degree. By slight changes in the measurement period of the analysis, these errors could be eliminated.

KEYWORDS

DETERMINATION
OXYGEN
ACTIVATION ANALYSIS
STEELS
NUCLEAR REACTIONS
OXYGEN 16
NEUTRON BEAMS
PROTONS
NITROGEN
GAMMA DETECTION
SENSITIVITY
ERRORS
METALS

CORRIGENDUM

P. 57 - Par. 4 - line 7 : ... takes up oxygen ...
read : ... Takes up air oxygen ...

P. 59 - Line 10 - col. 4 : ... 13 h ...
read : ... 10 d ...

P. 59 - Line 19 - col. 5 and col. 6 : interchange with line 20 same columns

P. 60 - Line 7 - col. 2 : ... 31.5 ...
read : ... 51.5 ...

P. 60 - line 7 - col. 5 : β^+ 2.4

P. 60 - Line 7 - col. 6 : 0.59; 1.53

P. 60 - Line 8 - col. 5 : β^+ 0.90

P. 60 - Line 10 - col. 5 : 5.4

P. 60 - Line 10 - col. 6 : 1.4

P. 60 - Line 15 - col. 5 : β^+ 1.15; β^+ 1.35

P. 60 - Line 15 - col. 6 : 0.04; 0.07; 0.10; 0.15; 0.16

P. 63 - Par. 3 - line 1 : ... Fujii (15) has ...
read : ... Fujii (15) have ...

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LIST OF FIGURES

THE DETERMINATION OF OXYGEN IN METALS BY 14 MeV NEUTRON ACTIVATION ANALYSIS(+)

1. INTRODUCTION.

In the present state of the metallurgical industries a rapid and accurate determination of oxygen is of extreme importance. The production of a great variety of metals makes it desirable to develop a method, suitable for various matrices. In the steel industry, where oxygen-poor steels and alloys of the most different composition are produced, this situation is of the highest urgency.

Untill quite recently oxygen in those materials was determined by a reducing fusion method, where the samples are melted in a graphite crucible in vacuum or in an inert gas atmosphere (nitrogen-argon). Oxygen combines with carbon to form CO, which is measured directly or after oxidation to CO_2 by an appropriate detection method, such as infrared, micro coulometry, etc.

This rather slow method has an important blank value and uses quite small samples (200 mg up to 5 g). Inherent to this technique are difficulties in recovering the CO especially because of the wellknown getter-effect. Low melting materials evaporate and deposit on the walls of the apparatus, e.g. high manganese steels frequently suffer from considerable negative errors in the oxygen determination (1-3).

Matrices with high melting point need the addition of fluxes which apart from enhancing the blank value, are sometimes very expensive. The determination of oxygen in Nb and Ta for instance uses some grams of platinum per analysis (4).

The existing fusion apparatus do not always satisfy the needs of the industry, especially when together with the control of the finished products, intervention during the production is desired. In this situation for routine analyses a method and apparatus are needed, which possess speed, reliability, accuracy, sensitivity and even universality, together with ease of operation for technical people and the possibility to accept substantial samples.

(+) Manuscript received on June 23, 1967.

For the activation analysis of oxygen, several nuclear reactions are available, however the $^{16}O(n,p)^{16}N$ ($T_{1/2}$: 7.4 sec) is of the most practical value. The oxygen determination applying this reaction has been the subject of many investigations (5-29).

The purpose of the work, described hereafter, was with the given reaction to develop a method and an apparatus adapted to the needs of the modern metallurgical industries. More specifically this study was directed towards the steel industry, where process-control in production is of highest urgency.

As the given nuclear reaction only succeeds with fast neutrons, a nuclear reactor apart from being intollerable in a steelwork, is quite useless. Neutrons with an energy of about 14 MeV, are produced in a so-called neutron generator of reasonable cost. The produced radioisotope ^{16}N with its short half life necessitates a fast transport system for moving large samples from irradiation to measurement stations in as short as possible times. An advantage of this short half life is the possibility to repeat the analyses on the same sample in a non destructive way. Computing results in activation analysis is transposing a recorded activity into a concentration or weight of the analysed element. In order to speed up the analysis time it is therefore necessary to obtain the results by a simple calculation, or to introduce the recorded activities into a small calculator, printing the result as weight of oxygen.

It is also obvious that an industrial equipment of practical value should provide the possibility to automate the procedure and to be able to accept a number of samples for analysis without any intervention from an operator. Therefore the imposed sequence of operations should be reliable and free from erroneous results, due to any mishap in the analysis cyclus.

2. PRINCIPLE OF THE METHOD.

2.1. Activation analysis.

The principle of activation analysis is based on the measurement of the radioactivity produced by bombarding stable nuclei with adequate particles. This activity A_t, expressed as desintegrations per second, is given by the following equation

$$A_t = f \sigma N (1 - e^{-\lambda t}) \qquad (1)$$

with

$$N = \frac{g}{M} N_A \qquad (2)$$

where f = irradiation flux in number of particles per cm^2 per sec;

σ = cross-section, for the reaction under consideration, in cm^2; (practical unit : barn = 10^{-24} cm^2);

N = number of irradiated stable nuclei;

λ = $\frac{\ln 2}{T_{1/2}}$ = desintegration constant of the produced isotopes, with half life $T_{1/2}$;

t = irradiation time;

g = weight of irradiated element;

M = atomic weight of the element;

N_A = Avogadro's number : $6.02 \; 10^{23}$.

From eq. (1) an exponential growth of the radioactivity is expected, with a limit value of $f \sigma N$. Therefore the term $(1 - e^{-\lambda t})$ is the so-called "saturation factor". It is obvious that for $t \gg T_{1/2}$ saturation is obtained and the activity in the irradiated sample is not increasing anymore.

Although with eq. (1) the weight of the element determined can be calculated from the observed activity, generally a relative method, is used, where under identical conditions a sample (X) together with a standard (S) of the element with known weight are treated. Under this condition, eq. (3) can be applied

$$\frac{g_X}{g_S} = \frac{A_{t_X}}{A_{t_S}} \qquad (3)$$

so that the weight of element in the unknown sample can be determined from the ratio of the recorded activities in sample and in standard.

2.2. Nuclear data.

A great variety of nuclear reactions are at least of theoretical value in activation analysis for the determination of oxygen :

$^{18}O(p,n)^{18}F$	(30)
$^{18}O(n,\gamma)^{19}O$	(31)
$^{17}O(n,\alpha)^{14}C$	(32)
$^{16}O(d,n)^{17}F$	(33)
$^{16}O(t,n)^{18}F$	(34)
$^{16}O(\gamma,n)^{15}O$	(35)
$^{16}O(^{3}He,p)^{18}F$	(36)
$^{16}O(n,p)^{16}N$	(5-29)

The isotopic abundances of the oxygen isotopes ^{16}O, ^{17}O and ^{18}O are 99.7%, 0.037% and 0.20% respectively. It is obvious that in order to achieve the highest sensitivity a reaction with ^{16}O is to be considered.

On the other hand reactions with charged particles suffer from a double draw back. Only costly accelerators produce them and their range of penetration in the irradiated samples is very low. As in the determination of oxygen only surface layers of up to some hundred microns would be detected, the results for materials with surface oxidation would be without value. Special precautions would have to be taken, e.g. working in an oxygen-free atmosphere, so that sample-taking and analysis would be of no use as a routine method. From these considerations follows that the reaction

$$^{16}O(n,p)^{16}N$$

is the most promising possibility. As the threshold energy E_{eff} for the reaction is of about 10 MeV, the monoenergetic 14 MeV neutrons from a neutron generator are quite adequate for the activation analysis of oxygen.

A survey of the most important nuclear reactions with 14 MeV neutrons on oxygen iron and the most frequent steel constituents is given in Table 2, I (37).

As appears from the desintegration scheme given in Fig. 2, 1, ^{16}N emits high energy γ-rays of about 6 and 7 MeV. Although also high energy β's are emitted, it is appropriate to use γ-energy discrimination with a reasonable high counting efficiency.

The iron matrix mainly produces ^{56}Mn with γ-rays of max. 3.20 MeV. The other steel constituents do not produce γ-active isotopes with energies above 3.2 MeV. It is obvious that energy discrimination at the 4.5 MeV level will allow a practically trouble-free ^{16}N counting for approx. 40% of its activity, even if sum peaks are taken into account. Fig. 2, 2, where the γ-spectra of ^{16}N and ^{56}Mn are given, illustrates this possibility.

2.3. Irradiation and measurement time.

The short half life of ^{16}N (7.4 sec) imposes the shortest possible delay between the end of the irradiation and the start of the activity measurement in order to achieve the highest sensitivity. Therefore the transport in the pneumatic system must be as fast as possible.

However this same short half life permits short irradiation periods, which speed up the analysis time. From eq. (1) giving the induced activity as a function of irradiation time, one calculates a saturation of 40% after 5 sec, and of 83% after 15 sec.

The counting period of the activated samples can also be rather short. When the delay between activation and measurement is 2 sec. then counting for 7, 20 and 30 sec yields resp. 40, 70 and 78% of the total produced activity. It is obvious that further increasing the counting period only has a negative effect on the counting statistics by multiplying the background of the detectors.

FIG. 2.1

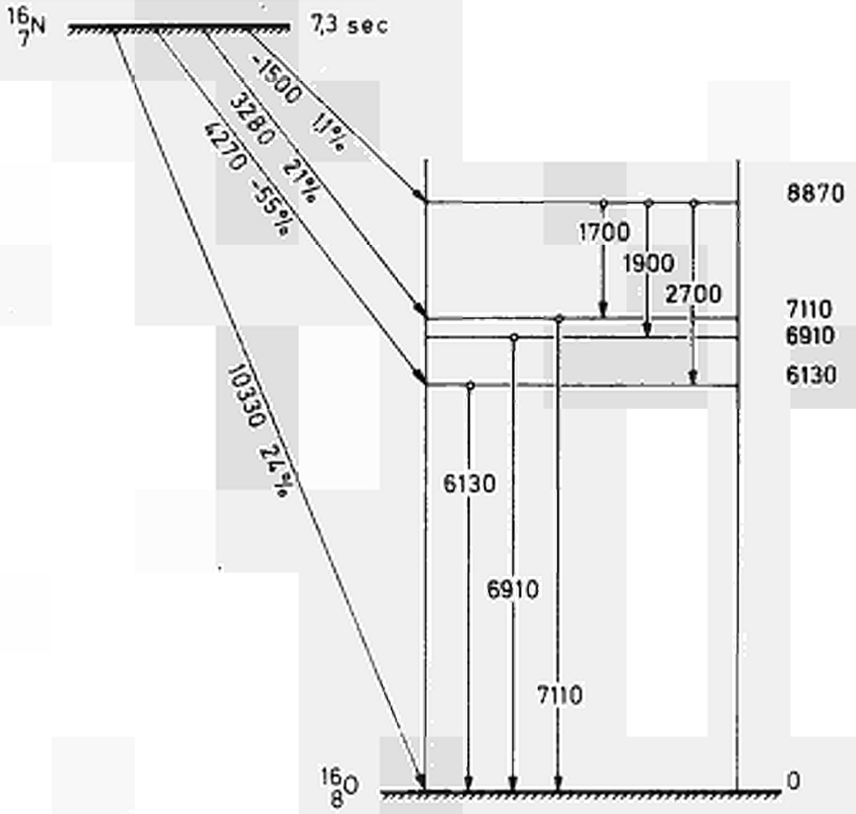

16/7 N
7,3 sec
~1500 1,1%
3280 21%
4270 ~55%
10330 24%
8870
1700
1900
2700
7110
6910
6130
6130
6910
7110
16/8 O
0

FIG 2.2

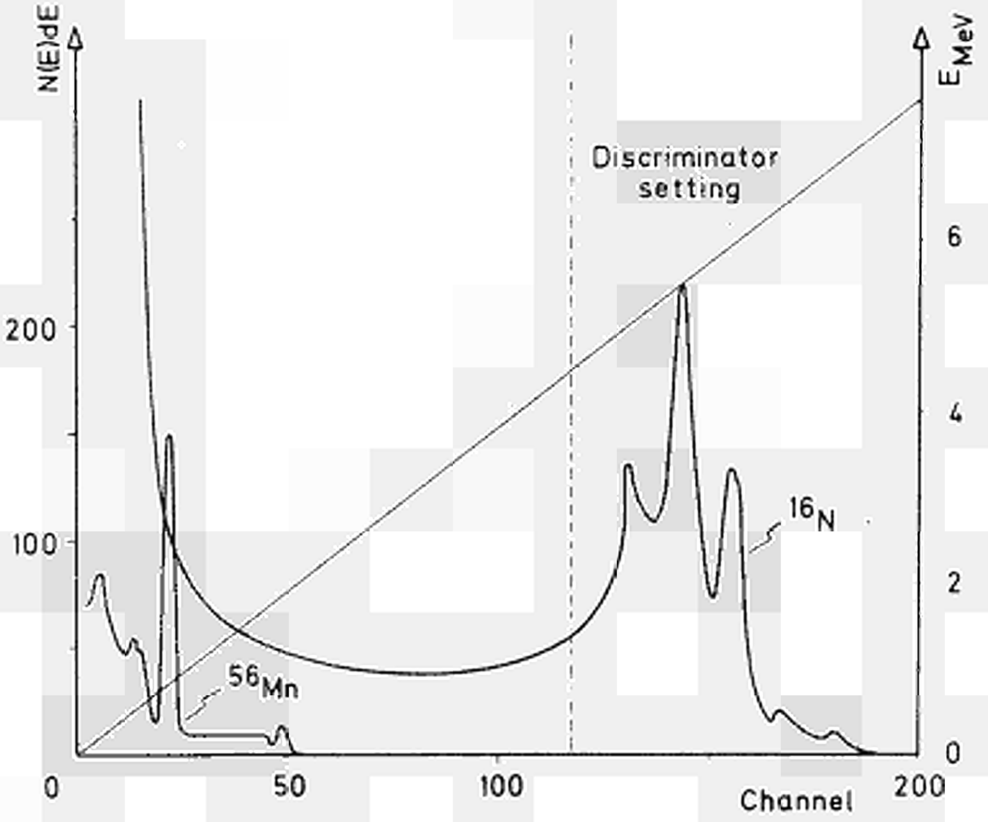

N(E)dE
E MeV
Discriminator setting
200
100
6
4
2
0
16N
56Mn
0
50
100
Channel
200

TABLE 2, I.

Reaction	Irradiated isotope			Reaction product	
	%	mb	$T_{1/2}$	E_{max} β (MeV)	E_{γ} (MeV)
$^{16}O(n,p)^{16}N$	99.7	40	7.4 s	10.3; 4.3; 3.2	6.13; 6.90; 7.11
$^{16}O(n,2n)^{15}O$	99.7		118 s	β^+ 1.73	-
$^{54}Fe(n,\alpha)^{51}Cr$	5.8	200	27.8 d	-	0.33
$^{54}Fe(n,2n)^{53}Fe$	5.8	15	8.9 min	β^+ 2,40; β^+ 2,70	0.38
$^{56}Fe(n,p)^{56}Mn$	91.7	110	2.6 h	2.86; 1.05; 0.70	3.20;2.93;2.69;2.56; 2.10;1.80;0.84
$^{57}Fe(n,p)^{57}Mn$	2.2	60	1.7 min	2.60	0.13; 0.12
$^{55}Mn(n,p)^{55}Cr$	100	40	3.5 min	2.85	-
$^{55}Mn(n,\alpha)^{52}V$	100	35	3.8 min	2.73	1.44
$^{59}Co(n,p)^{59}Fe$	100	81	45 d	1.56; 0.46; 0.27	1.29; 1.10; 0.19
$^{59}Co(n,\alpha)^{56}Mn$	100	30	2.6 h	see $^{56}Fe(n,p)^{56}Mn$	
$^{59}Co(n,2n)^{58m}Co$	100	800	9.2 h	-	0.025
^{58}Co		385	72 d	β^+ 0.48	1.62; 0.81
$^{58}Ni(n,p)^{58m}Co$	67.7	40	9.2 h	see $^{59}Co(n,2n)^{58}Co$	
^{58}Co		560	72 d		
$^{58}Ni(n,2n)^{57}Ni$	67.7	35	36 h	β^+ 0.85; β^+ 0.72	1.89;1.36;0.40;0.13
$^{52}Cr(n,p)^{52}V$	83.8	100	3.8 min	see $^{55}Mn(n,\alpha)^{52}V$	
$^{52}Cr(n,2n)^{51}Cr$				see $^{54}Fe(n,\alpha)^{51}Cr$	
$^{28}Si(n,p)^{28}Al$	92.3	360	2.3 min	2.86	1.80
$^{32}S(n,p)^{32}P$	95.1	220	14.3 d	1.71	
$^{31}P(n,p)^{31}Si$	100	80	2.6 h	1.48; 0.82	1.26
$^{31}P(n,\alpha)^{28}Al$	100	120	2.8 min	see $^{28}Si(n,p)^{28}Al$	
$^{31}P(n,2n)^{30}P$	100	10	2.5 min	β^+ 3.24	-

Finally the short half life of ^{16}N has another advantage as its allows repeated analyses on the same sample. Indeed 1 min. after the end of irradiation the activity has decreased to less than 0.5% of the original value.

2.4. Geometry factors at the irradiation- and γ-counting sites.

As a neutron generator is in fact a disk neutron source, an important flux gradient will exist as a function of the distance between the neutron source and the irradiated sample. For samples with finite dimensions the highest activity will be induced at the face nearest to the tritiumtarget. Furthermore as the counting efficiency of the NaI(Tl) detectors is also influenced by the distance between sample and crystal, the most activated face of the sample must be nearest to the detector to achieve the highest possible count rate. In this way the highest sensitivity for the analysis is obtained. Several authors (14, 22, 24, 27, 38) prefer to spin the samples during activation and counting in order to achieve isotropic irradiation and measurement. This method lowers the obtainable sensitivity as the mechanical setup increases the distances between sample and neutron generator and(or) the γ-detector. An additional setback is the difficulty to construct a reliable tool to spin heavy samples of 40 g for the steel analysis

A simple solution of these geometry problems has been achieved by constructing a transport system with aluminium tubes of rectangular cross section. In this way the samples necessarily present the same face nearest to the neutron generator and the detector.

An additional advantage of the transport system introduced here is the possibility to analyse the samples on both sides, thus allowing the detection of important oxide inclusions.

2.5. Neutron monitoring and standardisation.

As an absolute activation method is difficult to realise, a relative analysis method is generally adopted, where the oxygen concentration of the sample is measured versus a standard with known oxygen content. In most published procedures standard and sample are irradiated successively, whilst the neutron flux or a related quantity is measured. Afterwards the induced activity in sample and standard is corrected for differences in neutron output of the generator.

Two possibilities are exploited for the flux monitoring : measuring the activity induced in a suitable target simultaneously with sample or standard or direct neutron counting during the irradiation time.

In the first case, general use is made of the reaction $^{63}Cu(n,2n)^{62}Cu$ ($T_{1/2}$: 9.9 m) with a cross section of 0.5 barn and the annihilation radiation of ^{62}Cu is measured (39). The differences of the excitation function for ^{63}Cu and ^{16}O have no influence on the accuracy of the determination as long as no different neutron energy degradation arises on successive irradiations.

The direct neutron counting may be achieved with organic plastic scintillators(14, 23, 24) or with a BF_3 counter, surrounded with a paraffine layer to thermalise the neutrons (12, 20, 25, 40). An advantage of this method is the almost complete insensitivity of the counter for the important capture γ-flux associated with the neutron production. However it should be noted that the γ-detection system for ^{16}N differs from the neutron counting chain, thus a different drift is possible as a function of time and temperature. Also the neutron flux must be constant during the irradiation as the ^{16}N half life is short compared to the activation period. Various authors (12, 14) proposed as a solution to this problem the use of an integrating device, with a time constant equal to the mean half life of ^{16}N, i.e. $T_{1/2} \times \ln 2$.

In this work a procedure is proposed taken from the classical activation analysis techniques, where sample and standard are irradiated at the same time. Thus the standard in fact has a double function :

flux monitoring and standardisation. Whereas it is possible to irradiate sample and standard next to each other (27, 41), here the standard is placed behind the sample. By doing this the sample, with the lowest oxygen content, gets the highest neutron flux, and the lower flux in the standard is easily compensated by introducing a higher oxygen quantity. Afterwards the activities of sample and standard are measured simultaneously with two separate but identical detector systems. The oxygen concentration in the unknown sample is then to be computed with the classical activation analysis formula

$$(\text{mg O})_X = \frac{(\text{mg O})_S}{K} \cdot \frac{(\text{Act})_X}{(\text{Act})_S} = K' \frac{(\text{Act})_X}{(\text{Act})_S} \qquad (4)$$

where subscripts X and S respectively indicate sample and standard; Act the induced ^{16}N activity and K' represents the analysis factor. The K-factor is governed by the ratio of the neutron fluxes in X and S at the irradiation sites and by the difference in counting efficiencies of both counting systems. The determination of K is easily achieved with two oxygen standards as will be explained in 8.

It should be noted that this procedure does not demand additional apparatus as the neutron monitoring equipment is simply replaced by a classical γ-counting system.

Duplication of the rectangular transport system is fully compensated by minimalisation of the errors in standardisation, the simplicity of calculating the results and the omission of a spinning system. It is indeed obvious that the automatic computation of the analysis results does not present important technical difficulties.

It is also quite clear that the standard can be used repeatedly, provided the frequence of analysis is not higher than 1 analysis per minute. At that moment the residual activity of ^{16}N is lower than 0.5%. No danger of oxygen "burn-up" exists as ^{16}N decays by β - γ desintegration to the original ^{16}O.

3. APPARATUS.

3.1. Neutron generator.

When deuterons are accelerated in a high vacuum to 150 kV and bombard a tritium target, they give rise to 14 MeV neutrons from the fusion reaction

$$^{2}H + ^{3}H \longrightarrow ^{4}He + ^{1}n$$

The neutron generator used in this work was a SAMES Type J 150 kV 1 mA accelerator, which is shown in Fig. 3, 1 and schematically presented in Fig. 3, 2.

In this apparatus the deuterium gas flow is obtained by heating a palladium leak attached to the gas container. In the ion source the gas is atomised and ionised by a 100 Mhz - 60 W RF generator, with up to 90% of monoatomic deuterons. The deuteron plasma is condensed by a magnetic field and extracted by applying a variable positive voltage into the accelerating tube. From here the acceleration.takes place, whereupon the deuteron beam bombards a tritium target, producing the desired neutrons.

It should be noted that a positive potential is applied throughout the whole processus, so that the tritium target is at earth potential, and a metallic transport tube can be placed as near as useful to the accelerator tube, without electrical shielding. The 150 kV voltage is electrostatistically produced and protected against excessive voltage or current, which prevents electrical hazards on body discharges. In a first version of the accelerator, the accelerating potential was applied in 2 steps, the first one, variable from 0 to -45 kV serving also as focalisation potential. Adjusting this focalisation produced a beam with a diameter from 2 to 12 mm. As a tritium target has a useful diameter of 20 mm, it was impossible to obtain a maximum neutron yield. Also a 2 mm beam causes considerable damage to the tritium target by excessive local heating. Lastly as the accelerating electrodes were isolated by organic polymer material, a suitable vacuum was only obtained after pumping for at least 6 h when air has entered the vacuum system.

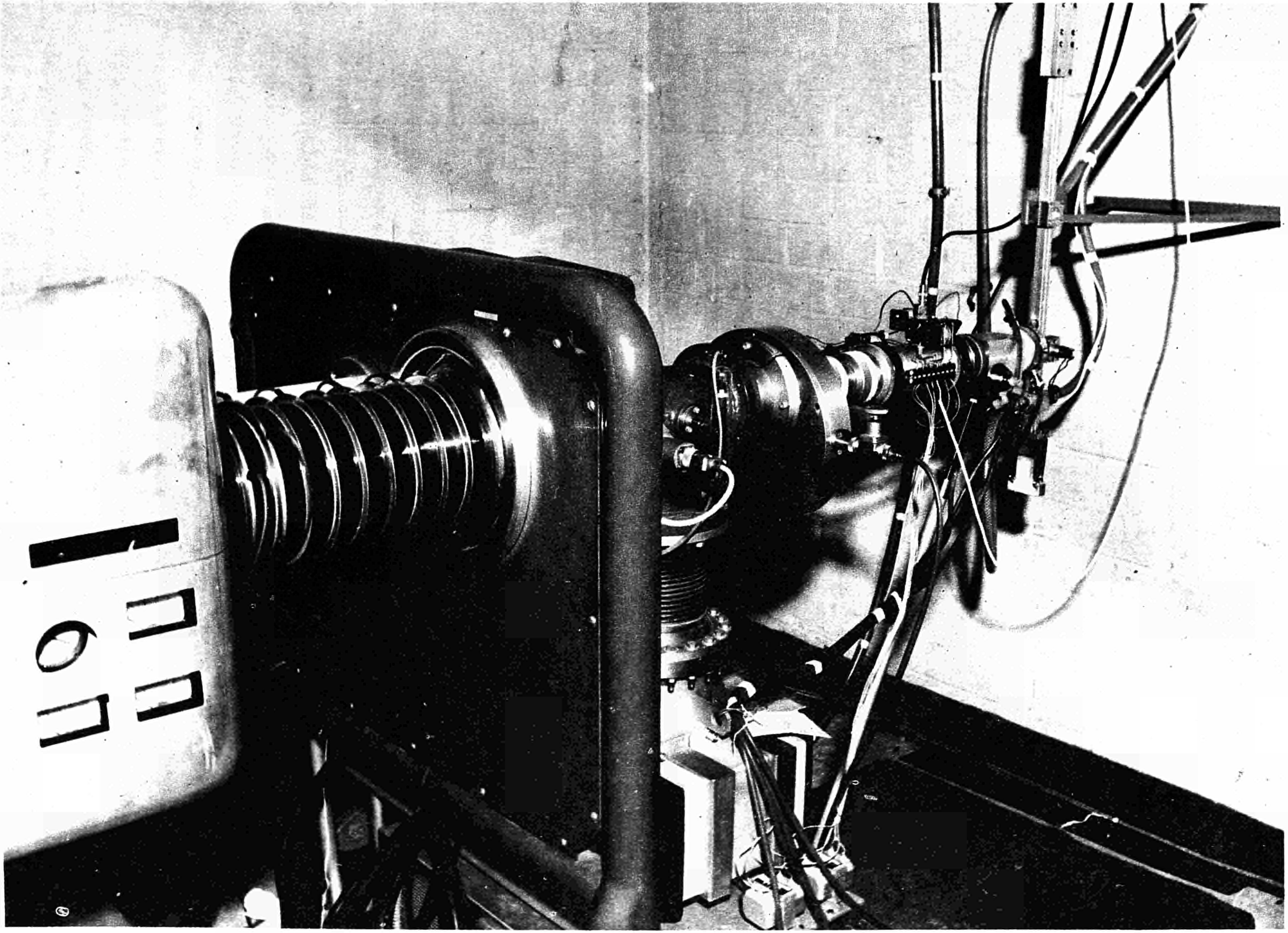
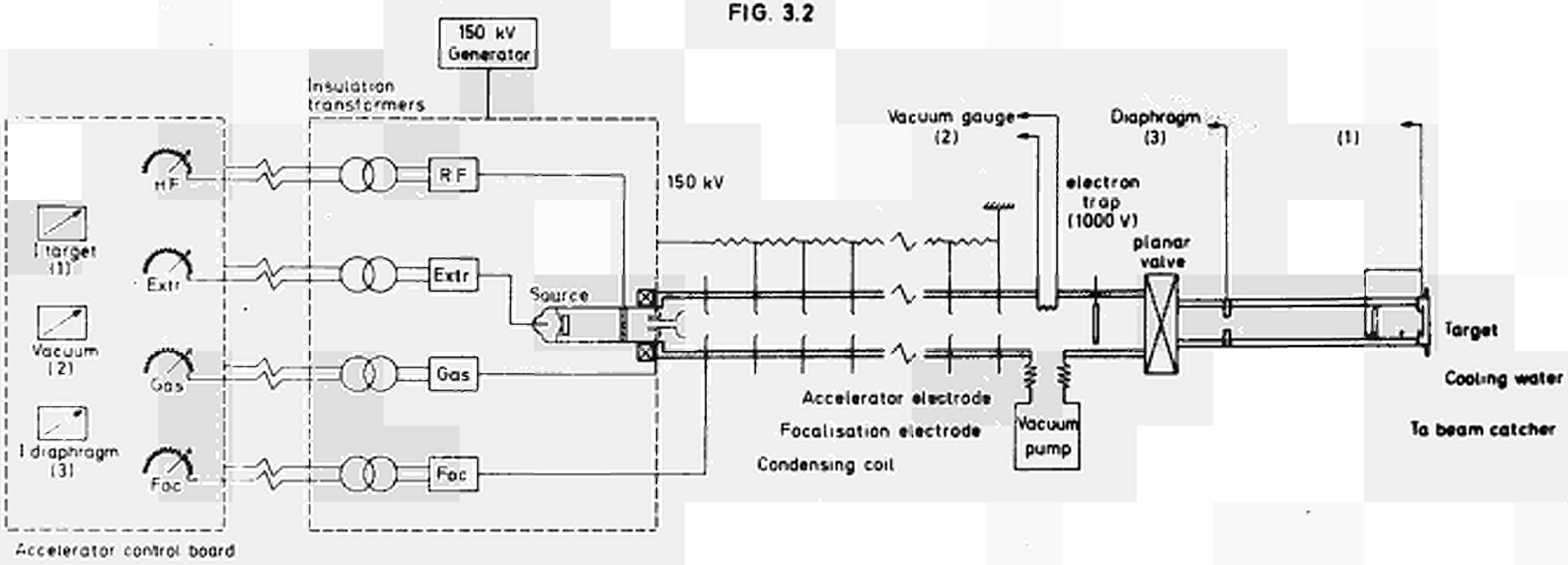


FIG. 3.2


150 kV
Generator
Insulation
transformers
HF
I target
(1)
Extr
Vacuum
(2)
Gas
I diaphragm
(3)
Foc
RF
Extr
Gas
Foc
Source
150 kV
Vacuum gauge
(2)
Diaphragm
(3)
(1)
electron
trap
(1000 V)
planar
valve
Target
Cooling water
To beam catcher
Accelerator electrode
Focalisation electrode
Condensing coil
Vacuum
pump
Accelerator control board

For all these reasons, a new accelerating tube was developped, where 10 accelerator electrodes are present, isolated by ceramic material. In this "constant field" tube a high vacuum is obtained in 10 minutes. Focalisation provides a beam with diameters varying from 6 to 25 mm.

A 10^{-6} torr vacuum is obtained with an ion-pump, with 200 l sec^{-1} capacity. An extremely clean vacuum is thus obtained and no deposits on the electrodes or tritium target are noticeable, as can happen with oil-diffusion pumps. The ion pump is continuously working, also when no neutrons are generated, thus preventing soiling the palladium leak or the ion source. A prevacuum of the order of 10^{-3} torr is obtained by a classical double rotating pump. The vacuum is monitored on the accelerator control by a built in vacuum-gauge.

The target section of the generator can be isolated from the rest of the accelerator by means of a planar valve, allowing the replacement of a tritium target without destroying the vacuum in the accelerator tube, in about 20 minutes. Farther on a diaphragm protects the tube against possible deuteron bombardment and its consequent damage. The incident deuteron beam is monitored on the control panel and gives a rough idea of the defocalisation of the beam.

The water-cooled target holder closes the accelerator. The tritium target consists of a copper or silver backing, 0,1 mm thick, on which approximately 200 µ of titanium or zirconium is evaporated and more or less saturated with tritiumgas. The total tritium activity varies from 1 to 15 Ci. In this work 2 to 5 Ci targets of different origin were used.

Upon repeated bombardments the target is depleted (42) and the half life can be established, i.e. the time necessary to obtain at constant beam current a neutron output, half of its original value. Experimentally it was established that a 4 Ci target does not produce a neutron flux, double of a 2 Ci target, but its half life was somewhat greater. This is probably due to regeneration by diffusion of tritium from the lower layers of the titanium or zirconium deposit. This same phenomenon was noted when the accelerator was rested. The decay of the target was also less pronounced with short irradiations, at constant integrated beam current. Consequently as many parameters influence the target half life, this value is of limited significance. One can however accept as typical for a "good" 2 Ci target a figure corresponding to 30 mA.minutes for irradiation times of 5 sec at 300 µA.

The target current is measured with a µA-meter in the control panel. The relation between beam current and induced activity in a oxygen standard on sample and standard irradiation sites is given in Fig. 3, 3.

Starting with 300 µA beam, 5 sec irradiations and if the beam intensity is gradually increased to achieve approximately constant neutron output, a 2 Ci tritium target is adequate for approx. 5,000 oxygen analyses at a price of 0.02 U$ target cost per analysis.

The neutron flux has been determined according to the Texas-convention (43). A copper target of 1 cm diameter and 0.25 mm thickness is irradiated and the absolute activity of ^{62}Cu determined. The neutron flux at the irradiation site of the sample was approx. 8.10^8 n/cm^2.sec at a beam intensity of 300 µA. The neutron generation is controlled by a mobile watercooled tantalum screen. Between neutron productions this screen intercepts the deuteron beam and is pneumatically lowered for the irradiations. This set up presents various advantages :

- it permits the adjustment of the accelerator parameters, such as R.F., extraction and focalisation without unnecessary bombardment of the tritiumtarget, the incident beam being monitored by the same µA meter of the target current;
- the accelerator is continuously in working conditions, enhancing remarkably the reproducibility of the beam output. In generators of other types the neutron production is regulated by switching on and off the R.F. generator or even the high voltage; this method imposes heavily upon the electronic circuits of the accelerator.

The accelerator control panel in the counting room consists of the H.V. control, the vacuum meter and the potentiometers for gas-flow, R.F., extraction and focalisation. These parameters are highly interdependent and their relation to the beam intensities is given in Fig. 3, 4.

3.2. Counting apparatus.

The sample to be analysed and the oxygen standard possess separate but identical γ-counting systems, consisting of a common H.V. supply, a 7.5 x 7.5 cm NaI(Tl) detector, preamplifier, linear amplifier with discriminator and scaler. An automatic background correction is included in the scaler : the reset at the start of the counting is made on the compliment of the adjustable background, approx. 40 counts per 30 sec. It is indeed necessary to correct for the background at low oxygen contents. The detectors are shielded with a 5 cm Pb ring, and a 60 cm concrete wall separates the two counting stations. As no long-living isotope with a γ-energy of above 4.5 MeV exists, the discriminator settings are adjusted with the help of the 1.12 MeV γ-energy of ^{65}Zn, and afterwards the gain of the amplifiers is reduced by a factor of 4.

3.3. Pneumatic transport system.

Aluminium tubes with rectangular section have been used to construct this transport system, thus providing the same geometry for the samples at the irradiation and the counting stations. As the analysis of sample and standard is simultaneous a double system was necessary. At the irradiation site the tubes are placed one after the other, the sample being nearest to the tritium target, at the measuring site the tubes are evidently separated and at a distance of approx. 100 cm.

At the beginning of the work, the transport system accepted samples of dimensions 20 x 17 x 7 mm, or equivalent to 18 g steel. However on suggestion by the European Coal and Steel Community commission

FIG. 3.4

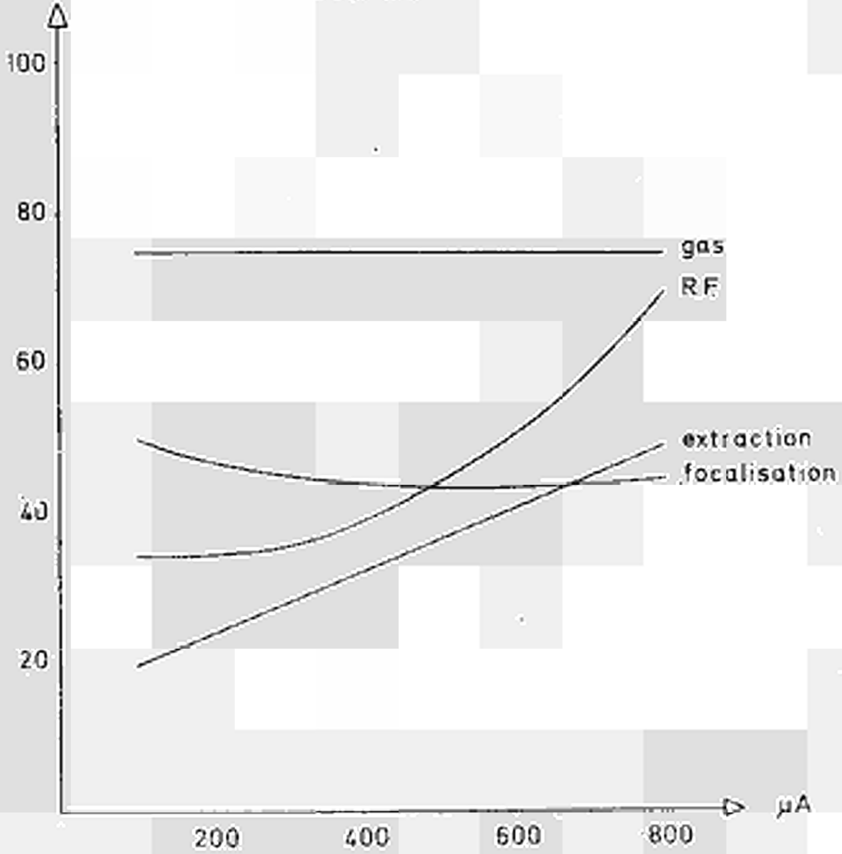
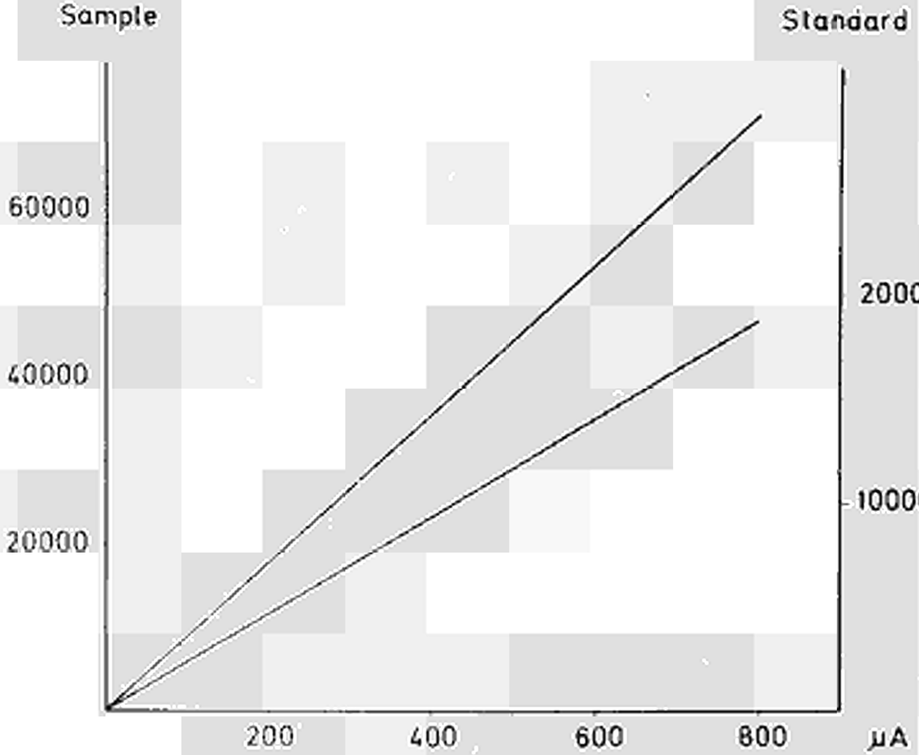

100
80
60
40
20
gas
R.F.
extraction
focalisation
200
400
600
800
µA

FIG. 3.3


Sample
Standard
60000
40000
20000
20000
10000
200
400
600
800
µA

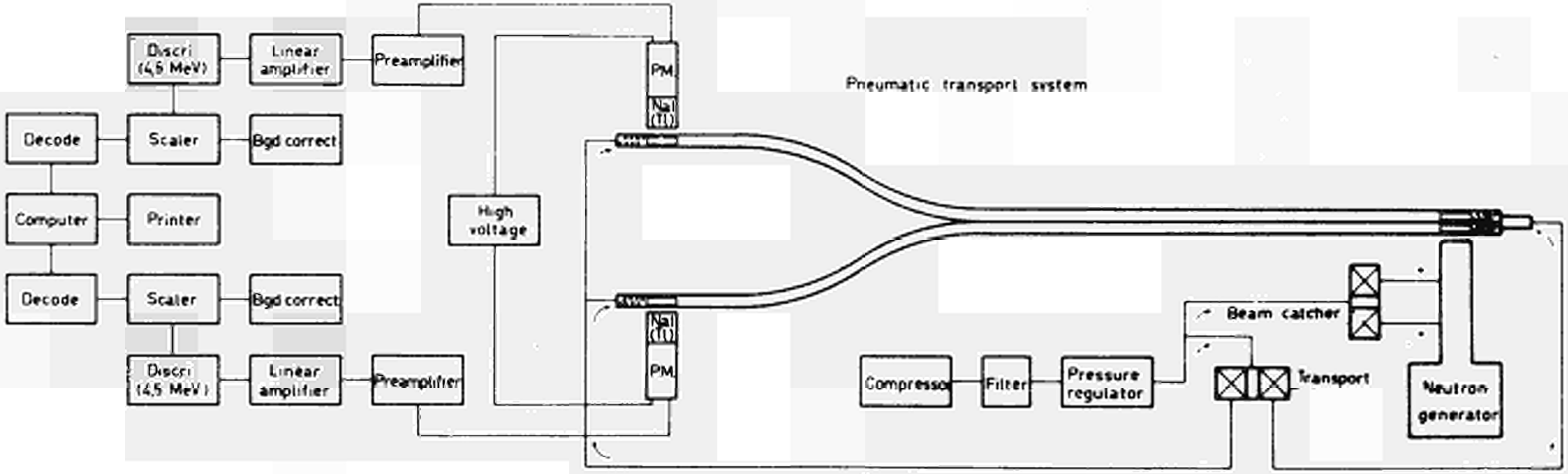
for the determination of oxygen in steel, the use of cylindrical samples, more readily available, was considered, and a new transport system for samples 26 mm in diameter and 9 mm thick, or approx. 38 g was constructed.

The direction of transport is reversed by means of double magnetic-pneumatic valves. In order to arrive at very short transit times, the transport is always done under pressure, approx. 1.7 atmosphere. Typical values are 1.6 sec for 12 m with the 18 g system and 0.8 sec for 5 m with the 38 g samples.

At this high speeds stopping the samples is achieved with nylon bumpers supported by spiral springs. The presence of the samples is photoelectrically controlled. As the same oxygen standard serves continuously, no exchanging mechanism is provided in its transport system. In the sample system a sample changer of classical design is mounted at the measuring station. The aluminium tube is connected to one of four chambers of a revolving block. When the block is moved over 90° a new sample is introduced in the transport tube, and the analysed sample is ejected in a shielded container. The number of samples in the charger is unlimited but has been kept for practical purposes to 15. The complete design of the system is given in Fig. 3, 5 and is pictured in Fig. 3, 6.

The geometric reproducibility of the transport system was checked with reactor activated steel samples, with a total activity of about 100,000 c/min. The samples were counted with a NaI(Tl) detector at the 2 measuring stations and at the irradiation station. Standard deviations were calculated for 10 stationnary countings and for 10 measurements after transport. Results are given in Table 3, I. From these results it appears that in the most unfavourable situation the standard deviation in only 0.3% higher than for stationnary measurements, which error is well inside the overall error of the method.

FIG 3.5


Discri (4,5 MeV)
Linear amplifier
Preamplifier
Decode
Scaler
Bgd correct
Computer
Printer
Decode
Scaler
Bgd correct
Discri (4,5 MeV)
Linear amplifier
Preamplifier
High voltage
PM
NaI (Tl)
NaI (Tl)
PM
Pneumatic transport system
Beam catcher
Compressor
Filter
Pressure regulator
Transport
Neutron generator

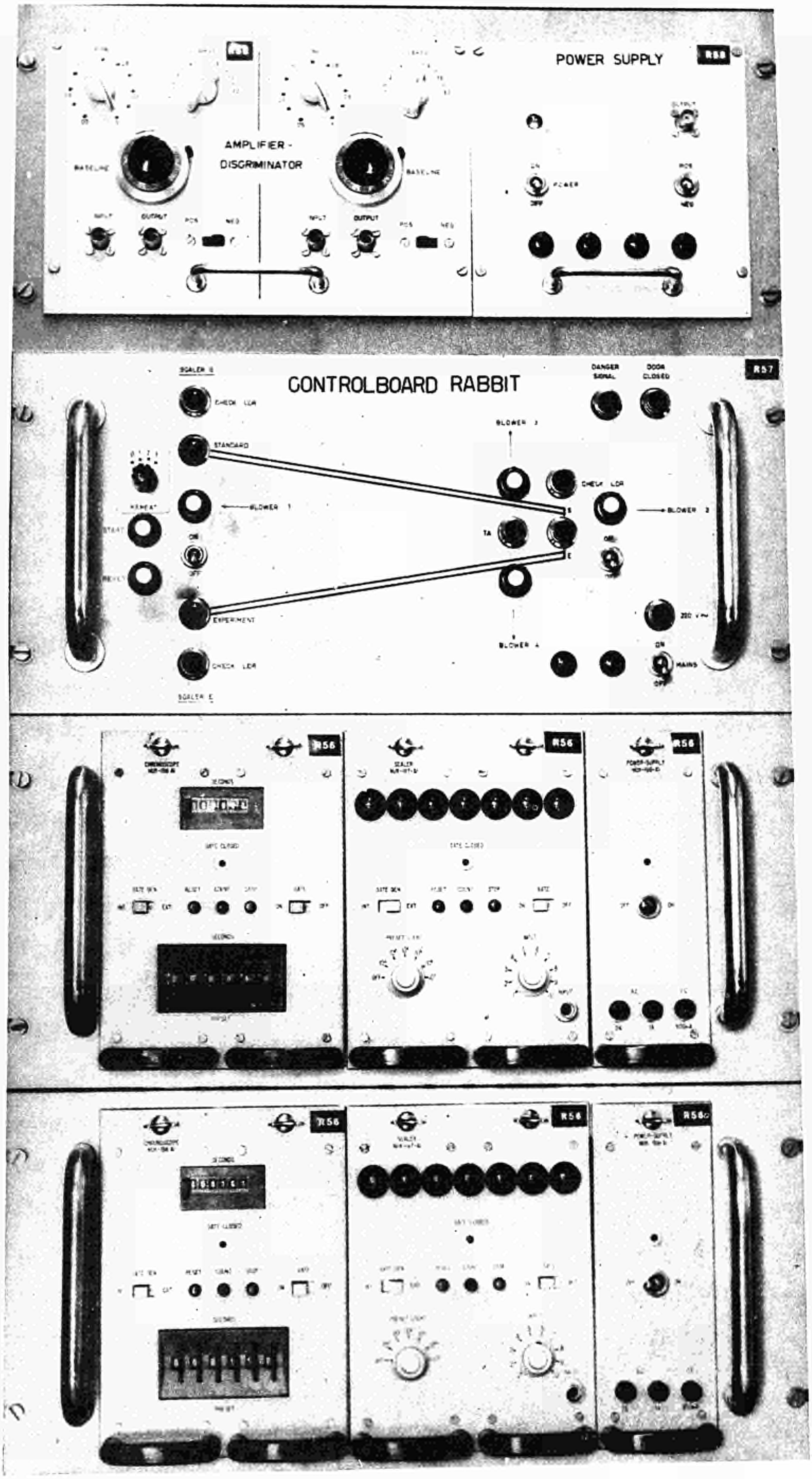

AMPLIFIER - DISCRIMINATOR
BASELINE
INPUT
OUTPUT
POS
NEG
POWER SUPPLY
R58
ON
POWER
OFF
CONTROLBOARD RABBIT
R57
SCALER S
CHECK LDR
STANDARD
BLOWER 1
BLOWER 2
BLOWER 3
BLOWER 4
REPEAT
START
EXPERIMENT
SCALER E
DANGER SIGNAL
DOOR CLOSED
TA
S
E
220 V~
MAINS
R56
GATE CLOSED
RESET
COUNT
STOP
GATE
SECONDS

TABLE 3, I.

	cpm ± standard deviations (mean of 10 measurements)	
	Stationnary counting	Counting after transport
Counting position		
sample	78,780 ± 240 0.31%	78,560 ± 350 0.45%
standard	88,470 ± 220 0.25%	89,500 ± 500 0.56%
Irradiation position		
sample	81,770 ± 210 0.26%	81,170 ± 380 0.46%
standard	79,960 ± 230 0.29%	79,990 ± 210 0.26%

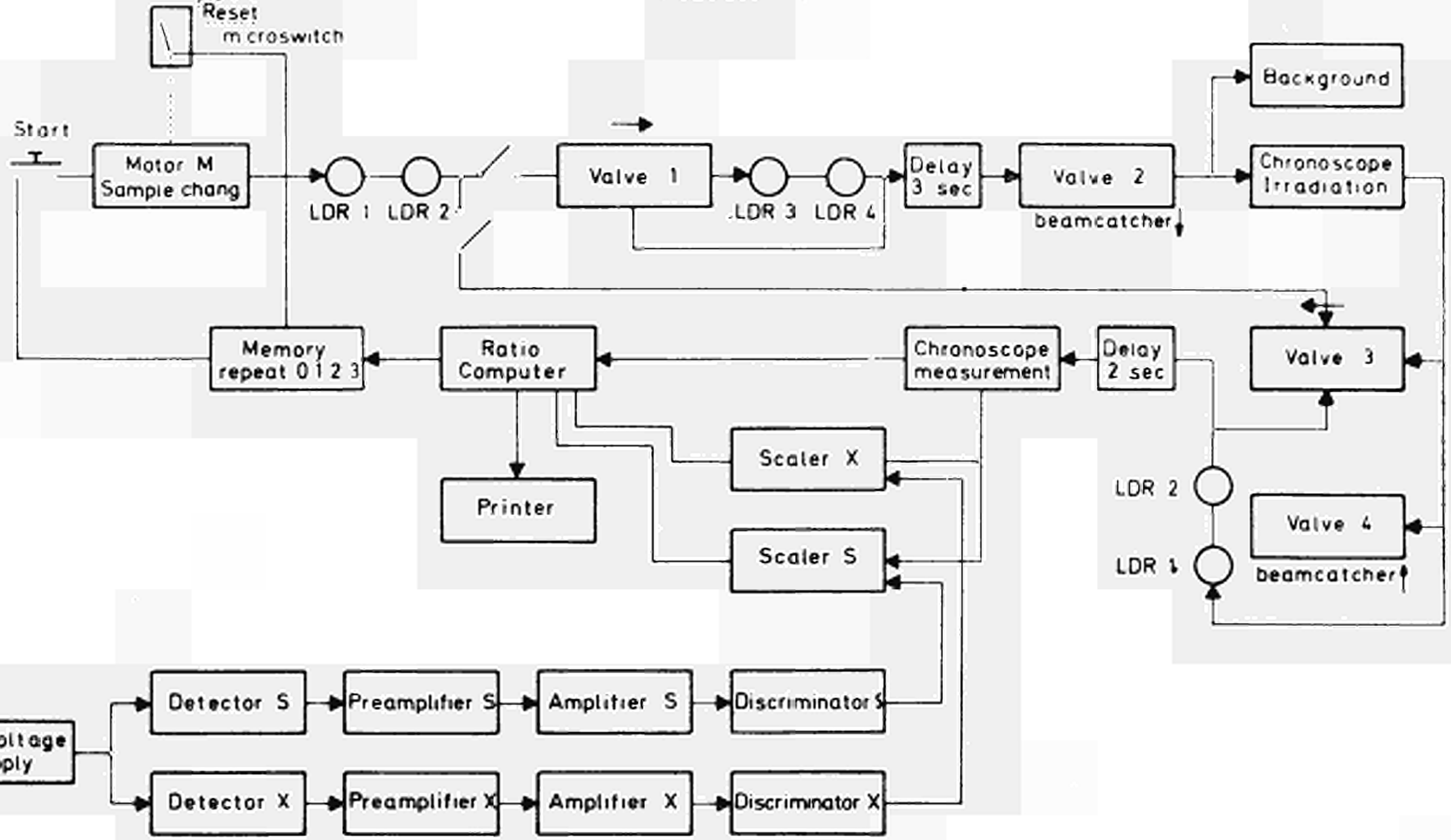
3.4. Analysis control panel.

In order to automate the complete analysis a control panel was designed, directing all manipulations in such a way that one intervention of the operator commands the analyses of a series of samples. As all actions have been connected in a serial way any faulty situation stops the cyclus and prevents the recording of erroneous results.

An outline of the control system is given in Fig. 3, 7. Provision has been made for manual intervention at the transport stage and also for action on the tantalum shield.

At the "start" order by the operator, the sample changer introduces a sample in the transport tube and a microswitch resets the whole apparatus. The presence of both sample and standard at the measuring site is photoelectrically controlled by means of light dependant resistors (L.D.R.) . If a positive reaction is obtained, a magnetic valve opens and the transport to the irradiation site is made. The arrival of sample and standard is again photoelectrically sensed and the air pressure is no longer applied. After a 3 sec delay the tantalum shield is lowered and the irradiation timer started. This 3 sec delay gives ample time to allow both samples to obtain their rest positions, thus preventing geometrical

FIG. 3.7


Reset
microswitch
Start
Motor M
Sample chang
LDR 1
LDR 2
Valve 1
LDR 3
LDR 4
Delay
3 sec
Valve 2
beamcatcher
Background
Chronoscope
Irradiation
Memory
repeat 0 1 2 3
Ratio
Computer
Chronoscope
measurement
Delay
2 sec
Valve 3
Printer
Scaler X
Scaler S
LDR 2
LDR 1
Valve 4
beamcatcher
High Voltage
supply
Detector S
Preamplifier S
Amplifier S
Discriminator S
Detector X
Preamplifier X
Amplifier X
Discriminator X

uncertainties of the irradiation. Three irradiation times are optional, 5, 10 and 15 sec. At the end of the period the tantalum target is brought into the deuteron beam, the return-magnetic valve is opened and the background correction is introduced in both scalers. When the presence of sample and standard at their respective measuring station is detected and an imposed delay of 2 sec has passed both scalers are started for 30 sec.

At the end of the activity measurements, the counts obtained are recorded and the result of the analysis calculated. The possibility exists also of decoding both scalers into an electronic computer, where the ratio of the recorded activities is multiplied by the analysis factor K', thus producing the result in mg oxygen, which is afterwards printed out.

The whole cyclus takes up about 45 sec. In order to obtain complete decay of the ^{16}N activity, an additional delay of 15 sec is then introduced. Hereafter two possibilities exist :

- or a new sample is introduced by revolving the sample changer;
- or the sample is analysed again up to 2 times before a new sample is introduced.

The complete system accelerator, control panels and measuring equipment has been installed in 3 adjoiningrooms of 3 m x 5 m. The neutron generator is separated from the rest of the apparatus by the middle room where the aircompressor and the magnetic valves are located, together with the concrete shielding as will be described below.

4. BIOLOGICAL PROTECTION.

As 14 MeV neutrons represent an important radiological hazard, the upper limit for a 40 hr week has been internationally established not to exceed 10 neutrons/cm^2/sec.

Whereas distance is by far the least expensive and most effective flux reducer, its limitations are quite obvious. Additional protection can be provided by low Z, high hydrogen content materials, such as water, paraffine, polythene and concrete (8, 44, 45). In this instance common concrete blocks (s.g.: 2.2) of 20 x 19 x 40 cm have been adopted. They lend themselves easily to be built into walls of any desired shape.

Although calculation taking into account distance and wall-thickness with associated stopping power of the concrete, showed that the biological protection was more than adequate, flux measurements have been made at the most important and most dangerous points of the final set-up.

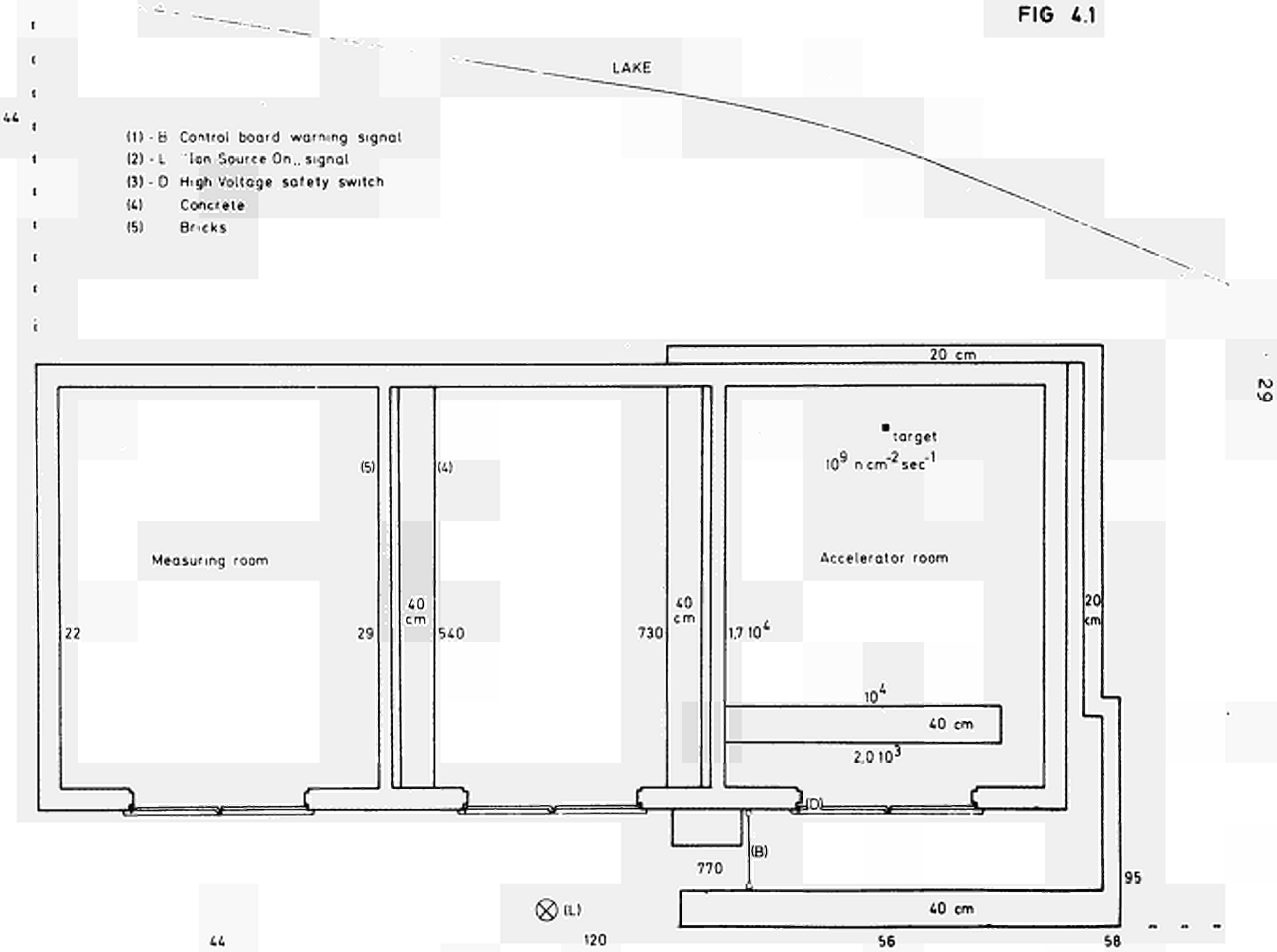
In order to achieve this a BF_3-counter surrounded by 5 cm of paraffine was calibrated with a Cu-foil activated by the $^{63}Cu(n,2n)^{62}Cu$ reaction and absolutely measured. A value of 0.5 barn was adopted as cross section for this reaction. Absolute counting was by gamma spectrometry using a 3 x 3 inch crystal according to the procedure recommended by Heath (43).

The results of this flux distribution survey have been mapped in Fig. 4,1, together with the actual implantation of the complete activation apparatus.

The plotted values are expressed in n/cm^2/sec for a flux at the sample irradiation site of 10^9/n/cm^2/sec. At a maximum beam intensity, on a new tritium target of 4 Ci, the actual flux at the sample site, can be estimated at 5 times this value.

As the neutron production in actual working conditions is only for 5 sec per min, the flux levels in the counting room are well below the accepted tolerance levels. Furthermore no energy degradation of the 14 MeV neutrons has been considered, although, this fact raises the tolerance levels.

FIG 4.1


LAKE
44
(1) - B Control board warning signal
(2) - L ''Ion Source On,, signal
(3) - D High Voltage safety switch
(4) Concrete
(5) Bricks
29
20 cm
target
10^9 n cm^{-2} sec^{-1}
(5)
(4)
Measuring room
Accelerator room
40 cm
40 cm
22
29
540
730
1,7 10^4
20 cm
10^4
40 cm
2,0 10^3
(D)
(B)
770
95
(L)
40 cm
44
120
56
58

As additional safety measures for unauthorised persons

- an external signal lamp flashes its light when the ion source is switched on;
- a warning signal on the accelerator control board is switched on when barrier B is passed;
- the High Voltage supply is automatically cut off when door D is opened, thus stopping all neutron generation.

5. NUCLEAR INTERFERENCES AT THE OXYGEN ANALYSIS IN STEEL.

5.1. Direct interferences.

Most nuclear interferences are eliminated by the short irradiation times and the high γ-energy of ^{16}N. Only a radioactive isotope of half life longer than 0.5 sec associated with β- or γ-energies of more than 4.5 MeV will interfere. Isotopes with these characteristics are few, only two being of reasonable interest.

5.1.1. Fluorine interference.

^{19}F with an isotopic abundance of 100% gives rise to activities with 14 MeV neutrons, according to the following reaction

$$^{19}F(n,\alpha)^{16}N.$$

It is obvious that no intervention can eliminate this interference. In order to evaluate its importance, a NaF sample was activated and its activity measured under standard conditions. From this it was calculated that 2.44 mg F produce the same activity as 1 mg of oxygen. This results in a 100% error on the oxygen determination when the F/O ratio in a sample is 2.44.

It should be noted that this experiment does not corrobate the values for the cross sections of this reactions as given in the literature (37). Indeed the ratio of the induced activities should be identical to that of the cross sections divided by the resp. atomic weights given as resp. $\frac{57}{19}$ and $\frac{40}{16}$ or a 0.85 O/F ratio, a discrepancy of a factor 3. A similar ratio was found by Vogt (24).

As in most steel samples fluorine is not present, this interference can be neglected. However should F be present in important concentrations, corrections can be applied as follows. Fluorine can be determined by the $^{19}F(n,p)^{19}O$ reaction giving rise to an isotope with $T_{1/2} = 27$ s and γ-energies of 0.2 and 1.37 MeV. The recorded oxygen concentration can then be corrected according to the equation

$$\text{ppm}_{\text{O present}} = \text{ppm}_{\text{O recorded}} - \frac{1}{2.44}\,\text{ppm}_{\text{fluorine}}$$

5.1.2. Boron interference.

Boron interferes (10, 13, 21) with the oxygen determinations by 2 reactions on the ^{11}B isotope, with 81% isotopic abundance.

$$^{11}B(n,\alpha)^{8}Li$$

$$^{11}B(n,p)^{11}Be$$

^{8}Li with a $T_{1/2}$ 0.84 sec is a pure β-emitter with a maximum energy of 13 MeV. The observed interference is due to the Bremsstrahlung and the direct interaction of the β's with the NaI(Tl) detector.

^{11}Be with a $T_{1/2}$ 13.6 sec is a β-emitter with max. energy of 11.5 MeV and γ-emitter of 9.3 and 4.5 MeV. A triple interference is therefore to be observed. Bremsstrahlung, β- and γ-interaction.

In order to measure the interference an oxygen-free boron compound was necessary. Nuclear grade boron carbide was available. After irradiation with 14 MeV neutrons, the induced activity was measured under standard conditions and compared with the pure oxygen produced activity of a standard. The decay curve analysis of the activity above 4.5 MeV allowed this correction for any oxygen present in the B_4C as is shown in Fig. 5, 1.

Results of the interference measurements are given in Table 5, I.

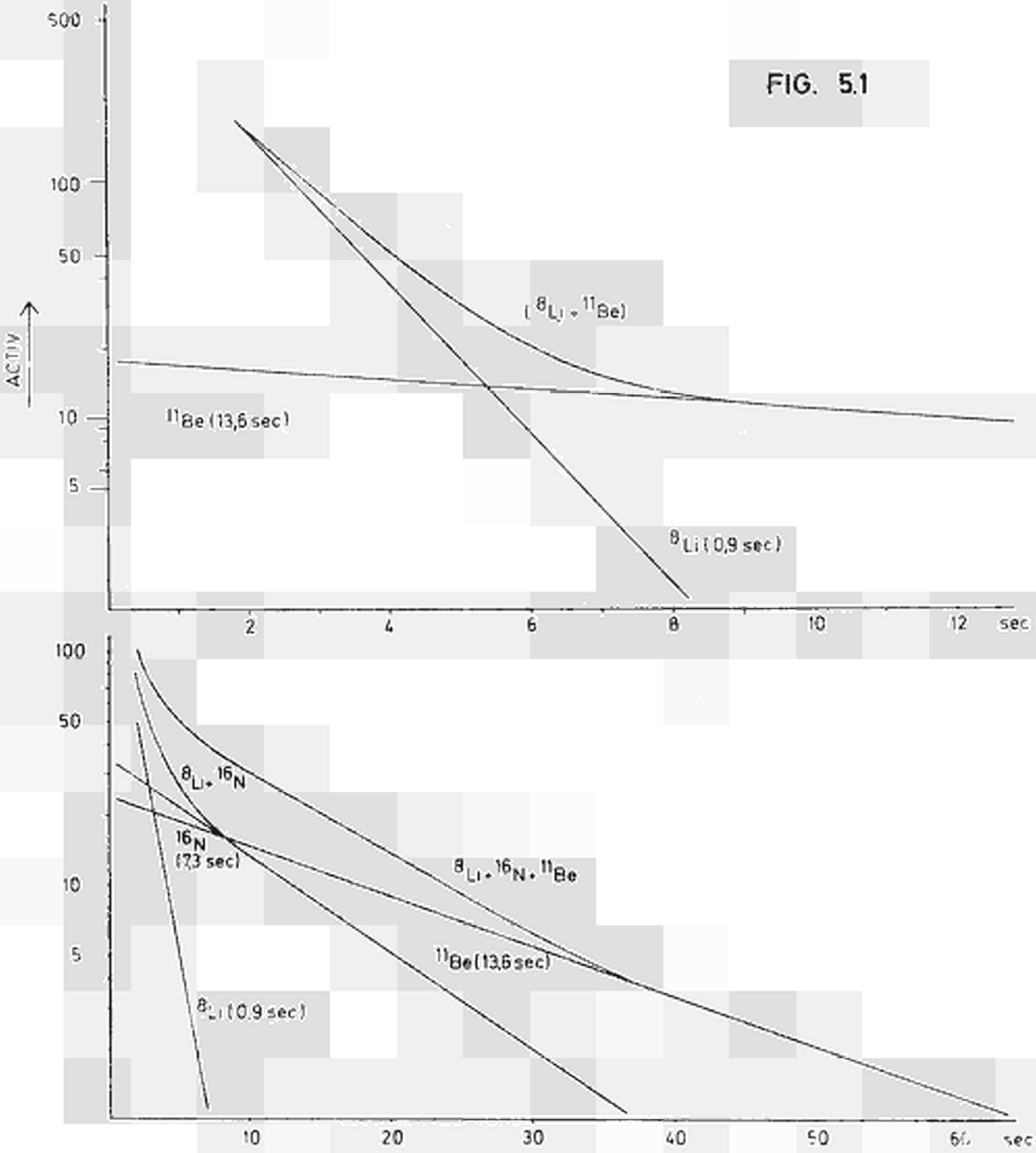


FIG. 5.1
500
100
50
10
5
ACTIV
(^{8}Li + ^{11}Be)
^{11}Be (13,6 sec)
^{8}Li (0,9 sec)
2
4
6
8
10
12
sec
100
50
10
5
^{8}Li + ^{16}N
^{16}N
(7,3 sec)
^{8}Li + ^{16}N + ^{11}Be
^{11}Be (13,6 sec)
^{8}Li (0.9 sec)
10
20
30
40
50
60
sec

TABLE 5, I.

Counting conditions			mg B giving rise to the same activity as 1 mg O	
Irradiation time (sec)	Delay between end of rradiation and counting (sec)	Counting time (sec)	Without Pb	With Pb
5	2	30	12	33
5	2	7	11	40
5	7	7	19	38

Under standard conditions, 12 mg B produces the same activity as 1 mg oxygen. However as the ^{8}Li half life is much shorter than that of ^{16}N and as the inverse applied to the ^{11}Be half life, the interference could be lowered by introducing a delay before the start of counting greater than the standard 2 sec, so as to let decay the ^{8}Li, and by choosing a counting time shorter than the normal 30 sec, the ^{16}N activity would be favored versus the ^{11}Be, As an example a counting time of 7 sec after 2 sec delay enhances the interference as only 1 half life of ^{16}N is counted together with all the ^{8}Li. A 7 sec delay and counting time lowers the interference as practically all ^{8}Li has decayed. However the effect is not very important as already one ^{16}N half life has passed before the counting is started.

A more efficient method however is to make use of the β-absorption in a Pb-shield of 2 mm thickness between sample and detector. The ^{16}N activity drops only for 15%, whereas as can be seen from Table 5,I, the boron interference is noticeably lowered. Combining the appropriate choice of a 7 sec counting time and 2 sec delay together with the β-absorption, an 100% error on the oxygen determination is obtained with a B/O weight ratio of 40, whereas in standard conditions a ratio of 12 gives the same error.

As boron is only present in special steels, the interference is generally to be neglected. When however B is present as an alloying element, corrections have to be made. This car be achieved by analysis of the decay curve of the induced activities or by double activity measurements. In the last method sample and standard are to be counted for 7 sec after a 5 sec delay and again 15 sec after the end of irradiation. From these two countings, the exact oxygen content of the sample may be calculated in a simple way.

5.2. Indirect interferences.

Important errors can be introduced in the ^{16}N measurement by coincidence and saturation effect in the detectors or electronic circuits. This will be the case when a very intense source is presented to the detector, even when the energy of the source is well below the discriminator level.

When activating steel samples the most important source of activity is ^{56}Mn with a $T_{1/2}$ of 2.6 h, produced by an (n,p) reaction on ^{56}Fe with cross section of 100 mb, as can be seen from Table 2, I.

Although the irradiation time of 5 sec is relatively short compared to the half-life, the ^{56}Mn activity will be quite high upon repeated activations. However even after a whole day of routine analysis with the same oxygen standard, no interference could be detected, as was established by a normal background count at the end of the working period.

An interference of the same kind can also be produced by an alloying element present in high concentration and having an important cross section for 14 MeV neutron reactions with the production of an isotope with a reasonable half life. This is most likely to happen for copper. It gives rise to ^{62}Cu with a cross section for the (n,2n) reaction of 0.5 barn and a half life of 9.9 m.

As will be shown later, this interference in the oxygen determination in copper samples could only be detected after the 4th consecutive irradiation. It is obvious then that even for steel with high copper content no errors will be introduced, even at a triple analysis.

As a conclusion, it is safe to state that oxygen determinations will be erroneous only in boron steel, and even for these samples correction can be made by decay curve analysis or by double activity measurements.

6. REPRODUCIBILITY AND ACCURACY.

Errors of reproducibility on the determination of oxygen will be based on two different causes :

- geometry variations of the positionning of sample and standard during irradiation and measurement;
- statistical errors associated with the radioactivity phenomenon.

6.1. Geometry errors.

The internal section of the transport tubes has a width of 7.5 mm. In order to avoid excessive wear of the aluminiumwalls a sample thickness has been imposed of 7.0 mm. In this way, sample and standard can position themselves within 0.5 mm, and even within 1.2 mm for the samples at the measuring station, as it is kept in the sample changer. This situation induces several causes of error at the irradiation and at the measurement.

6.1.1. Irradiation.

The neutron flux at the irradiation site presents an important gradient along the accelerator tube axis. The flux variations have been experimentally measured in the following way.

Copper foils have been wrapped around steel samples and introduced in the sample and standard irradiation positions, the neutron generator being positionned at different distances from the transportation system. The β^+ activities arisen from the reaction

$$^{63}Cu(n,2n)^{62}Cu \qquad T_{1/2}\ 9.9\ min.$$

have been measured, corrected for changes in neutron output by BF_3 monitoring and plotted on a log-log diagram versus the square of distance in mm (Fig. 6, 1).

From this figure it is seen that in the vicinity of the sample the flux gradient follows a 1/d law, whereas in the standard area the flux obeys a $1/d^2$ law.

It is obvious that a small change in position of the sample will have a much greater influence than the same change for the standard. This is most easily experienced in the determination of the factor K e.g. when the neutron generator has been moved.

Furthermore both faces of the sample to be analysed, being 7 mm apart, will not receive the same neutron flux. If the sample is homogeneous, this effect will pass unnoticed. If however an important oxygen inclusion is assymmetrically present on one side of the sample, a double activation of both faces of the sample will show the heterogeneity. Apart from an axial flux gradient, one has to take into account the fact that the disk source also gives rise to a lateral gradient (46). The lateral flux distribution, normalized to flux unity, as a function of lateral displacement d and as a function of axial distance R was computed by Op de Beeck (47) and is given in Fig. 6, 2.

The effect of both gradients has to be taken into account in the preparation of oxygen standards as is discussed under 7.

FIG. 6.1

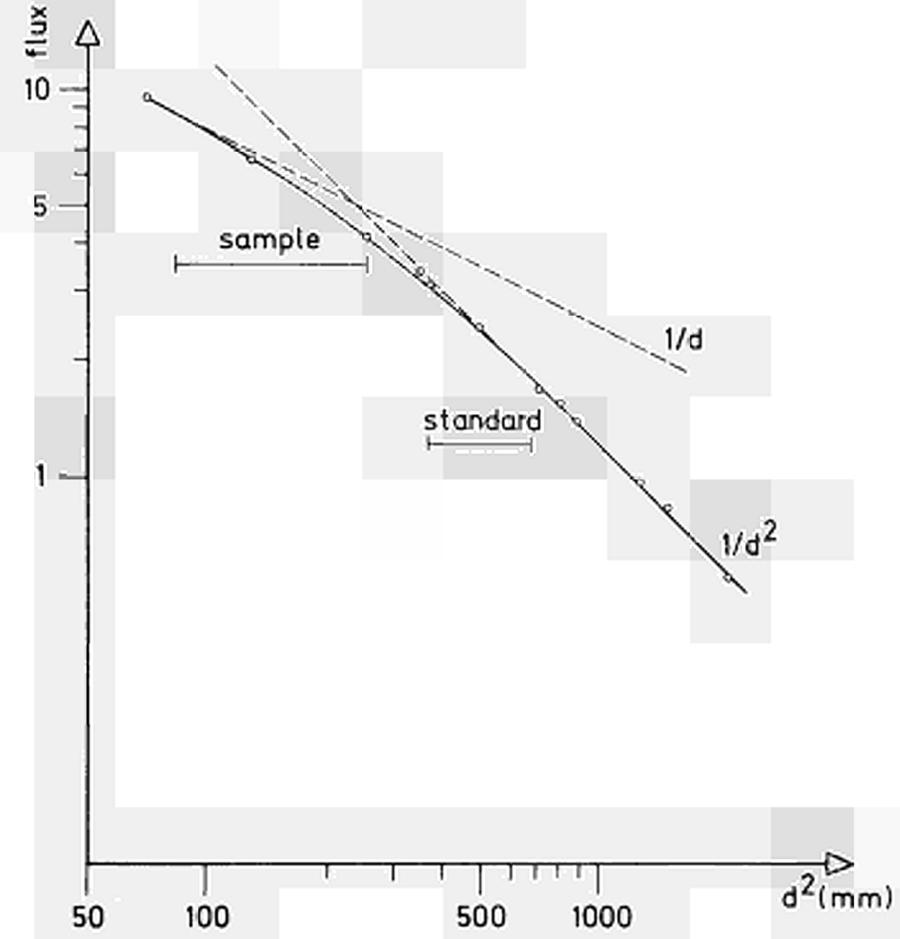
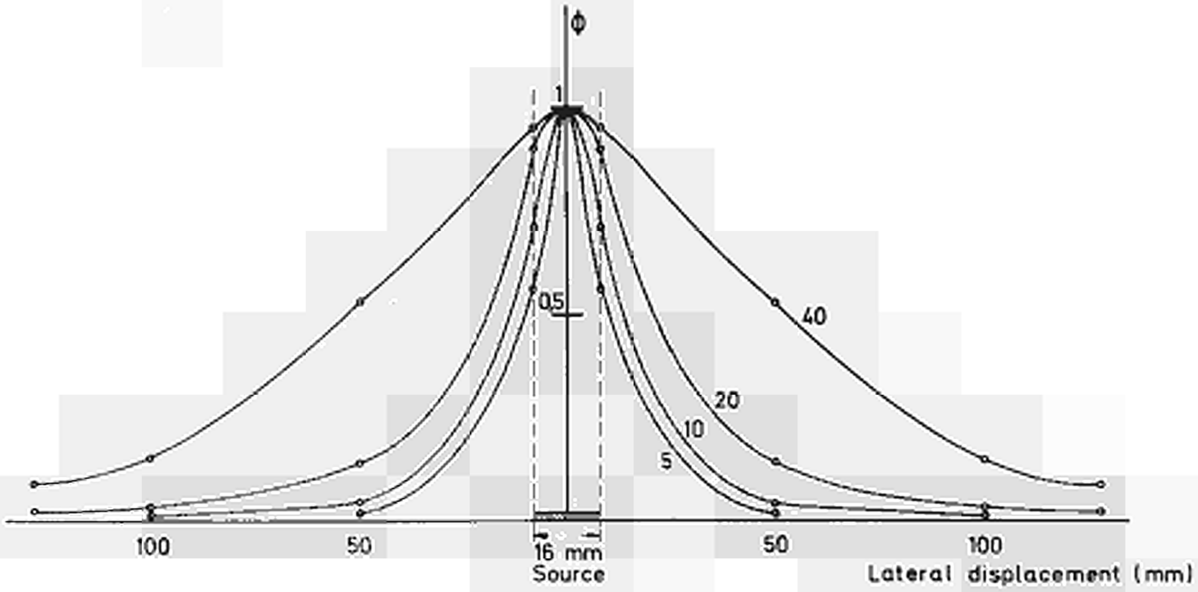

flux
10
5
1
sample
standard
1/d
1/d^2
50
100
500
1000
d^2(mm)

FIG. 6.2


ϕ
1
0.5
40
20
10
5
100
50
16 mm
Source
50
100
Lateral displacement (mm)

6.1.2. Activity measurement.

The solid angle under which the γ-rays of the ^{16}N enter the NaI crystals, will also vary with the positionning of sample and standard at the measuring stations.

It is obvious that the combined geometry errors will influence the value of the ratio factor K, already defined. As this influence is hard to calculate, experiments have been carried out where sample and standard where artificially forced to taken up one of the positions here under :

- normal position : sample and standard on irradiation and measurement are placed in the middle of their respective available spaces;
- maximum position : a maximum distance is imposed between sampl and standard at the irradiation, and at the measurement the sample is as near as possible and the standard as far away as possible from their detector;
- minimum position : sample is as far away as possible from the tritium target and the detector, the inverse applies for the standard.

Theoretically sample and standard can take the extreme positions. In actual analysis it is however obvious that a preferential and more or less reproducible positionning will occur, thus reducing errors due to this cause.

Results from this experiments show that :

K normal = 5.23
K maximum = 5.43
K minimum = 5.09

From this one concludes that the error on the oxygen determinations resulting from geometry errors will be at most -3.8% and +2.7%. It is clear that this "apparatus error" is independent from the oxygen content

6.2. Radioactivity measurement errors.

Radioactivity being a statistical phenomenon, the standard deviation on the measurement is given by $s = \sqrt{\text{recorded counts}}$.

As already has been seen, the oxygen content of a steel sample is calculated from a formula, where intervene

- counts recorded for the sample N_X;
- counts recorded for the standard N_S;
- weight of oxygen in the standard;
- ratio factor K.

The error on the oxygen content of the standard is to be neglected. The error on K, being determined with 2 standards, giving a sufficient high number of counts, is also negligible in relation with the error on the number of counts from the sample to be analysed.

Thus the error on the oxygen content expresses itself as follows

$$\frac{s_x}{x} = \sqrt{\left(\frac{s_{N_X}}{N_X}\right)^2 + \left(\frac{s_{N_S}}{N_S}\right)^2}$$

When the standard contains sufficient oxygen, an activity is therein produced under normal working conditions, so that

$$s_{N_S} \ll s_{N_X}$$

and finally the error on the determination is almost solely given by the error on the activity produced in the sample. This error is only dependent on the oxygen content, but can be reduced by increasing the produced activity, i.e. the neutron output.

As a result of analyses done on some 200 samples, a graph has been plotted where, as a function of the oxygen content, the standard deviation on one sample on at least 9 determinations is given in Fig. 6,3.

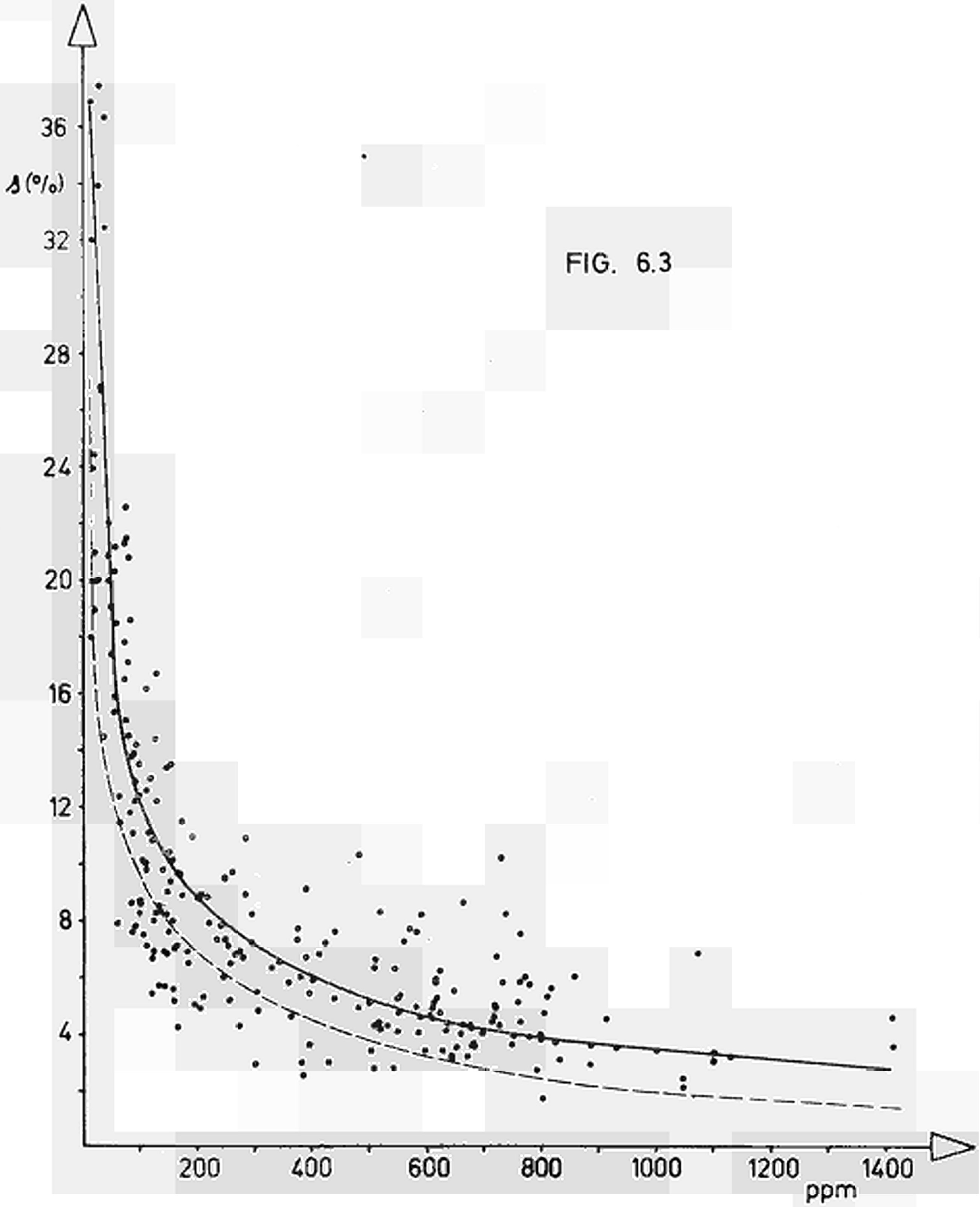


FIG. 6.3

The most probable line has been drawn through these points. A dotted line gives the error to be found when only the statistical phenomenon of radioactivity is taken into account.

The spread between the two lines is to be attributed to the "apparatus error" already mentionned, and is approx. of 1.5 to 2%. Points which are well out are produced by samples, which later on proved to be very inhomogeneous.

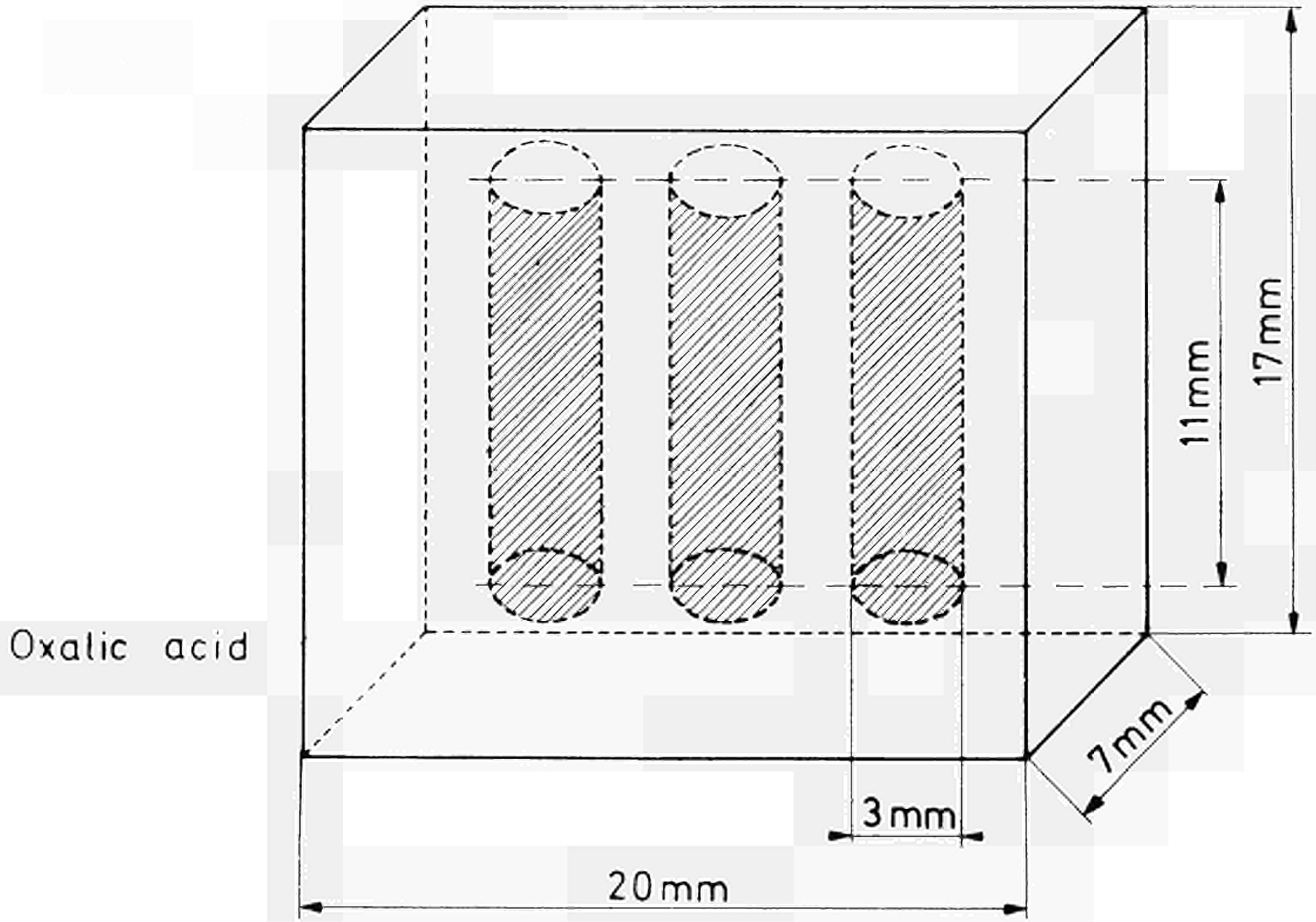
7. STANDARDS.

As has been previously described, due to the flux gradient, the specific activity produced upon irradiation in the standard will be lower by a factor of approx. 5 than in the sample. Also the error on the determination will be greatly influenced by the error on the activity measurement of the standard.

Combining both facts, the standards must contain a sufficient amount of oxygen to be of practical value, e.g. between 200 and 300 mg. This amount of material does not cause neutron shadowing, self shielding nor coincidence losses during the measurements, as was experimentally checked.

It is also necessary that the oxygen in the standards is as homogeneously distributed as possible. However steel with an oxygen content as high as and as exactly known as desired is not available. Therefore the standards in this work were prepared from ordinary steel, machined to the exact dimensions of the samples to be analysed. In this pieces, 3 holes were drilled, filled with a weighed amount of $(COOH)_2.2H_2O$ or Fe_2O_3 and stoppered with screws, as represented in Fig. 7, 1. Thus were obtained standards with approx. 200 mg of oxygen.

FIG. 7.1



This non-uniform distribution of the oxygen in the standard could cause errors when comparing with a homogeneous sample, as a biaxial flux gradient is present in the irradiation area. Dams and Adams (48) calculated that placing the oxygen in a layer in the middle plane of the sample causes a negative error of approx. 3.0%, due to the axial flux gradient. Concentrating however the oxygen in three holes, as shown in Fig. 7, 2, causes an error of +2.2%, due to the lateral flux gradient as shown by Op de Beeck (47). The resulting error can thus be estimated at -0.8%.

To check this influence experimentally, the specific activity ratio factor K was measured in 3 different ways :

- a "real" K_1 determined with two homogeneous samples = 3.00
- a "determined" K_2 as in activation analysis work with two standards; = 2.90
- an "analysis" K_3 as present in an activation, a homogeneous sample with a standard = 2.89

As can be seen from this values, the use of non homogenous standards, but prepared in the way described, introduces a negative standarisation error of 0.3% through the use of K_2 instead of K_3. The experimental sense of difference between K_1 and K_2 is in agreement with the calculated values.

8. SENSITIVITY.

From the preceding chapters it could be established that the following working conditions would be adequate for practically all steel samples to be analysed :

- a 300 µA irradiation for 5 sec at 150 kV;
- a 30 sec counting after a 2 sec delay.

This conditions typically yielded with a 2 Ci target 80 net counts for 1 mg oxygen or for 55 ppm in a 18 g sample.

The limit of detection can be set much lower. A 15 sec irradiation at a feasible beam current of 1.2 mA on a 5 Ci tritium target yields 1100 net counts for 1 mg of oxygen and adopting as limit half the background counts (40/30 sec) establishes with sufficient confidence the limit of detection at 1 ppm of oxygen in a 18 g sample or approx. 0.02mg.

This limit of detection could nowever be practically limited by two sources of contamination. One could conceive that the samples are contaminated by carying Al_2O_3 from the pneumatic tube at the irradiation site. It could be shown, that manual transport of the sample at the freshly polished irradiation site and pneumatic return of the sample, gives rise to the same results at a 10 ppm oxygen level. Moreover it has been stated (22) that ^{16}N recoil atoms introduce a positive error on the used polythene containers. Although the present method makes no use of containers, one can conceive that recoil can also occur on steel samples, which are slightly greased with vaseline, to insure a smoother transport. Samples irradiated in or without a steel box showed no different oxygen content at the 10 ppm level. Consequently it can be concluded that if the above effects exist at all, they do not affect the results for oxygen quantities of 0.2 mg or higher.

9. COMPUTATION OF THE AMOUNT OF OXYGEN IN AN UNKNOWN SAMPLE.

Starting with the classical activation analysis formula

$$\frac{g_X}{g_S} = \frac{Act_X}{Act_S} \qquad (3)$$

expressing the ratio of weight of element in experiment and in standard being equal to the ratio of the measured activities for the element, two conditions have to be fulfilled :

- the γ-detection efficiencies have to be the same for both samples;
- the flux in experiment and standard have to be identical.

As has been explained previously, this is not the case in the present experimental set up.

The actual calculation of the oxygen content of the unknown sample is therefore to be made with the following equation

$$g_X = g_S \cdot \frac{Act_X}{Act_S \cdot K} \tag{5}$$

where K is the factor correcting for differences in neutron flux and γ-detection.

10. DETERMINATION OF K.

When two identical standards are available it suffices to irradiate and count them at the same time, the ratio of the recorded activities giving K.

When 2 non identical standards even with unknown oxygen content, are available, K is determined by irradiating and counting them in sample and standard position (1) and again after switching their positions (2). Then

$$K = \sqrt{\begin{pmatrix}\text{ratio of}\\ \text{activities}\end{pmatrix}_1 \cdot \begin{pmatrix}\text{ratio of}\\ \text{activities}\end{pmatrix}_2} \tag{6}$$

Practically, for every series of analyses K was redetermined with 2 known but different oxygen standards. A typical value of K with the 18 g transport system was 4.19 $\pm$ 0.04 for 5 determinations. The observed values of K are highly dependent on the position of the accelerator relatively to the transport system, due to the already described flux gradients. The neutron generator parameters influence also the K-value, as the quality of the deuteron beam, incident on the tritium target, varies accordingly. When all conditions for K remained constant, the mean value of K over a 5 week period was 4.24 with extremes of 4.09 and 4.36.

11. RESULTS.

From the approx. 3,000 analyses on more than 200 steel samples of different origin and composition, some results are presented hereunder. It will appear clearly that the proposed oxygen analysis method does accept steel samples with oxygen contents ranging from a few ppm up to more than 1000. Results are also given for high-alloy steels and alloys where the other analysis methods failed up to now to give reliable results. A complete series of analyses given indicate the excellent corrolation between activation and the fusion method in the 400-800 ppm region. Lastly two graphs are presented which indicate the help by the activation analysis in improving the working conditions of the fusion method.

All results were obtained on 18 g samples.

Fig. 11, 1 represents the correlation between fusion and activation for 15 carbon steels ranging from 12 up to 1170 ppm. Crosses indicate the respective extreme values obtained by the two methods.

In Table 11, I together with the composition of the samples, results are given for the activation analysis for at least 9 determinations, together with fusion results when available.

$$s = \sqrt{\frac{\Sigma \Delta \bar{x}^2}{n(n-1)}}$$

with n being 9 or 12.

The excellent precision obtained, even for the low concentrations, should be noted.

The important differences for 2 samples of Lab. II must be attributed to the rather poor quality of the fusion technique used, as the same discrepancies were observed for carbon steels.

TABLE II, I.

Lab I.

% C	S	P	Si	Mn	Cu	Al	Cr	Ni	Co	Mo	W	Ti		ppm activ.	ppm fusion
1.57	0.05	0.12	0.32	0.44			12.28	0.11		0.78			0.51V	52±2	
0.06	0.10	0.20	0.47	1.26	0.13		16.50	11.91		2.25		0.30		30±2	
0.38	0.15	0.10	0.42	0.82			20.49	20.74	43.13	4.16	4.00			19±1	
0.06	0.09	0.20	1.34	0.36		1.48	23.50	0.18						30±2	
0.13	0.05	0.05	0.46	0.48			27.12	24.16	47.83					26±1	
0.05	0.05	0.10	0.64	0.45		0.03	20.59	77.22						106±2	
Lab. II.															
0.44			0.92	0.49	0.08		26.96	4.56		0.01				396±2	190
0.07		0.02	0.78	0.85	0.32		17.31	13.01		2.48			0.47Nb	98±2	90
0.09			0.42	0.56	0.27		17.28	2.62		0.16				206±2	201
0.06			0.90	0.48	0.04		28.55	0.20		0.02				321±3	250

FIG. 11.1

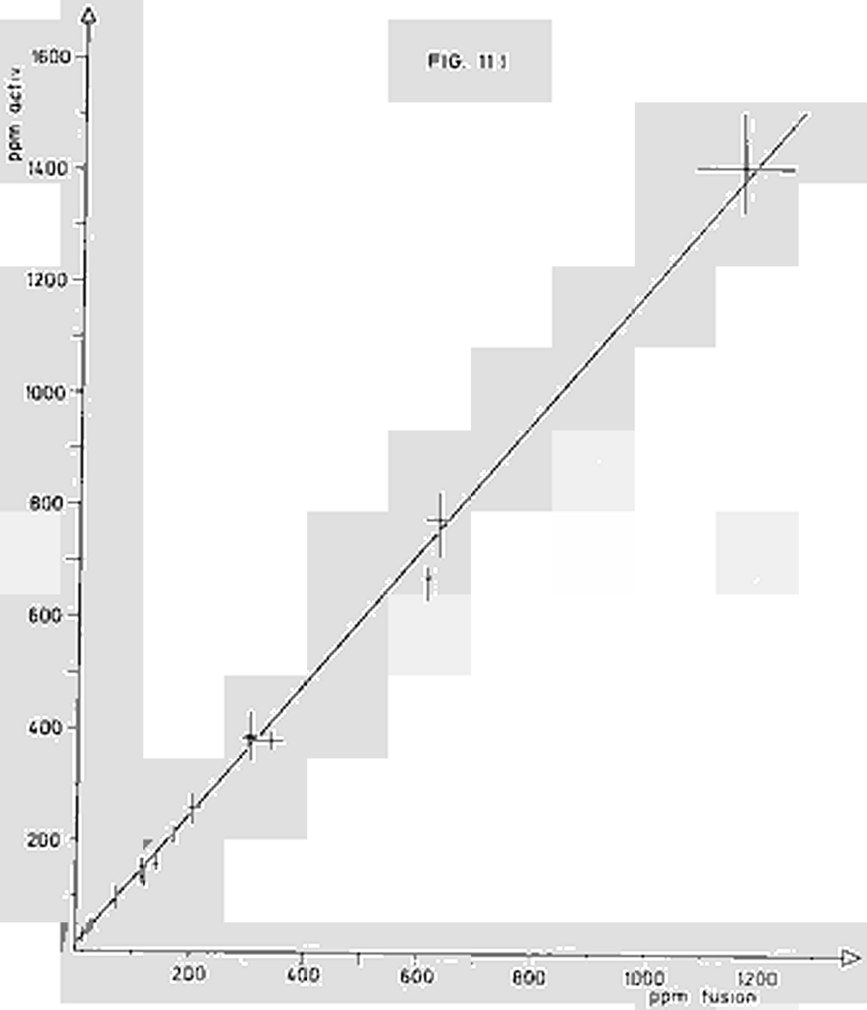


FIG. 11.2

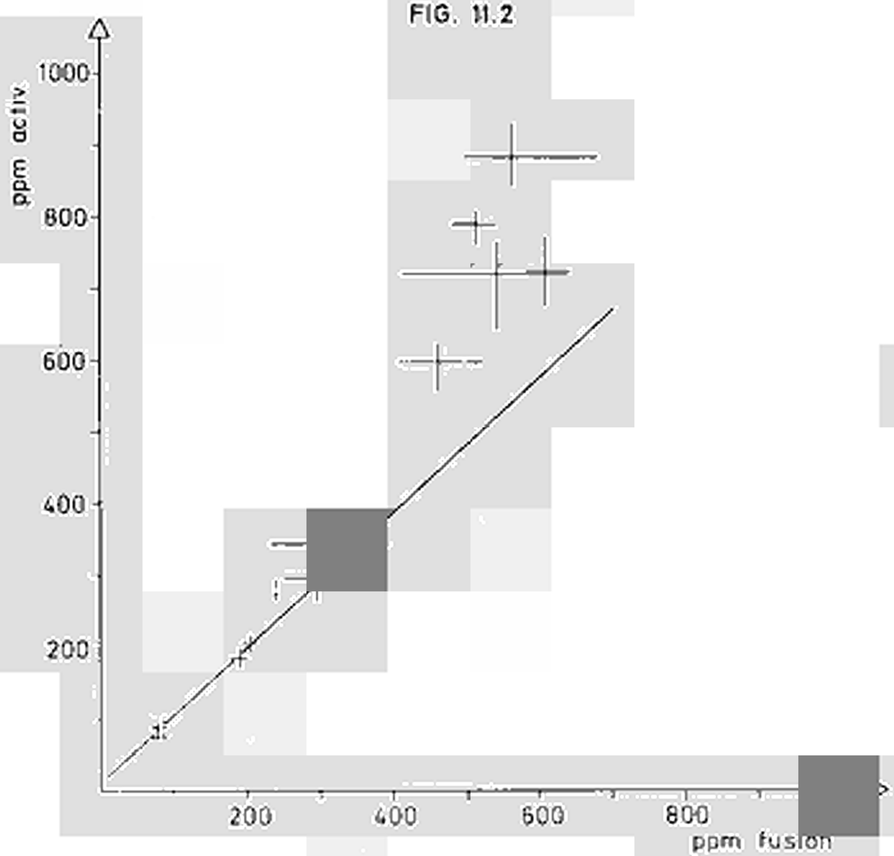
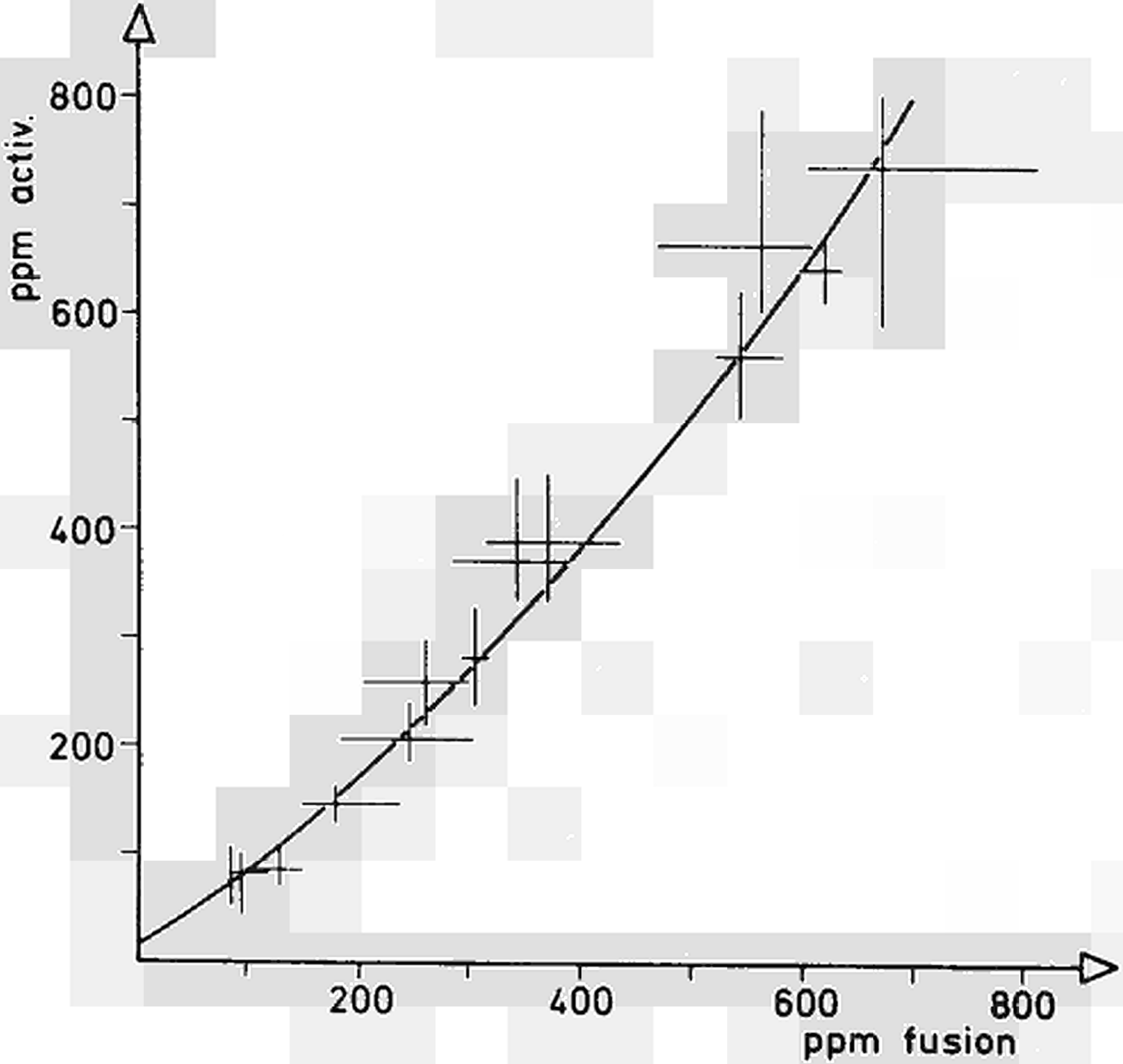


FIG. 11.3



In an investigation sponsored by the International Committee for the Study and Rationalisation of the Methods of Gas determination in Iron and Steel, 60 carbon steels were repeatedly analysed in an 8 day period. In order to present the reproductibility of the results in time and the possibility to detect inhomogeneous samples, all the individual results for both faces of the samples are given in Table 11, II together with the results from the fusion method in 2 or 3 laboratories.

As can be seen, the correlation between the two methods is excellent. For samples where results for both faces of the sample differ notably, the inhomogeneity of these samples was quite often proved by the fusion method (49).

When the correlation between the two methods was studied on carbon steel samples from an industrial laboratory, very poor results were obtained, especially when the oxygen content was higher than 300 ppm as shown in Fig. 11, 2. When later on this same laboratory changed its working conditions, e.g. increasing gas extraction time and temperature, the results improved remarkably as is shown in Fig. 11, 3, where the upper limit of the oxygen was increased to 600-700 ppm. Still later on, the correlation between the activation results and those obtained by the perfected fusion technique was of the same quality of these presented in Fig. 11, 1.

As a final conclusion, it was possible to establish an equation to express the corrolation between results obtained by the here proposed activation analysis method and by the well known reducing fusion technique.

$$\mathrm{ppm}_{\mathrm{Activ.}} = 15 + f.\mathrm{ppm}_{\mathrm{fusion}}$$

The equation factor f varies from one laboratory to the other, with a mean value of 1.02 for 7 laboratories, the extremes being 1.15 and 0.98. No explanation however is offered for the 15 ppm residual oxygen. As has already been explained, this quantity of approx. 0.25 mg cannot be attributed to Al_2O_3 from the transporttubes or from recoil ^{16}N.

Sample (1)	1st face (2)		2nd face (3)		fusion (4)	Sample (5)	1st face (6)		2nd face (7)		fusion (8)
2A	431		401			2B	362		394		
	440	422	419	412			407	380	400	395	
	396		415		400		371		392		340
	377				448		404				383
	481	428					404	397			
	427						382				
		421 s=30			424			391 s=16			362
4A	803		759			4B	800		823		
	825	812	800	768			838	819	778	794	
	809		746		830		819		782		770
	819		787		745		825		779		755
	796	807	781	783			901	835	747	773	
	807		782				780		792		
	810 s=11		776 s=20		787		827 s=41		783 s=25		762
6A	599		642			6B	648		582		
	666	638	556	596			661	636	591	560	
	650		590		590		600		508		570
	622				587		569		566		603
	600	619					588	592	562	555	
	636						619		536		
		618 s=35			588		614 s=35		557 s=31		587
8A	744		703			8B	736		739		
	737	731	658	684			757	738	732	758	
	713		691		720		722		803		730
	737		707		685		754				720
	774	750	722	701			710	733			
	738		673				734				
	740 s=20		692 s=25		702			713 s=27			725
10A	504		526			10B	589		564		
	561	540	528	541			602	592	557	576	
	554		568		520		585		606		540
	550				514		624		580		542
	566	549					562	603	547	566	
	531						622		571		
		543 s=22			517			584 s=25			541

(1)	(2)		(3)		(4)	(5)	(6)		(7)		(8)
12A	607		572			12B	585		563		
	632	621	529	541			606	585	568	563	
	625		522		540		564		559		570
	541		540		538		538				568
	572	563	565	544			649	583			
	577		527				562				
	592 s=35		544 s=21		539			577 s=33			569
15A	907		856			15B	1007		1004		
	873	892	877	871			1012	1018	1042	1038	
	895		880		860		1034		1067		920
	896		861		722		1026				1016
	913	899	846	859			1074	1059			
	887		870				1077				
		880 s=20			791			1038 s=29			978
16A	587		508			16B	634		593		
	661	619	592	552			600	607	551	601	
	610		556		590		586		659		560
	554		535		562		624				598
	579	568	603	578			600	629			
	570		595				662				
		579 s=38			576			612 s=36			579
19A	743		737			19B	820		805		
	803	795	745	753			854	841	736	778	
	840		777		720		848		793		690
	764				742		823		761		852
	726	764					881	849	780	784	
	803						844		812		
		771 s=38			731		845 s=22		781 s=29		771
20A	793		743			20B	725		650		
	864	825*	720	726			717	720	696	699	
	819		715		720		718		750		610
	763		700		735		695				672
	719	750	745	728			699	711			
	769		739				739				
		735 s=23			728			710 s=29			641

* Results omitted for the calculations.

(1)	(2)		(3)		(4)	(5)	(6)		(7)		(8)
21A	628		569			21B	602		514		
	605	614	591	571			617	606	564	547	
	610		554		590		598		562		515
	608		594		588		596		583		597
	643	629	639	610			587	598	557	576	
	636		597				610		588		
		606 s=28			589		602 s=11		561 s=26		556
22A	621		655			22B	666		675		
	572	615	640	643			659	677	655	677	
	653		633		625		705		702		625
	627				643		658				582
	649	643					662	680			
	652						720				
		634 s=26			634			678 s=24			603
23A	672		598			23B	606		589		
	587	622	664	608			610	607	576	588	
	607		563		520		586		599		595
	631				595		618				595
	623	618					631	642			
	599						677				
		616 s=35			558			610 s=30			595
24A	591		642			24B	771		722		
	633	622	627	638			793	787	737	727	
	643		645		650		797		711		710
	589				634		756		819		761
	632	619					755	752	735	782	
	635						744		791		
		626 s=21			642			761 s=34			736
25A	682		614			25B	649		660		
	645	661	614	617			675	671	614	655	
	655		623		610		690		691		585
	639		643		655		630				705
	645	633	684	638			681	654			
	614		589				652				
		637 s=28			633			660 s=27			645

(1)	(2)		(3)		(4)	(5)	(6)		(7)		(8)
26A	754		780			26B	728		759		
	704	738	765	763			797	752	759	741	
	755		744		685		730		725		740
	715				747		847				728
	795	748					831	823			
	734						791				
		750 s=29			716			772 s=46			732
27A	520		587			27B	789		691		
	557	534	517	562			739	768	690	701	
	526		581		555		775		723		690
	520		595		538		777				717
	538	529	557	576			664	703			
	530		575				667				
	532 s=14		569 s=27		547			724 s=49			704
28A	776		792			28B	749		652		
	758	790	731	767			727	713	723	692	
	837		778		740		664		700		705
	698		714		709		754				712
	725	721	772	756			692	739			
	741		783				771				
		758 s=39			724			714 s=41			709
29A	760		682			29B	693		712		
	765	736	734	713			667	684	729	718	
	682		722		645		693		713		665
	779				712		724				697
	679	745					702	735			
	778						780				
		731 s=42			679			713 s=31			681
30A	578		537			30B	528		493		
	602	584	524	533			467	513	474	477	
	571		539		605		543		464		550
	545		565		541		504		535		524
	521	522	576	569			522	504	520	539	
	499		597				486		563		
		552 s=30			573			508 s=32			537

(1)	(2)		(3)		(4)	(5)	(6)		(7)		(8)
01A	538		513			01B	493		525		
	544	519	481	511			525	496	508	512	
	575		540		515		471		502		522
	501				490		494				490
	456	501			560		490	494			580
	546						497				
		511 s=34			522			501 s=17			531
02A	604		608			02B	674		666		
	653	622	600	603			693	690	695	669	
	609		601		623		713		647		725
	667		575		560		691				620
	615	644	661	625	670		715	685			680
	651		639				649				
		624 s=29			618			682 s=25			675
03A	535		552			03B	608		564		
	531	526	540	542			521	561	529	553	
	511		535		498		555		565		554
	526				490		521				475
	557	521			550		492	527			550
	480						567				
		530 s=23			513			547 s=35			526
04A	610		555			04B	618		618		
	602	604	612	581			669	620	589	616	
	601		576		617		572		642		593
	563				550		581				560
	555	569			560		629	602			550
	588						595				
		585 s=23			576			613 s=31			568
05A	694		685			05B	689		640		
	733	714	707	702			648	675	668	656	
	715		714		665		689		659		643
	647				600		588				570
	665	677			620		635	607			600
	719						597				
		698 s=28			628			645 s=36			614

(1)	(2)		(3)		(4)	(5)	(6)		(7)		(8)
06A	654		662			06B	703		723		
	651	648	638	657			672	679	661	699	
	638		670		631		662		714		674
	639				560		672				680
	697	651			580		667	659			610
	618						637				
		652 s=23			590			679 s=28			655
07A	526		525			07B	519		562		
	521	528	553	524.			547	530	544	554	
	537		493		535		525		555		522
	487				520		537		539		520
	512	496			470		522	531	556	553	560
	490						535		564		
		516 s=23			508			542 s=15			534
08A	642		659			08B	614		689		
	681	661	621	640			694	662	698	678	
	661		641		680		678		648		666
	633				590		659				670
	635	630			630		670	655			670
	623						635				
		644 s=20			633			665 s=29			669
09A	835		861			09B	835		784		
	786	800	746	821			868	838	857	821	
	781		856		726		812		822		774
	787				655		824				755
	808	797			910		847	841			760
	795						852				
		806 s=38			764			833 s=26			763
10A	517		491			10B	519		538		
	555	534	522	516			496	502	516	525	
	529		535		505		490		524		500
	506				500		494		513		565
	553	508			540		499	504	514	510	510
	465						518		503		
		519 s=22			515			510 s=14			525

12. OXYGEN ANALYSIS IN NON-FERROUS METALS.

12.1. Introduction.

As a normal extension of the proposed steel analysis method, the oxygen analysis in various non ferrous materials was considered. It is well-known that for the reducing fusion method these matrices can present several difficulties : e.g. gettering effect for Zn, Cu, Al, Pb, etc. or high melting points for Nb, Ta, etc.

Whereas in steel analysis no container was used, the lack of mechanical stability of some metals made the use of a container necessary. A frame or a box was machined for this purpose, from carbon steel, with a blank value of approx. 0.5 mg oxygen. This frame accepted samples of 18 x 15 x 7 mm, whereas the box accomodated 17 x 14 x 5 mm samples.

While most elements do no cause nuclear interferences, for some of them, Pb, Zr, Cu and Al, changes in the analysis procedure had to be introduced to eliminate or to correct for sources of errors.

Surface oxidation for several of the metals studied was an important cause of positive errors, especially for the low oxygen contents encountered. Cleaning the samples with abrasive silicon carbide paper under perchloro-ethylene, and keeping them afterwards in the same solvent was an adequate solution to this problem. It must be noted that metals like Ta, Nb, Cu, Pb and Zn do behave quite differently in this aspect. Where a Ta sample with 17 ppm oxygen takes up oxygen very rapidly (4 min) yielding a 25 ppm concentration, a Zn sample has an oxygen content increasing slowly (10 min) from 15 to 20 ppm under the same working conditions.

As it was desirable to use the same oxygen standards as for the steel analysis, an extensive study was made of this point. Indeed, according to Anders (14) and Fujii (15) important errors are introduced when the samples of different material are analysed with an unique standard, the reason being differences in neutron adsorption, -scattering and energy degradation.

12.2. Matrices without nuclear interferences.

From the study of the nuclear data given in Table 12, I, it appears that for Bi, Zn, Cd, Co, Nb, Ta and Ti no nuclear interferences for the oxygen determination were to be feared. Indeed upon irradiation with 14 MeV neutrons no radioactive isotopes are produced in these matrices with a β- or γ-energy exceeding the choosen energy discrimination of 4.5 MeV. Even more, or the cross sections for the given reactions are so low or the half-lives of the radioactive species are so long that no high intensity sources are formed which could saturate the detection systems. It was therefore possible to determine the oxygen contents of the given materials in the same way as in the steel analysis. It was however frequently necessary to step up the beam intensities, 600-900 µA, to obtain sufficient precision at the low concentrations found.

12.3. Matrices with nuclear interferences.

In the oxygen analysis of Pb, Zr, Cu and Al, nuclear interferences were encountered. The most probable nuclear reactions with 14 MeV neutrons for these materials are given in Table 12, II. Although no isotopes are produced with energies (β or γ) greater than 4.5 MeV, several short living species with intense activities are formed which then cause errors by coincidences or saturation. It should indeed be remembered that, depending on the density of the metals, 10 to 40 g samples are irradiated.

Lead and zirconium give resp. rise to the isotopes ^{207m}Pb and ^{90m}Zr with half-lives of about 0.8 sec. It is obvious that with a 5 sec irradiation practical saturation is achieved. In standard conditions, with a counting delay of 2 sec, in the first seconds of the measurement an important activity is recorded, only due to coincidences and saturation of the detector and the electronic circuits. Introducing a 10 sec delay should permit unhindered ^{16}N activity measurements. This was experimentally checked

TABLE 12, I.

Reaction	Irradiated isotope		Reaction product		
	%	(mb)	$T_{1/2}$	E_{max} β (MeV)	E_{γ} (MeV)
${}^{09}\mathrm{Bi}(n,p){}^{209}\mathrm{Pb}$	100	1	3.2 h	0.63	-
${}^{09}\mathrm{Bi}(n,\gamma){}^{206}\mathrm{Tl}$	100	1	4.2 min	1.51	-
${}^{4}\mathrm{Zn}(n,p){}^{64}\mathrm{Cu}$	48.9	350	12.8 h	0.57; β^+ 0.66	1.34
${}^{4}\mathrm{Zn}(n,2n){}^{63}\mathrm{Zn}$	48.9	180	38.3min	β^+ 2.32; β^+ 1.40	2.60; 1.90; 0.97
${}^{6}\mathrm{Zn}(n,p){}^{66}\mathrm{Cu}$	27.8	80	5.1 min	2.63; 1.65	1.04
${}^{8}\mathrm{Zn}(n,p){}^{68}\mathrm{Cu}$	18.6	25	32 s	3.00	-
${}^{3}\mathrm{Nb}(n,\alpha){}^{90g}\mathrm{Y}$	100	9	64 h	2.26	-
${}^{3}\mathrm{Nb}(n,2n){}^{92}\mathrm{Nb}$	100	500	13 h	-	1.84; 0.93
${}^{81}\mathrm{Ta}(n,p){}^{181}\mathrm{Hf}$	99.9	2.5	46 d	0.40	0.61; 0.48; 0.14
${}^{81}\mathrm{Ta}(n,2n){}^{180m}\mathrm{Ta}$	99.9	1100	8.1 h	0.71; 0.61	0.11
${}^{14}\mathrm{Cd}(n,p){}^{114}\mathrm{Ag}$	28.9		2 min		
${}^{14}\mathrm{Cd}(n,\alpha){}^{111g}\mathrm{Pd}$	28.9	0.51	22 min	2.15;1.04;0.80; 0.70	0.34; 0.24
${}^{12}\mathrm{Cd}(n,2n){}^{111m}\mathrm{Cd}$	24.07		48.6min	-	0.25; 0.15
${}^{10}\mathrm{Cd}(n,p){}^{110}\mathrm{Ag}$	12.4		24 s	2.84; 2.16	0.94
${}^{9}\mathrm{Co}(n,p){}^{59}\mathrm{Fe}$	100	81	45 d	1.56;0.46;0.27	1.29; 1.10; 0.19
${}^{9}\mathrm{Co}(n,\alpha){}^{56}\mathrm{Mn}$	100	30	2.6 h	2.86;1.05;0.70	3.20;2.93;2.69; 2.56;2.10;1.80;0.84
${}^{9}\mathrm{Co}(n,2n){}^{58m}\mathrm{Co}$	100	800	9.2 h	β^+ 0.48	1.62; 0.81
${}^{58}\mathrm{Co}$		385	72 d	-	0.025
${}^{8}\mathrm{Ti}(n,p){}^{48}\mathrm{Sc}$	73.5	66	44 h	0.64	1.33; 1.05; 0.98
${}^{6}\mathrm{Ti}(n,2n){}^{45}\mathrm{Ti}$	7.9	20	3.07h	β^+ 1.02	-
${}^{7}\mathrm{Ti}(n,p){}^{47}\mathrm{Sc}$	7.7	200	3.43 d	0.62; 0.44	0.18
${}^{9}\mathrm{Ti}(n,p){}^{49}\mathrm{Sc}$	5.5	55	57 m	2.05	-

TABLE 12, II.

Reaction	Irradiated isotope	Reaction product			
	%	(mb)	$T_{1/2}$	$E_{max}\ \beta$ (MeV)	$E\ \gamma$ (MeV)
$^{208}Pb(n,p)^{208}Tl$	52.3	0.96	3.1min	2.37; 1.79; 1.28	2.61;0.86;0.58; 0.51;0.27
$^{208}Pb(n,\alpha)^{205}Hg$	52.3	1.58	5.5min	1.60	-
$^{208}Pb(n,2n)^{207m}Pb$	52.3	1700	0.84 s	-	1.01; 0.50
$^{207}Pb(n,p)^{207}Tl$	22.6		4.8min	1.44	-
$^{90}Zr(n,2n)^{89m}Zr$	31.5	80	4.4m	-	0.59
^{89}Zr		700	79 h	β^+ 2.43; β^+ 0.90	0.91
$^{90}Zr(n,n')^{90m}Zr$	51.5		0.83 s	-	2.30
$^{94}Zr(n,p)^{94}Y$	17.4	10	16.5min		-
$^{94}Zr(n,\alpha)^{91}Sr$	17.4	5	9.7 h	2.70; 1.40; 0.80	1.41;1.02;0.93; 0.75;0.64;0.55
$^{91}Zr(n,p)^{91m}Y$	11.2	17	50 min	-	0.55
^{91}Y		180	61 d	1.55; 0.36	1.16
$^{91}Zr(n,2n)^{90m}Zr$	11.2		0.83 s	see $^{90}Zr(n,n')^{90m}Zr$	
$^{96}Zr(n,\alpha)^{93}Sr$	2.8	5	7 min		
$^{63}Cu(n,2n)^{62}Cu$	69.1	500	9.9min	β^+ 2.91	-
$^{65}Cu(n,p)^{65}Ni$	30.9	30	2.6 h	2.10; 1.01; 0.60	1.49; 1.12; 0.37
$^{65}Cu(n,\alpha)^{62g}Co$	30.9	7.5	14 min	2.80; 0.85	2.50;2.00;1.70; 1.50;1.17;1.00
$^{65}Cu(n,2n)^{64}Cu$	30.9	1000	12 h	0.57, β^+ 0.66	1.34
$^{27}Al(n,p)^{27}Mg$	100	60	9.5min	1.75; 1.50	1.02; 0.84; 0.17
$^{27}Al(n,\alpha)^{24}Na$	100	120	15 h	1.40	2.76; 1.38
$^{27}Al(n,2n)^{26m}Al$	100		6.6 s	β^+ 3.20	-

as given in Table 12, III with a zirconium sample where the oxygen concentration is given as function of the delay between end of irradiation and start of counting.

TABEL 12, III.

	Irradiation (sec)	Delay (sec)	Counting (sec)	ppm
A	5	2	30	4,670
B	1	1,5	3	47,960
C	5	2	7	7,330
D	5	10	30	1,110

When the activity, measured under standard conditions (5 sec irradiation, 2 sec delay and 30 sec counting), is normallised as 100% of the total activity for both ^{90m}Zr and ^{16}N, then in experiment B 100% of the zirconium activity is recorded with only 8% of the ^{16}N counts, thus giving extremely high results. Although in experiment C still 100% of the ^{90m}Zr is counted, measuring 53% of the total oxygen produced counts decreases the error. In the finally choosen conditions, where no ^{90m}Zr is counted, 50% of the ^{16}N activity is registered.

For lead analyses, the activity of the matrix is lower than for zirconium, so that a delay of 5 sec suffices to insure an interference free oxygen determination.

In the copper analysis a saturation effect is noticeable, due to the very intense 9.9 m annihilation radiation produced in the matrix. The interference was experimentally checked when the same copper sample was irradiated 10 times for 5 sec at 300 µA at a rate of 10 sec per cycle. After the complete ^{16}N decay, repeated background measurements were made as a function of time for both sample and oxygen standard and their ratios compared to those obtained with non activated samples. The results are given in Table 12, IV.

TABLE 12, IV.

	Ratio background sample/standard
original	1.03
after 5min	1.27
15	1.19
25	1.08
35	1.03
45	1.00
55	1.03

From this results it can be concluded that only after 4 consecutive irradiations at the standard periodicity (1 analysis per minute) the Cu interference will be measurable.

While analysing Al samples it was noticed that the recorded ^{16}N activity increased continuously upon repeated irradiation. As appears from Table 12, II ^{27}Mg, because of cross-section and β - γ energies can be excluded from the possible interferences. Upon analysis of the decay curve above 4.5 MeV a long-living species was found and could be attributed to the 15 h ^{24}Na isotope with a 2.75 γ-ray. By double counting this error can be corrected. Gammaspectrometry showed also the presence of the 511 MeV β^+ annihilation radiation of ^{26m}Al. Decay curve analysis above 4.5 MeV did not yield information about the possible, but unlikely, interference of the 3.20 MeV β^+ activity when measuring ^{16}N. This impossibility of course is due to the small difference in half-life : 6.6 sec versus 7.4 sec. As however even for aluminium with very low oxygen content the measured half-life was always larger than 7 sec, the errors caused by the matrix itself will be unimportant. (*)

(*) When writing this report, the authors read an article by Fujii, who came to similar conclusions (Japan Analyst, 15, 1245 (1966)).

From the above considerations the following analysis procedure was finally adopted : 5 sec irradiation, 2 sec delay, first counting during 30 sec, 1 min delay, second counting for 30 sec. The second counting result is directly substracted from the first, as the decay of ^{24}Na is negligible in a 2 minutes interval.

12.4. Standards.

The materials studied in this part of the work have widely varying physical and nuclear properties. This densities range from 2.7 for Al to 16.6 for Ta, their atomic densities varying by a factor of 3. The total cross sections for 14 MeV neutrons vary from 1.7 to 5.5 barns, their macroscopic cross sections varying by a factor of 2.7. A survey is given in Table 12, V.

Anders (14) and Fujii (15) has shown that matrix effects on 14 MeV neutrons are not to be neglected, regarding differences in scattering effect and energy degradation. However it would be very interesting if an unique oxygen standard, such as prepared for the steel analysis, could be used throughout the whole range of materials under investigation.

Experiments were undertaken where a standard was irradiated in the sample position and backed by different materials; the activity in this standard recorded and related to a steel backing. The inverse was also done where a standard in the standard position was activated, being protected by the different materials under investigation, and its activity again related to the reference steel.

The different matrices were Al, Bi, Nb, Ta, Co, Cd and Cu. The results are given in Table 12, VI and Fig. 12, 1, and plotted versus ascending atomic density and total macroscopic cross sections. No significant influence of the matrix can be found outside the experimental errors. This was ascertained when a cobalt-oxygen standard was prepared in a manner described earlier, and Co-samples were analysed against both Co and steel standard.

FIG. 12.1

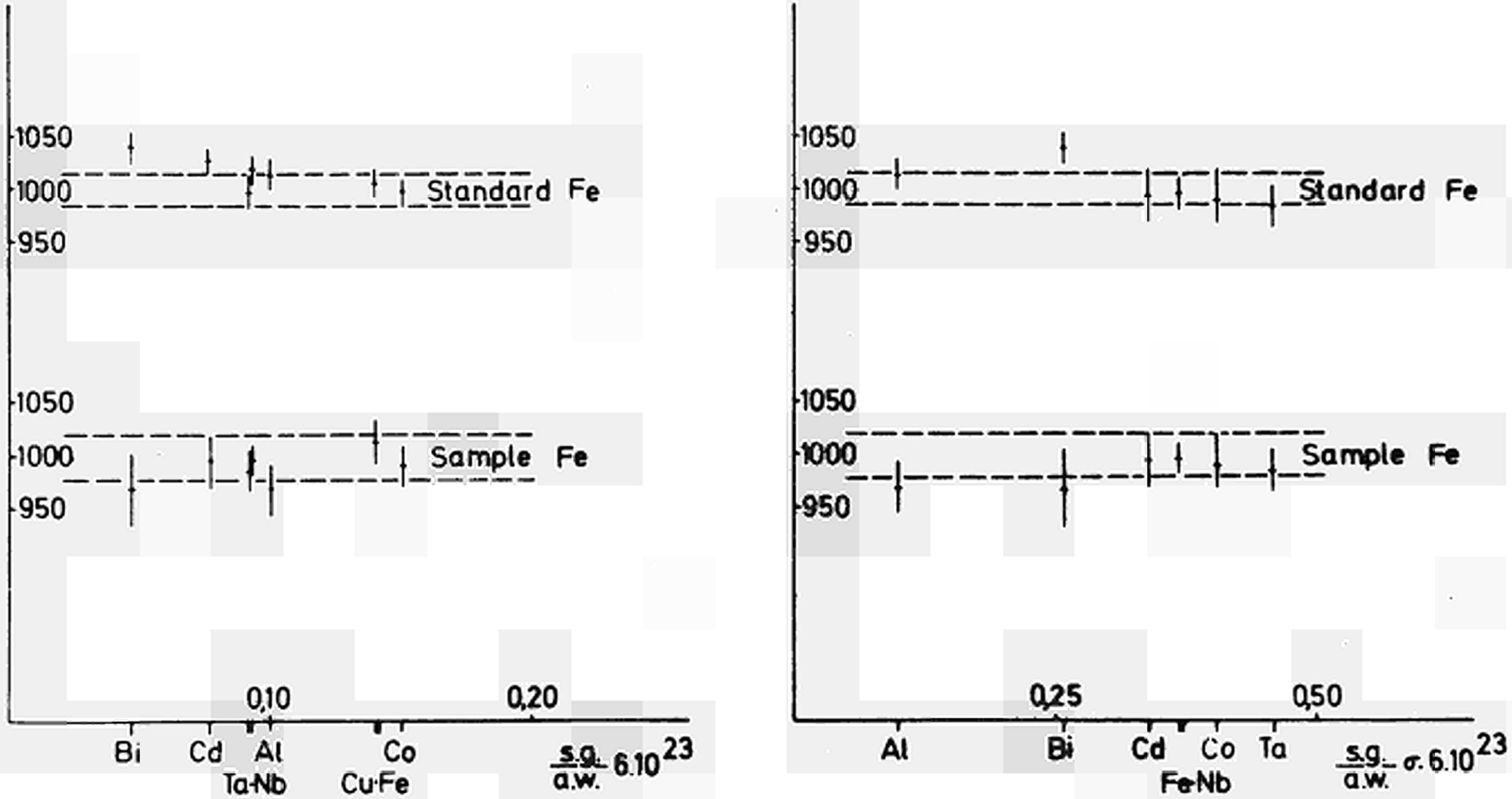

1050
1000
950
Standard Fe
1050
1000
950
Sample Fe
0,10
0,20
Bi
Cd
Al
Ta-Nb
Co
Cu-Fe
s.g./a.w. 6.10^23
1050
1000
950
Standard Fe
1050
1000
950
Sample Fe
0,25
0,50
Al
Bi
Cd
Co
Ta
Fe-Nb
s.g./a.w. σ.6.10^23

TABLE 12, V.

Element	Atomic weight a.w.	Specific gravity s.g.	σ total (b) σ_T	$\frac{s.g.}{a.w.} \times 6.10^{23}$	$\frac{s.g.}{a.w.} \times \sigma_T(b) \times 6.10^{23}$
Al	26.98	2.70	1.7	0.100	0.170
Ti	47.90	4.5	2.3	0.094	0.216
Co	58.94	8.9	2.7	0.151	0.408
Cu	63.54	8.92	2.95	0.140	0.413
Zn	65.38	7.14	3.1	0.109	0.338
Zr	91.22	6.4	4.1	0.070	0.287
Nb	92.91	8.55	4.0	0.092	0.368
Cd	112.41	8.64	4.4	0.077	0.339
Ta	180.95	16.6	5.0	0.092	0.458
Pb	207.21	11.3	5.3	0.055	0.290
Bi	209.0	9.80	5.5	0.047	0.258
Fe	55.85	7.86	2.6	0.141	0.367

TABLE 12, VI.

Metal	Sample	Standard	K
Fe	1000 ± 20	1000 ± 15	3.28 ± 0.08
Al	967 ± 25	1014 ± 14	3.13 ± 0.10
Co	989 ± 20	998 ± 14	3.23 ± 0.09
Cu	1011 ± 20	1006 ± 14	3.28 ± 0.09
Nb	995 ± 15	1018 ± 14	3.18 ± 0.07
Cd	994 ± 25	1026 ± 12	3.15 ± 0.10
Ta	984 ± 20	996 ± 16	3.22 ± 0.09
Bi	967 ± 35	1039 ± 16	3.03 ± 0.11
	m = 987	m = 1014	m = 3.18
standard	989 ± 10	1018 ± 16	3.16 ± 0.07

Furthermore two copper foils were irradiated separated by 7 mm air and also by 7 mm of the investigated metals. In no case a different ratio in the induced activities of the foils could be measured.

The apparent difference in specific activity of various matrices noticed by Anders and Fujii is therefore rather to be interpreted in the light of their neutron monitoring technique. Both authors employ plastic scintillators, which are sensitive not only to neutrons but also to gamma's. Obviously the presence of a different sample will vary the prompt and reaction product gamma flux, thus causing a variation in the neutron detection efficiency.

Hereafter unique steel standards were used for the oxygen determinations in the various materials.

12.5. Results.

In Table 12, VII results are given of the oxygen analyses in 11 non ferrous metals. As most of the metals studied present important difficulties for the fusion method, comparative results are rare and when available, have been included.

The samples had different origin and their overall purity varied from commercial quality to 99.9999%. Most samples were very homogeneous in regard to their oxygen content, only 1 niobium sample showed a clear change in oxygen concentration when it was analysed on its two faces.

It should also be noted that the weight of the samples varied from 6 g for Al to 38 g for Ta. Thus at the same concentration a tantalum sample contained 6.3 times more oxygen than an aluminium sample, therefore yielding 6.3 times more recorded ^{16}N counts, and improving in this way the reproducibility of the results.

Samples marked with * were transported in the already mentionned steel frame or box. The practical sensitivity obtained is quite sufficient for the oxygen concentration actually encountered.

Consequently the standard error $s = \sqrt{\frac{\Sigma \Delta \bar{x}^2}{n(n-1)}}$ (n = 9) on these results is much greater than for normally transported samples.

It was also possible to extend the "error-ppm" curve, given as Fig. 6, 3, into the lower concentration region.

TABLE 12, VII.

Oxygen Analysis of Non Ferrous Metals (ppm).

Metal	uality or origin	1st sample	2nd sample	fusion
Bi	1	8 ± 1		
	2	10 ± 1		
	3	10 ± 1		
	4	10 ± 1		
Cd	1	20 ± 1		
	2	16 ± 1		
	3	23 ± 1		
Co	1	402 ± 10	390 ± 4	
	2	110 ± 3	111 ± 2	
	3	15 ± 1	15 ± 1	
Nb	1	18 ± 1		
	2	49 ± 1		
	3	45 ± 1		
	4	228 ± 4 (1st face)	307 ± 11 (2nd face)	
Ti	1	770 ± 11	776 ± 9	
Ta	1	18 ± 1	18 ± 1	
	2	19 ± 1	17 ± 1	
	3	6 ± 1	16 ± 1	
Zn	1 *	12 ± 4		
	2	15 ± 1		
	3 *	9 ± 4		

(1)	(2)	(3)	(4)	(5)
Al	1	42 ± 8		
	2	35 ± 3		
	3	26 ± 5		
	4	31 ± 5		
	5	18 ± 2		
Cu*	1	67 ± 4		
	2	11 ± 3		
	3	312 ± 10		
	4	463 ± 8		
Pb*	1	29 ± 4		
	2	27 ± 5		
	3	8 ± 4		
	4	46 ± 8		
	5	30 ± 4		
	6	57 ± 12		
	7	100 ± 4		
	8	52 ± 13		
	9	37 ± 4		
Zr	1	1110 ± 15	1095 ± 12	1170 ± 30 (n=7)

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