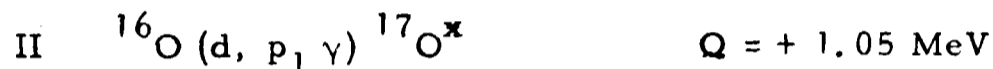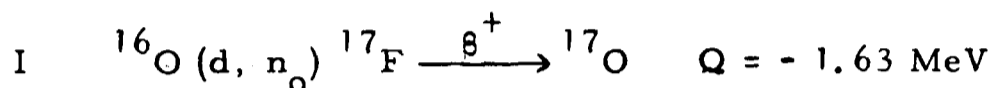# 4. DISTRIBUTION STUDIES OF CARBON, NITROGEN, OXYGEN AND FLUORINE IN METAL SURFACES BY MEANS OF PROTON AND DEUTERON INDUCED REACTIONS

Dag Brune and Joachim Lorenzen

4.1 Oxygen in zircaloy surfaces

Oxygen present in zircaloy surfaces has been determined be means of charged particle activation analysis, employing the following two reactions

$$\text{I} \qquad {}^{16}O\,(d,\,n_o)\,{}^{17}F \xrightarrow{\beta^+} {}^{17}O \qquad Q = -1.63 \text{ MeV}$$

$$\text{II} \qquad {}^{16}O\,(d,\,p_1\,\gamma)\,{}^{17}O^x \qquad Q = +1.05 \text{ MeV}$$

In the context of these two reactions oxygen can be identified from reaction I using:

1) Neutron time-of-flight measurement [1], [2]

2) Measurement of the induced β^+ activity from ${}^{17}F$ ($\Gamma_{1/2} = 66$ sec)

or from reaction II using:

3) Proton spectroscopy [3]

4) Measurement of prompt 0.87 MeV γ radiation

The present work has made use of techniques 2) and 4).

Thus, the detection limits for oxygen in zircaloy surfaces have been investigated both by measuring the promptly emitted 0.87 MeV gamma rays, and by measuring the 511 keV annihilation which arises from the β^+ decay of ${}^{17}F$.

Usually, the excitation functions for (d,n) and (d,p) reactions for light elements increase with the particle energies, up to a few MeV [4]. This implies an improved detection limit for the element in the surface with increasing particle energy. It should be noted, however, that the penetration depth of the particles also increases, so that a thicker surface layer is involved.

The correlation between the detection limit for oxygen in zircaloy, the particle energy and the surface thickness analyzed have therefore been evaluated. Measurement of the prompt gamma radiation arising from the (d, p) reaction gave a detection limit of $0.7 \cdot 10^{-7}$ g/cm^2 at a deuteron energy of 3 MeV (see Fig 4. 1).

A comparison of the two techniques used in this investigation indicates that the gamma-ray method is preferable, not only because of the better detection limits attained but also because of the shorter running time which is required. Thus the gamma peak is built up during an activation time of one minute, while it is necessary to follow the β^+ decay curves for periods which are at least three times longer. Furthermore, an analysis involving measurement of the area of a single peak (0. 87 MeV) is more rapidly performed than an analysis which involves the measurement of the several peak areas necessary for characterization of the decay curve (0. 51 MeV).

It is estimated that more than 10 analyses per hour can be performed using the reaction $^{16}O(d, p_1, \gamma)^{17}O^x$ in combination with a remote-controlled sample changer [5].

The technique is described in detail elsewhere [6].

4. 2 The application of time-of-flight measurement for depth distribution evaluation of carbon, nitrogen and oxygen in steel surfaces [2]

Light elements in metals can be studied successfully by means of deuteron induced reactions. The cross-section for a (d, n) reaction is often some orders of magnitude greater than that of a (p, γ) reaction, but no distinct resonances are observed.

The neutron energy within a certain solid angle of emission depends on the deuteron energy at the instant of reaction, which in turn depends on the primary deuteron energy and the depth to which the deuterons penetrate before they react. At a given depth, the corresponding neutron yield is proportional to the number of nuclear reactions. Since the different reactions between deuterons and light nuclei have essentially different Q-values, neutron groups corresponding to different reactions [C (d, n); O (d, n); N (d, n)] can be resolved. Cross-sections for heavy matrix nuclei are, moreover, low at a deuteron energy of a few MeV.

For purposes of calibration, use was made of the relationship between the values for the different channels as measured for surface reactions with carbon, oxygen and nitrogen, together with the Q-values for each reaction. This channel flight-time-energy relationship could be transformed into a depth scale by using the existing well-documented values for the stopping power of deuterons in iron. Ten-keV steps were used.

Analysis and results from experimental data

The neutron yield A_x from a (d,n) reaction at a given depth x from the surface and registered in channel k is given by

$$A_x = P(r,\Omega) \cdot i_D \cdot \epsilon(E_{nx}) \cdot N_c(x) \cdot \sigma(\theta, E_{dx}) \cdot dE_n \qquad (1)$$

where

$P(r,\Omega)$ = proportional factor depending on measurement geometry

i_D = incoming charged particle current density

$\epsilon(E_{nx})$ = detector efficiency for neutrons with energy E_{nx}

$N_c(x)$ = number of carbon atoms per unit volume at depth x

$\sigma(\theta, E_{dx})$ = differential (d,n) cross-section at particle energy E_{dx}

dE_n = energy interval of the neutrons in channel k

During the experiment $P(r,\Omega)$ is constant. Since the decrease of deuterons i_D due to reactions during the passage through the material can be neglected ($< x\ 10^{-6}$), and since $\epsilon(E_{nx})$ is approximately constant for neutron energies between 1 and 3 MeV the measured neutron flux from a depth x is proportional to $N_c(x) \cdot \sigma(\theta, E_{dx})$.

Theoretically it is possible to determine $N_c(x)$ by correcting the shape of the neutron energy spectrum for cross-section dependence. However, since $\sigma(\theta, E_{dx})$ is only known to an accuracy of 20 % this method does not produce satisfactory results. Since neutrons of a given energy will give rise to a signal in the same channel, it is much easier to compare a spectrum of an unknown sample (x) with a spectrum of a homogeneous standard. Since $dE_n \approx dE_d = (dE/dx) \cdot dx$ this gives

$$\frac{A_x}{A_{st}} = \frac{N_c(x) \cdot (dE/dx)_x \cdot dx}{N_c(y) \cdot (dE/ly)_y \cdot dy} \cdot \frac{i_{Dx}}{i_{Dst}}$$

where y is the depth in the standard sample which contributes neutrons in channel k.

If the standard has the same variation of stopping power with energy as the unknown sample, both dE/dx and dx will cancel out and after normalization and subtraction of the background the ratio of the two spectra (channel by channel) will automatically reveal the concentration profile.

Samples studied have been irradiated with deuterons at energies between 2.5 - 5.3 MeV in the 5.5 MeV VdG accelerator at Studsvik. A pulsed beam with a repetition frequency of 1 MHz gave a pulse of 3 ns width (FWHM). In order to keep down the heating effect in the samples, only currents up to 1 µA were used. At the same time forced air cooling was installed at the target.

The information about the elemental distribution is given by the neutron spectrum from the (d, n) reaction. The energy distribution of the outcoming neutrons was therefore measured at 0° and 20° using a time-of-flight technique. The detector used was a ϕ 5" x 2" NE 213 liquid scintillator coupled optically to an RCA 8850 photomultiplier. (n, γ) pulseshape discrimination was used and the data were collected in a 4 x 1024 channel analyzer. Recent experiments have been carried out with a PDP-15 computer using both on- and off-line programs.

Depths of some tens of microns were studied with a resolution of fractions of a micron. The detection limit is of the order of 100 ppm.

A concentration profile for a 4 µm carbon gradient in steel obtained with this technique is given in Fig 4.2.

4.3   Analysis of fluorine in zircaloy surfaces

The technique for the depth distribution analysis of fluorine in zircaloy surfaces previously described by Möller and Starfelt [7] has been extended to comprise fluorine analysis up to depths of about 8 µm. Measurements of the sensitivity of fluorine at various depths below the surfaces have been carried out using this technique. A simple nomogram for the evaluation of the fluorine content in the surface is also being developed.

4.4 Proton microprobe analysis

A proton microbeam arrangement supplied by AB Scanditronix, Uppsala, has been installed at the 5.5 MeV Van de Graaff accelerator at Studsvik. The system is at present being calibrated. The diameter of the beam spot is estimated to be 4 - 5 µm.

Proton microprobe analysis will be carried out using the following two approaches:

1. Nuclear reaction techniques for light elements such as carbon, nitrogen, oxygen and fluorine will be determined in the microprobes, utilizing the techniques of charged particle activation analysis which have already been developed [e.g. 2, 5, 6 - 8].

2. Proton X-ray analysis for heavy elements such as e.g. cobalt, nickel, manganese, and tungsten will be determined by means of measurements of characteristic X-rays produced from these elements by proton irradiation with the microprobe [9].

Studies have already been initiated for the evaluation of the sensitivities of various elements in steel surfaces, using this technique for thick targets and broad beam spots (in collaboration with R Akselsson et al., University of Lund).

The Studsvik micro-beam system has been described in ref [8].

4.5 Résumé of analytical results

A résumé of the results obtained in Studsvik in the development of charged particle activation analysis to serve as an analytical tool for metallurgical research is given in the table below.

Table 4.1 Charged particle activation analysis of carbon, nitrogen, oxygen and fluorine in steel or zircaloy surfaces

Fluorine in zircaloy [7]

Surface analysis
Depth distribution analysis

Detection limit:	0.005 %
Layer resolution:	0.2 µm
Depth analyzed	5 µm
Capacity:	Determination of 10 concentration profiles per 8 hours

<u>Carbon, nitrogen, oxygen in steel</u> [1, 2, 5]

Surface analysis

Depth distribution analysis

Detection limit: 0.001 % (surface analysis)

                                          0.005 % (depth distribution analysis)

Layer resolution: 0.2 μm

Depth analyzed: 15 μm

Capacity: Determination of 10 concentration

                                          profiles per 8 hours

<u>Oxygen in zircaloy</u> [8]

Surface analysis

Detection limit: 0.001 %

Capacity: 50 - 100 surface analysis per 8 hours

4.6   Compilation of excitation functions for charged particle induced reactions

A compilation of excitation function is being prepared [10] for about 70 charged particle induced reactions (proton, deuteron, alpha, and ^{3}He induced reactions), for use in the activation analysis of light elements.

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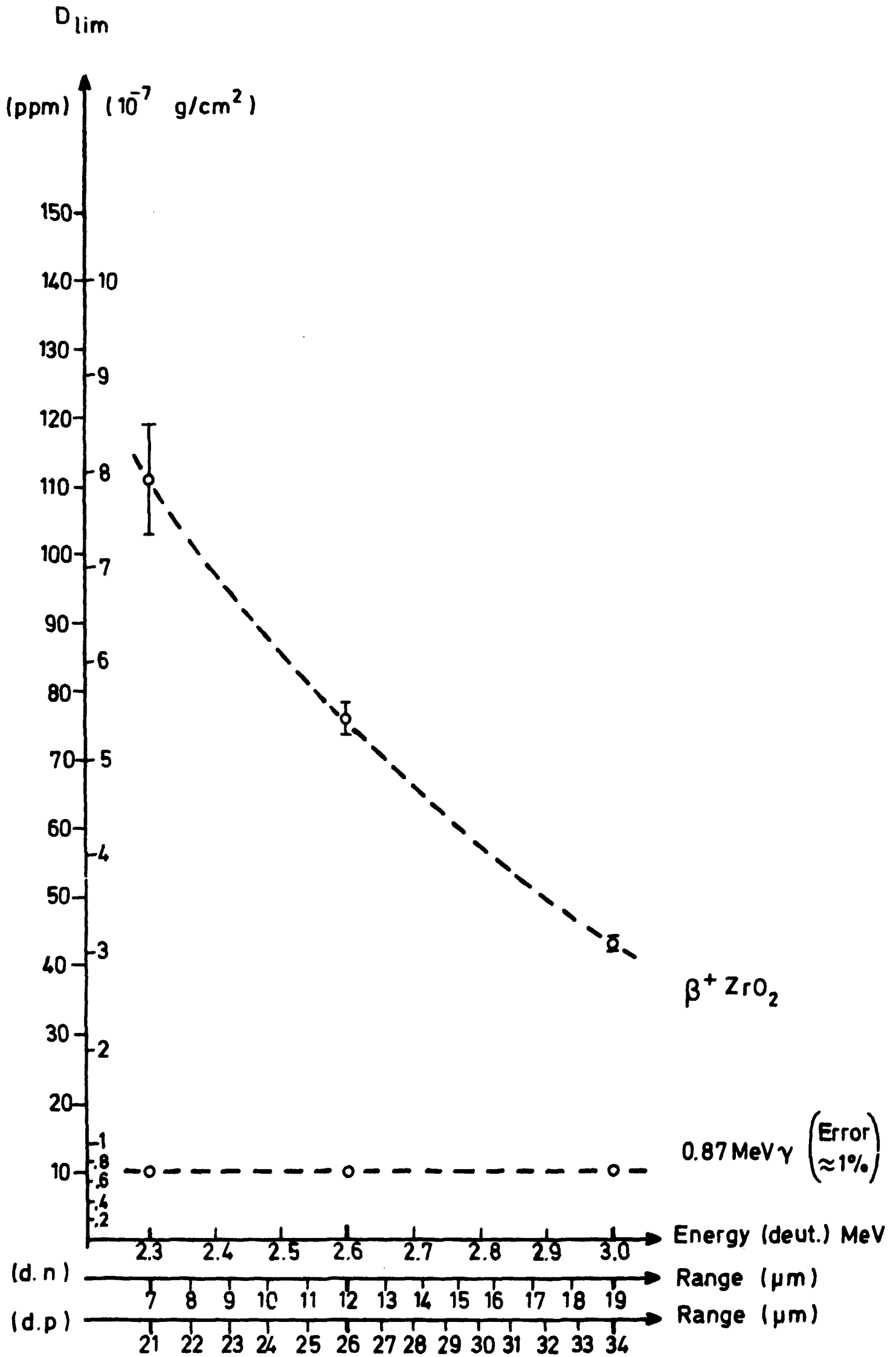
10. LORENZEN, J. and BRUNE, D. ,
    To be publ.

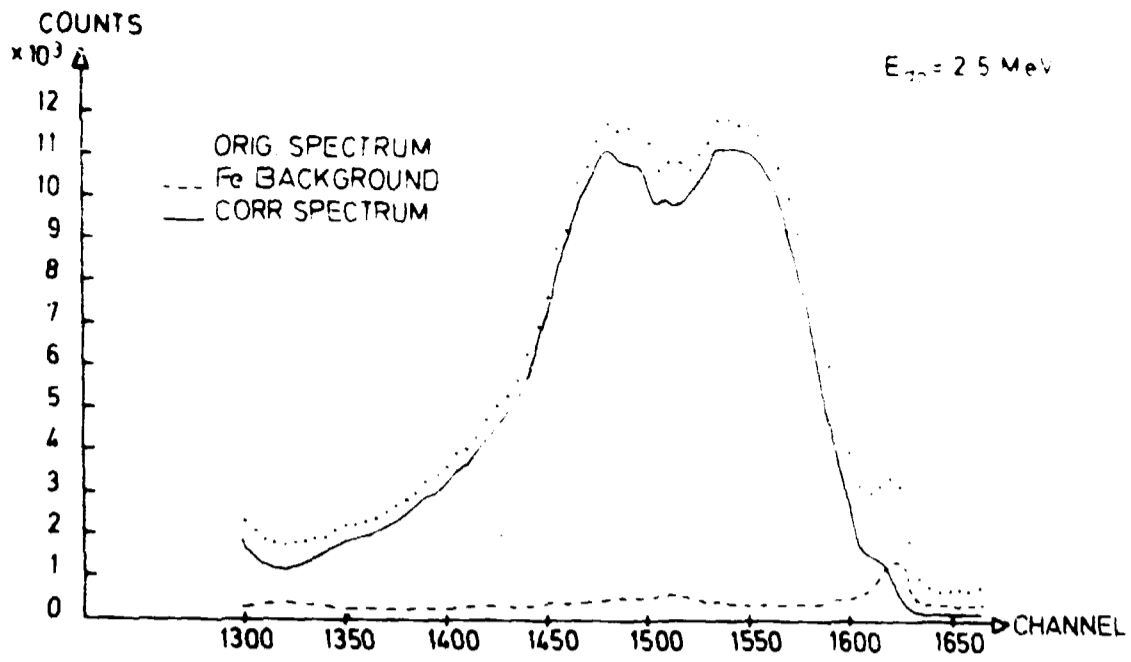Fig 4.1 Calculated detection limits obtained from the experimental values

Fig. 2a

Fig. 2b

Fig. 2c

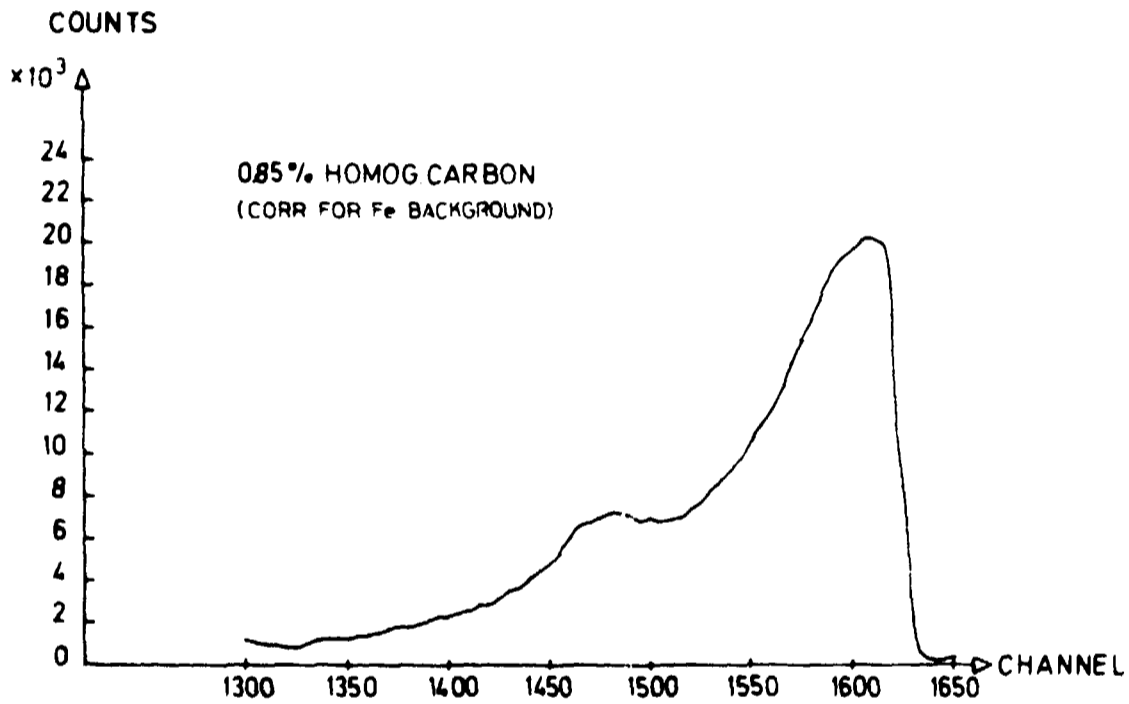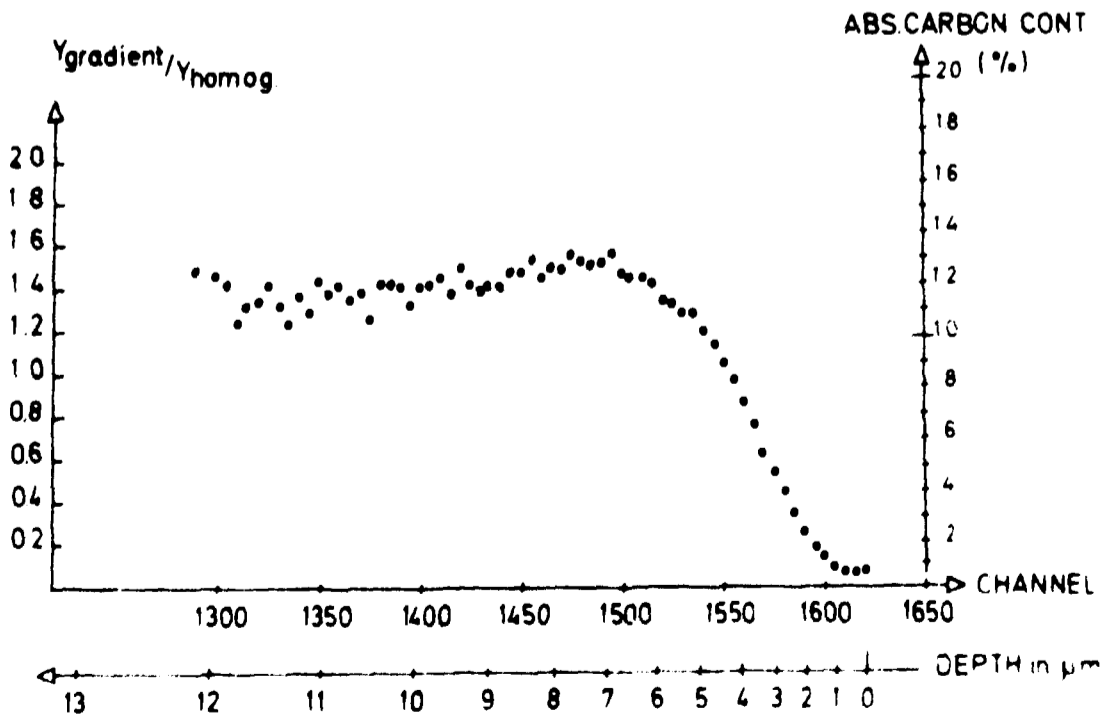Fig 4. 2   Concentration profile of a 4 μm gradient studied
with time-of-flight-technique