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Oxygen content analysis of metal surfaces with resonant α-scattering

by

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Abstract

The thicknesses of the thin native oxygen layers on some metals have been determined by making use of the 3.05 MeV resonance in the elastic scattering reaction $^{16}O(\alpha,\alpha)^{16}O$. The surfaces of iron have specially been studied for different ways of preparation e.g. evaporation, sputtering, passivation. The properties and possibilities of the method are discussed. Its advantageous application on interfaces is shown with a scanning investigation on an iron-aluminium sample.

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Introduction

Surfaces of metals, in general, become contaminated when exposed to the atomsphere; some of the usual contaminants are for example Oxygen and Nitrogen. These may in some cases lead to differences between the bulk and surface properties of a metal. Such is the case in the investigation of hyperfine interaction with the α-γ angular correlation method [1,2] in which the depth region to be studied is in the order of 10 $\mu g/cm^2$.

As oxygen in general is dominating on metal surfaces, there is a need to determine the thicknesses of the native oxide layers when extracting characteristic properties of a homogeneous metal.

The possibility to analyse samples with consideration to their oxygen contents may also be valuable within semiconductor technology and metallurgy. The analytical methods based on nuclear techniques are filling the demands of high sensitivity to low oxygen concentration. Activation analysis by neutrons [3] and charged particles [4] have been used to measure traceable quantities in the bulk of the samples. On the other hand, the direct observation of charged particles emitted in nuclear reactions yield possibilities to measure depth distributions of fairly small amounts of impurities. The (d,p) and (d,α) reactions have relatively high sensitivity and are easy to use. They have therefore been developed to be successful tools for element analyses [5,6]. However, the depth resolution can be improved considerably by making use of resonance reactions [7]. This approach implies also an improved facility to study interfaces between different layers of materials.

The 3.05 MeV resonance in the elastic scattering $^{16}O(\alpha,\alpha)^{16}O$ has been investigated already in 1953 by Cameron [8]. He investigated the elastic scattering from ^{16}O (gas target) in the energy interval 0.94 to 4 MeV. A sharp resonance was found at θ_{cm} = 168°.0 and E_α(lab) = 3.045 MeV corresponding to a 3^-, 7.218 MeV excited state in the compound nucleus ^{20}Ne. The experimental data were theoretically interpretated with partial wave analysis [9]. The differential cross section in the backwards direction is very large (~ 2b/Sr).

We have chosen resonant α-scattering to analyse the surfaces of the samples used in the earlier mentioned α-γ experiments. Beside the enhanced sensitivity for oxygen analysis a multielement analysis can be performed at the same time with conventional backscattering. It should also be mentioned that the method may be considered to be non-destructive; radiation damage is hardly detectable and no radioactivity is produced.

During the course of our investigation the use of this method has been presented by Mezey et al. at the Karlsruhe Conference on Ion Beam Surface Layer Analysis in 1975 [10]. The advantages over other techniques were demonstrated by investigations of layered structures such as Si on SiO_2 and simultaneously evaporated Co and Gd on quartz.

2. Experimental

The experiments were performed at the Van de Graaff accelerator, Studsvik. The backscattered α-particles were detected in an annular surface barrier detector. It had an area of 300 mm^2 with a 5 mm hole to let in the α-beam and the depletion region was 100 μm A tantalum collimator with a diameter of 17 mm was placed in front of the detector which distance to the target was 74 mm. This arrangement corresponds to a centre of mass backscattering angle between 175.1° and 178.6°. The detector resolution was 30 keV measured by a ^{226}Ra source (α-energy 4.78 MeV).

The scattering chamber is equipped with a collimator whose aperture was about a few tenths of mm. The current of the beam on the target was kept between 15 and 25 nA. A 1 m deep Faraday cup with a beam stopper made of graphite was used to minimize the background in the α-spectrum.

The target holder can be loaded with nine samples. The energy of the α-beam was changed over the resonance in steps of about 2-3 keV. The spectra of the backscattered α-particles were collected during 10 minutes by a PPP-15 computer, when Al-foils were investigated. The collecting times were longer for the Fe, Co and Gd-foils because of the higher Rutherford cross sections for these elements giving a higher background under the oxygen peak. In two cases a different normalization procedure had to be chosen as these samples were too thin to give a continous backscattering distribution. These were the 400 $\mu g/cm^2$ Ni foil and the 125 $\mu g/cm^2$ sputtered Fe sample. The normalization interval was here chosen in the Ni and Fe distributions.

A specification of the foils studied is presented in Table I. The thickness of the sputtered sample was 100 $\mu g/cm^2$ Fe supported on a 100 $\mu g/cm^2$ carbon foil.

The thicknesses of the sputtered and evaporated materiels were measured by a quartz crystal gauge. Before the experiments the samples were stored in an exicator and they were washed in ethanol just before the mounting in the scattering chamber.

3. Analysis of the backscattering spectra

Two typical spectra are shown in Fig. 1. The sample is an anodized Al-foil with an oxidized Al thickness of 1.34 $\mu g/cm^2$. The spectrum is Fig. 1a is at resonance and in Fig. 1b is a backscattering spectrum at a beam energy below the resonance.

The area of the oxygen peak in the backscattered particle spectra was analyzed with parabolic fitting of the background. The mean value of the Rutherford contribution in the energy regions, symmetrically on both sides of the oxygen peak was chosen for normalization, which also can be related to the heightof the forward edge in the α-spectrum. This parameter is defined by Ziegler and Chu [11], whose tables were used to get a relation between different metals. The conversion between the normalizations for Al and Fe has been made experimentally by evaporating Au layers of 80 $\mu g/cm^2$ on two foils of each element. The counting rates in our chosen normalization intervals were then determined as the area of the gold distribution in the spectrum. This experimental proportionality have been used in the evaluations of the Fe-results. The oxygen contents for the other samples are based on estimations from Ziegler and Chu tables [11].

4. Calibration

In order to convert the normalized area of the oxygen peak to oxygen content on the surface of the material a separate calibration experiment was performed. Anodic oxidized aluminium layers with known thicknesses were used. The anodizing procedure is described by Davies et al. [12]. Commercial (1.3 mg/cm^2 thick) Al-foils together with a few Al-plates (0.1 mm thick) were used. They were polished with a fine-grained diamond paste (3 μm). A preanodization and an etching off the natural oxide was made for each target.

The anodizing bath consisted of an aqueous solution of ammoniumcitrate (0.14 mol/ℓ) maintained at 25°C. The relationship between the thickness of the oxidized aluminium (W) and the applied voltage (V) is

$$W_{Al} = 0.25 \cdot (V+1.8)$$

where W is in $\mu g/cm^2$ and V is in volt.

The content of oxygen was obtained assuming that the oxide has the chemical formula Al_2O_3. This is reasonable when considering stochiometric measurements of anodized aluminium-oxide [13]. The result was $Al_2O_{(3.05\pm0.05)}$.

To make the self-supporting 10-24 $\mu g/cm^2$ Al_2O_3 targets the following technique was used. An etched Al-foil was on one side covered with bees wax and the other side was anodic oxidized. The wax was thereafter washed away and the aluminium was dissolved in hydrochloric axid. The remaining Al_2O_3 film constituted a very thin target, which was used to check the energy and the width of the resonance. (See Fig. 2). The width (19 keV) is narrower than that from the work by Cameron [8] in agreement with the results reported by Mezey et al. [10].

The resonance curves for different oxide thicknesses are illustrated in Fig. 3. A simplified analysis can be used, since the resonance is fairly broad compared to the energy spread of the accelerator ($<$ 1 keV), to the straggling and the energy loss in the oxide layer (2 $\mu g/cm^2$ Al_2O_3 corresponds to 2 keV). To obtain the oxygen content, it is sufficient to determine the maximum value of the resonance. The results of the calibration are presented in Fig. 4.

5. Results and discussion

The experimentally determined oxygen thicknesses for the investigated samples are presented in Table II. Oxide thicknesses can be calculated from the oxygen data, if it is assumed that all oxygen is occurring in oxides.

5.1 Iron

The 'old' Fe and the Fe-Al foils have been used at the α-γ angular correlation experiments [2]. They have been used repeatedly in a special implantation equipment, in which a high voltage was applied between the source and the foil in vacuum. Interesting to note is that vaporized iron has the largest oxygen content of the investigated iron samples. The 125 $\mu g/cm^2$ evaporated Fe layer evidently takes up oxygen to a large extent. Some of the oxygen has probably diffuesed to the inner surface between the iron and the aluminium, as the aluminium foil was etched just before the iron evaporation. The oxide layer of a pure aluminium surface grow rather slowly according to the dielectric measurements by Semov [14].

A well-known way to conserve surfaces is to cover them with an evaporated layer of gold. The thickness used was 80 $\mu g/cm^2$. The iron surface has in this case the smallest oxygen content. Possible explanations might be degassing out from the iron surface into the vaporized gold layer. This latter effect has been studied in connection with the manufacturing of silicon surface barrier detectors [15].

The large oxygen content of the vaporized iron is probably not an effect of the evaporation process as the oxygen layer of the gold-iron interface was thin. The evaporation process may give a more porous structure of the iron, which has made the sample more sensitive to corrosion. It should be mentioned that an investigation of the crystallinity of evaporated iron (enriched with ^{57}Fe) has been made at our institute with Mössbauer spectroscopy. There was no indication of non-crystallinity. An interesting fact is also that no iron oxide pattern was discovered in the Mössbauer spectrum, although the oxide thicknesses in Table II extends over the experimental resolution of the Mössbauer spectrometer. The oxygen on the surfaces of vaporized iron is evidently not completely bonded to iron oxides but occurs in another forms.

The sputtered iron, however, contains small amounts of oxygen on the surface and has evidently not taken up oxygen in the same extension as the evaporated iron.

All samples have also been checked by conventional backscattering analysis with consideration of the occurence of other impurities. Only the evaporated and sputtered ones contained measureable amounts (<0.5 o/oo) of Cu or Xe.

Another well-known way to conserve metal surfaces from corrosion is to use the method of passivation. The Fe-foils were immersed into conc. nitric acid. A thin oxide layer is then created on the surface, which prevents the metal from further oxidation. In Fig. 5 is a backscattering spectrum shown for a Fe foil with a passive oxide layer . The passivation has been performed at different temperatures of the acid bath; room temperature, just below and at the boiling point (83^{o}C). The foil treated at the highest temperature contained most oxygen on the surface (see Table II).

It should be mentioned that the samples have only been investigated once. It would be interesting to study the oxygen development versus time in connection with annealing [16] and ion implantations [17].

5.2 Aluminium, cobalt and nickel

Rolled aluminium contains a rather thick oxygen layer on the surface compared to thin films made by evaporation [14]. The sample was taken from an ultra-pure Al-rod, which was rolled at room temperature and in air to a thickness of about 3 mg/cm^2.

This procedure gives probably rise to rolling of oxygen amounts into the material. Then the oxygen might diffuse out to the surfaces of the samples.

The result for cobalt is presented in Table II. Its surface contains much oxygen which also is demonstrated by a backscattered spectrum at resonance in ref. [10].

The oxygen content for the Ni surface is rather large compared to earlier published results [16]. Our results obtained with thin Ni foils demonstrate that the method is most suitable to apply on thin selfsupporting foils consisting of elements which are heavier than oxygen. This is visualized in Fig. 6. The sensitivity of the method is improved as the oxygen peak is nearly free from background counts.

5.3 Gadolinium

The gadolinium foil contains considerable amounts of oxygen on the surface, which can be seen in Table II. The gadolinium surface has taken up oxygen to a much larger extent than the cobalt surface, which also has been demonstrated in ref. [10]. The metallurgical and chemical properties of gadolinium are still very little known. An investigation of gadolinium as a ferromagnetic host for hyperfine interaction experiments have recently been published [18], where the dependence of the magnetization of Gd-foils for different oxygen contents has been demonstrated.

5.4 Metal interfaces and depth resolution

Covered surfaces can also be studied with resonant α-scattering. A scanning investigation of vaporized iron on aluminium is shown in Fig. 7. Both the oxygen contents of the outer iron surface and of the iron aluminium interface have been determined with this resonance method. The incoming α-particles are given a somewhat higher energy to compensate for the energy loss when traversing the iron material. This gives a possibility to estimate the depth, where the resonance will take place. The depth resolution in iron can be estimated with the centroid shift method to about 2.5 $\mu g/cm^2$. One complication of the analysis is however the straggling of the incoming α-particles, which as is seen in Fig. 7 contributes to the broadening of the resonance at the interface.

5.5 Sensitivity

The non-destructive technique described here gives normal multielement analysis with backscattering plus an enhanced sensitivity of oxygen detection. As an introduction to this investigation a backscattering experiment at an α-energy of 2.5 MeV was performed. The sensitivity limit was about 4.1 $\mu g/cm^2$ Al_2O_3 for an anodized Al-foil. Calculations of cross sections with partial wave analysis [9] and Rutherford theory gave results which indicate that this sensitivity of oxygen can be improved with a factor of 35 by using the 3.05 MeV resonance.

The limitation of the method is that the oxygen peak has to be separated from its background. Therefore we can use the criterion applied by Peisach [19]; the minimum surface concentration of oxygen is the one, which gives a counting rate equivalent to three times the standard deviation of the background. For the most favourable case in this measurement namely the Ni-foil (Fig. 6) the sensitivity was $1.3 \cdot 10^{15}$ oxygen atoms/cm^2 (0.034 µg/cm^2), which for a fully developed nickel oxide corresponds to a thickness of 0.16 µg/cm^2 (2.5 Å). This statistically estimated sensitivity can of course be improved by working with longer time of measurement and higher target currents. However, it can lead to certain destructive effects from e.g. carbon build-up and sputtering of the oxygen on the surface. This was investigated for an energy scanning.

6. Summary

The present method of oxygen analysis has been shown to be useful for studies of surfaces and interfaces of different metallic samples. It is foremost characterized by following properties.

1) non-destructive; other physical methods can be applied on the samples.
2) multielement analysis; the contents of other impurities can be determined at the same experiment by conventional backscattering.
3) the sensitivity (2.5 Å oxide layer) is enough for corrosion studies.
4) the depth resolution (30-150 Å) makes the method valuable at oxygen content determinations of interfaces of layered structures.

The technique to combine Rutherford analysis with resonant methods can also be extended to other contaminants e.g. carbon and nitrogen. It will probably be a valuable analytical tool within metallurgy and semiconductor technology as the availability of low energy accelerators increases.

7. Acknowledgements

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Table I. Specifications of the foils

Foil	thickness mg/cm^2	manufacturer
Fe	9	Material Research Centre
Al	1.3	Johnsson, Matthew and Co.
Co	1.8	Good fellow Metals
Gd	18	Koch-light Labs.
Ni	0.4	Chromium Corp.

Table II. Oxygen content of metal surfaces

The iron foils denoted Fe (new) were directly delivered from the manufacturer. Fe (old) has been used repeated times at the α-γ angular correlation experiments [2].

			Oxide thickness (fully developed oxides)	
Sample surface	Oxygen thickness in µg/cm^2	Assumed formula	µg/cm^2	Å
Al rolled	1.56±0.16	Al_2O_3	3.33±0.10	105±11
Fe passivated in nitric acid at RT	0.63±0.08	Fe_2O_3	2.10±0.27	41±5
Fe passivated in hot nitric acid	1.10±0.13	"	3.66±0.43	71±8 x
	1.40±0.15	"	4.66±0.50	90±10 *
Fe new	0.42±0.07	"	1.40±0.23	27±4
Fe old	1.06±0.13	"	3.53±0.43	68±8
Fe vaporized	2.38±0.25	"	7.92±0.83	153±16
Fe sputtered	$\lesssim$ 0.30	"	$\lesssim$ 1.0	$\lesssim$ 20
vap. Fe-Al interface	2.08±0.22	—		
vap. Fe-Au	$\lesssim$ 0.30	—		
Co	2.83±0.31	CoO	13.2±1.5	205±22
Ni	1.16±0.12	NiO	5.42±0.56	81±8
Gd	4.78±0.60	Gd_2O_3	36.1±4.5	487±61

x below boiling temperature

* boiling

Figure captions

Fig. 1. Backscattering spectra for α-particle energy at and below the resonance. The foil is a 1.3 mg/cm^2 Al-foil with an anodized Al_2O_3 thickness of 50 Å.

Fig. 2. The resonance curve for a self-supporting 480 Å Al_2O_3 foil. The ordinate is the ratio of alpha particles scattered by ^{16}O to those scattered by ^{27}Al. Backscattering spectra at (b) and above (c) the resonance is also shown.

Fig. 3. Resonant alpha scattering for different anodized Al_2O_3 thicknesses on Al-foils.

Fig. 4. Maximums of the resonance curves (Fig. 3) as a function of the thickness of anodized aluminium oxide.

Fig. 5. A backscattering spectrum at resonance for an iron foil passivated in hot nitric acid.

Fig. 6. Backscattering spectrum for a 400 μg/cm^2 Ni-foil.

Fig. 7. An energy scanning investigation of a vaporized iron on aluminium foil. Backscattering spectrum at the resonance energy is also shown.

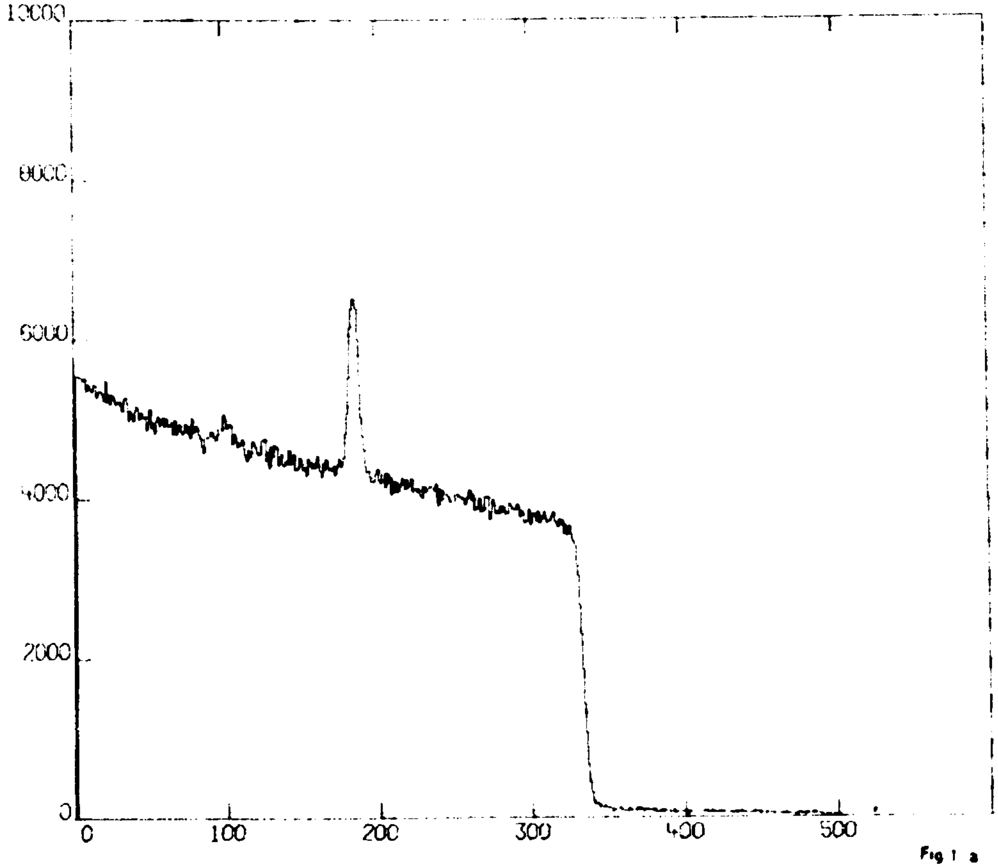
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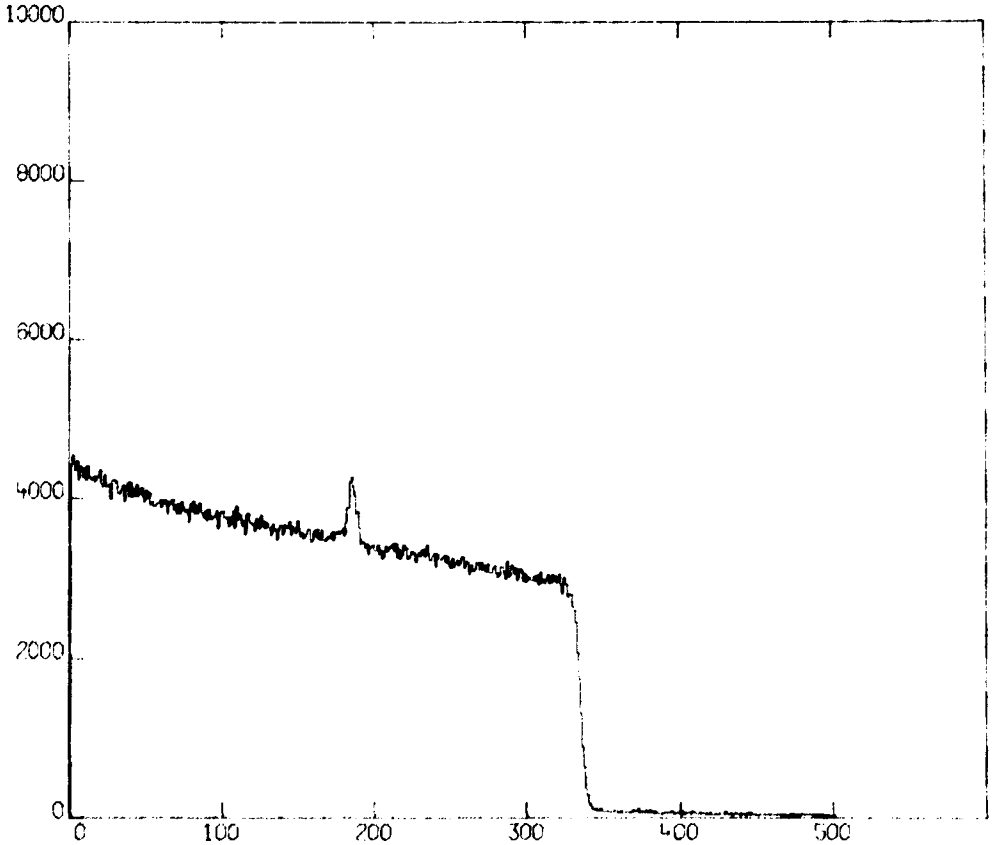
Fig 1 a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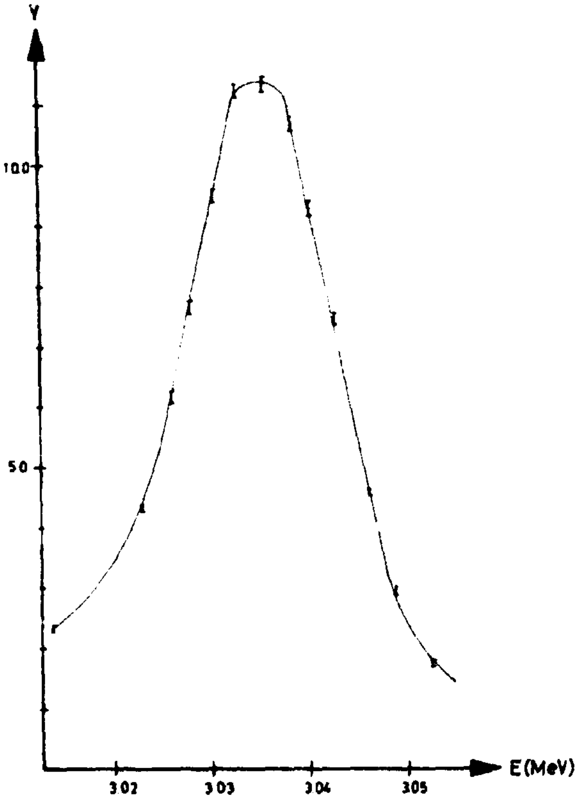
b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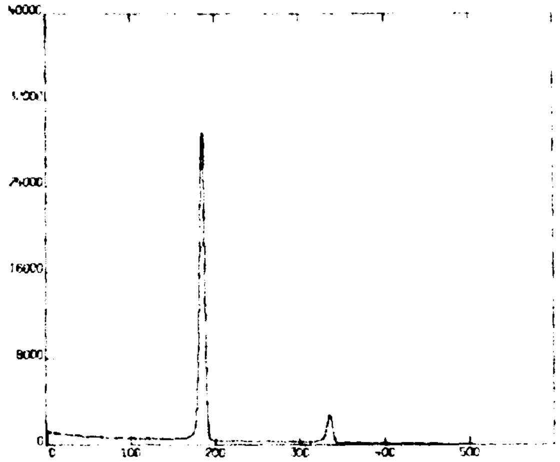
E(MeV)

Fig. 2 a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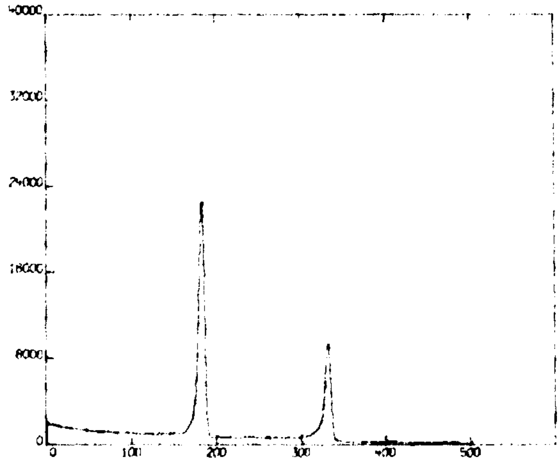
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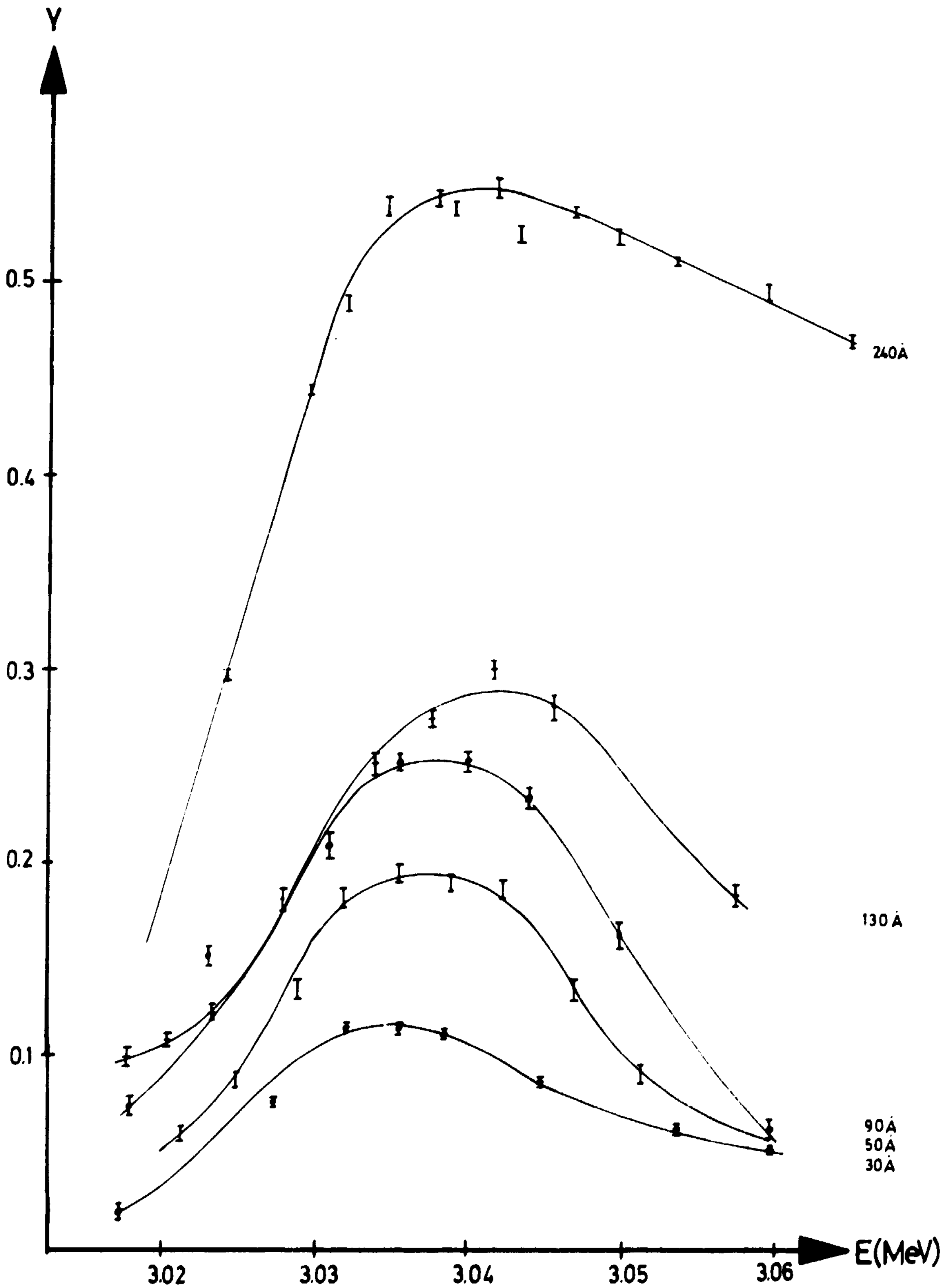


Fig. 3

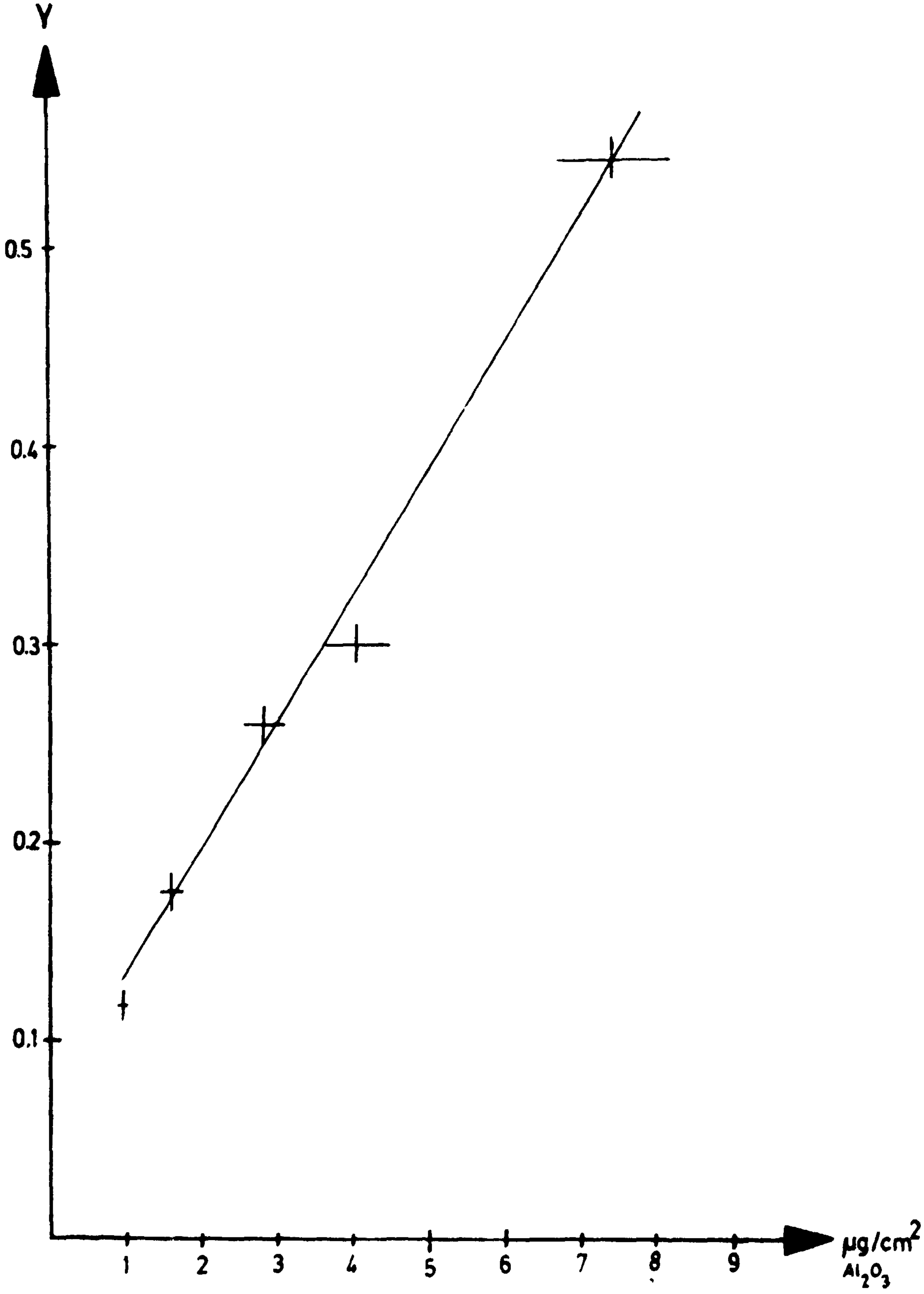


Fig. 4

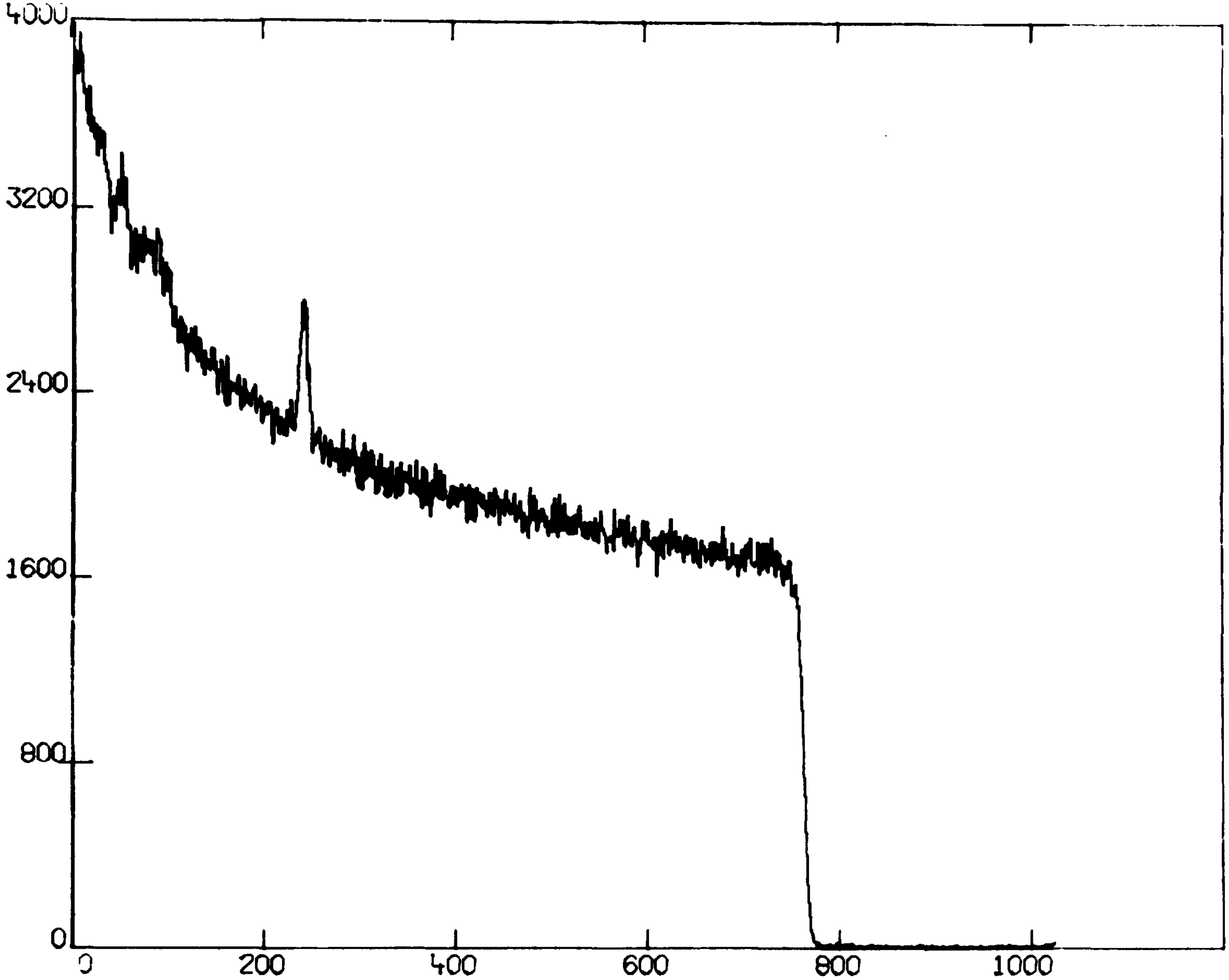


Fig 5

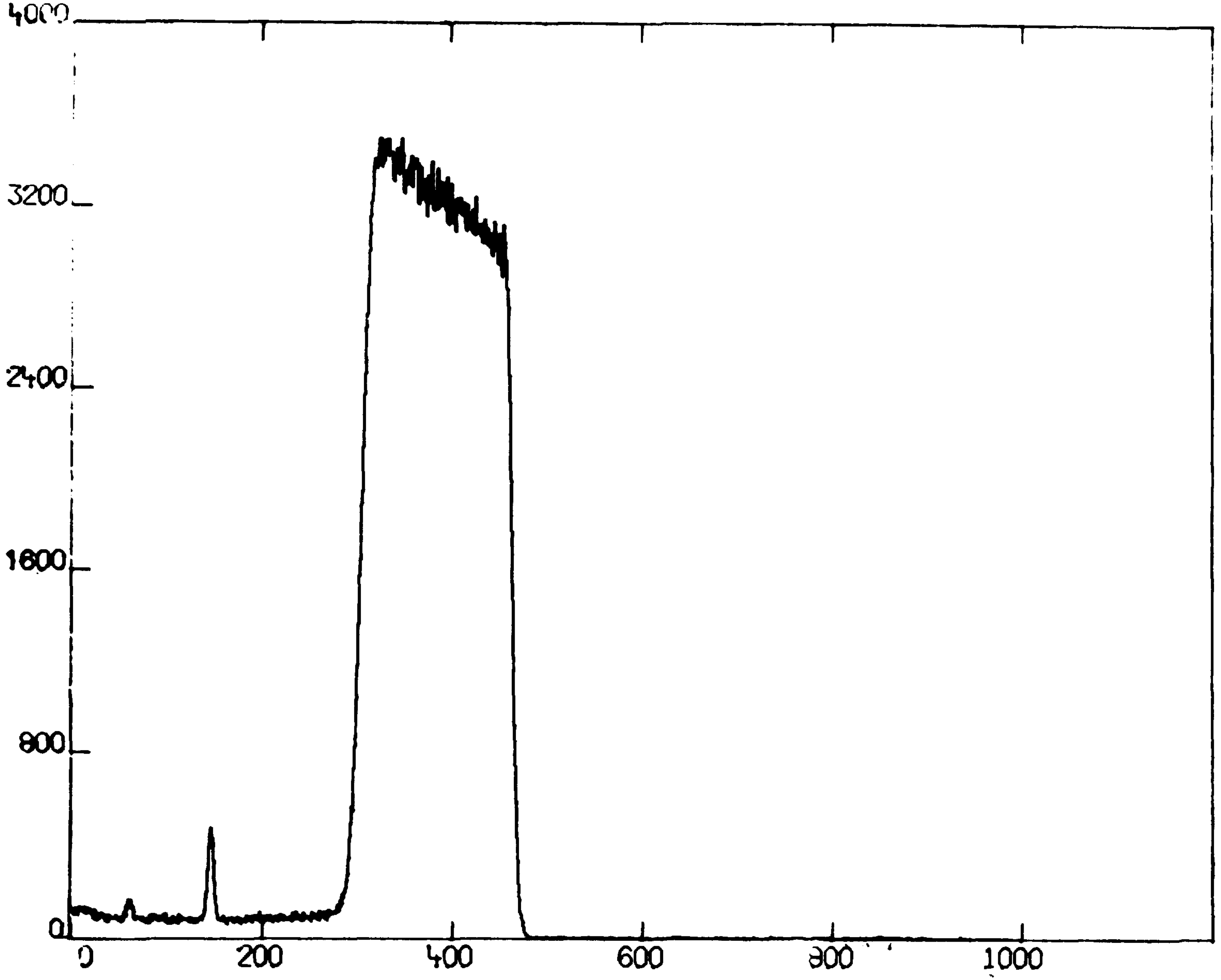
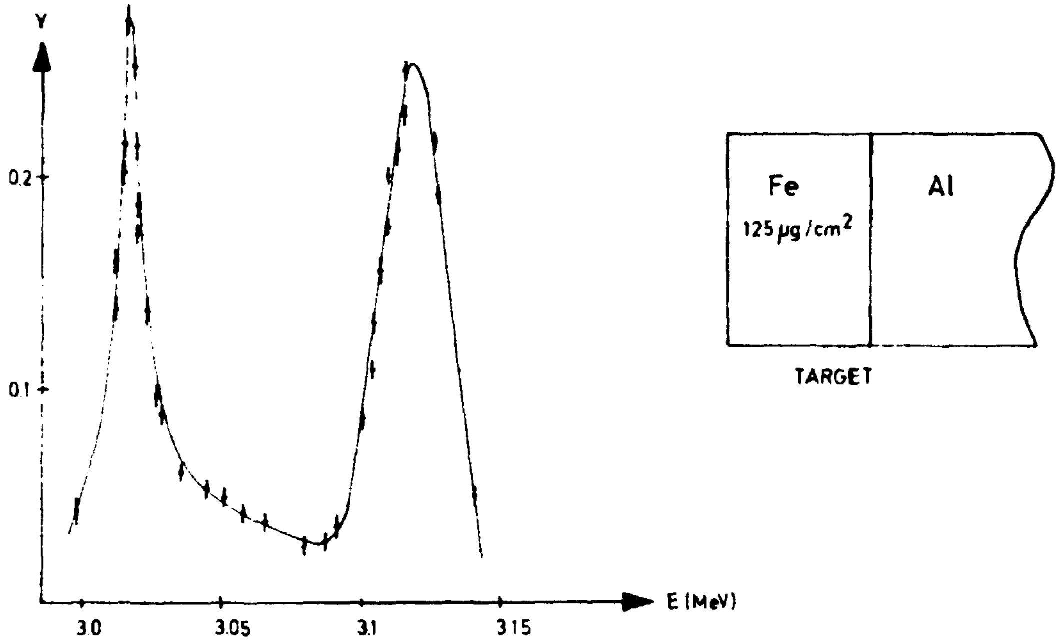


Fig. 6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Fe
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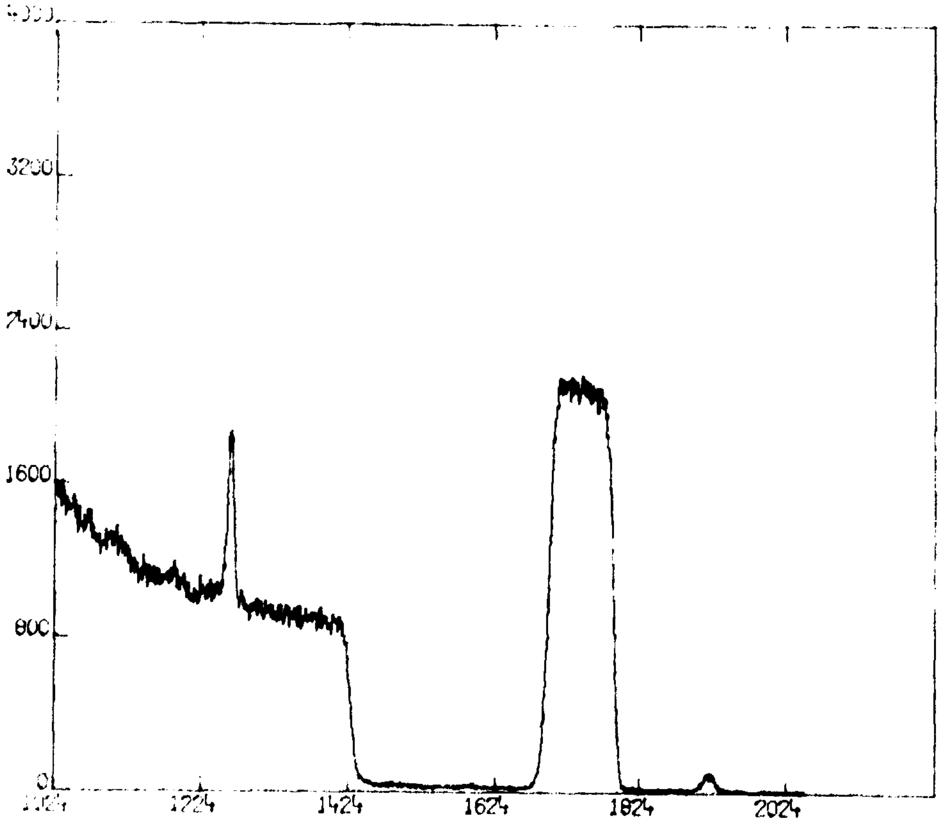
Al
TARGET

Fig. 7 a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