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THRESHOLD REACTION INTERFERENCE
IN NEUTRON ACTIVATION ANALYSIS

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by

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Chalk River, Ontario

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by

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SYNOPSIS

The high energy (>0.5 MeV) component of a reactor flux
can produce, via threshold reactions on the major constituents of
a sample, identical activities as those produced by the thermal
flux, through (n,γ) reactions, on the impurities being determined.
In order to predict these interferences in thermal neutron activa-
tion analysis, it is necessary to know:

1. The cross section of the threshold reaction in a pure fission
   neutron flux.

2. The fraction of the reactor thermal flux, nv_0, above about
   0.5 MeV which has the properties of a pure fission flux.

The latter has been determined in an empty fuel rod position in the
N.R.X. reactor using the reaction U-238 (n,f) as a monitor. Based
on this value, fission neutron cross sections have been measured for
several (n,p), (n,α), $(n,2n)$ and (n,n') reactions. The interferences
caused by the (n,p) and (n,α) reactions in this particular irradia-
tion position are given. An example of activation by $(n,2n)$ and
(n,n') reactions, when the (n,γ) reaction is not suitable, is also
discussed.

Chalk River Ontario
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1. INTRODUCTION

1.1 Fast Neutrons in a Reactor

The presence of high energy neutrons in thermal reactors creates a problem for the neutron activation analyst. Threshold reactions involving these neutrons can produce in the sample material the same radionuclide as the (n,γ) reaction on the impurity. At Chalk River, most of our analyses involve metallurgical specimens and we have found that interferences caused by (n,p) reactions on low mass metals present a serious problem. Although several of these reactions are exoergic they are classed with threshold reactions. The charged particle emitted has a coulomb barrier of several MeV to penetrate with the result that the reaction rate is negligible below about 0.5 MeV. In studying these reactions we are therefore concerned with the distribution of neutrons above this energy in the reactor spectrum. The N.R.X. reactor, in which most of our samples are irradiated, is fuelled with natural uranium and moderated with D_2O and is considered a 'well-thermalized' reactor.

ROY et al. (1) however were able to measure cross sections of $(n,2n)$ reactions in N.R.X. with thresholds between 6 and 20 MeV and they suggested that the neutron spectrum in this region was similar to that of a pure fission spectrum. If indeed the reactor neutron spectrum contained a pure fission component that held down to about 0.5 MeV before changing to the $1/E$ spectrum, then the effect of interfering threshold reactions could be calculated. This flux could be measured using a threshold detector with a known fission neutron cross section. MELLISH, et al. (2) found this hypothesis successful for the graphite moderated reactor Bepo. Using the S-32 (n,p) reaction cross section that had been measured by

HUGHES (3) in a pure fission neutron spectrum as a reference standard, they determined fission neutron cross sections of other threshold reactions.

1.2 Fission Neutron Cross Section

In a fission neutron flux the rate of a threshold reaction is

$$\int_{E_t}^{\infty} \sigma(E) \, nv(E) dE = \bar{\sigma}_{f.s.} \int_{0}^{\infty} nv(E) dE$$

The integral on the right is the integral flux in a pure fission neutron source. The fission neutron cross section, $\bar{\sigma}_{f.s.}$ is an average cross section which gives the correct reaction rate in such a flux. When the integral fission flux is normalized to one neutron cm^{-2} sec^{-1} using the distribution of WATT (4),

$$nv(E) = e^{-E} \sinh (2E)^{1/2} ,$$

then the fission neutron cross section is

$$\bar{\sigma}_{f.s.} = \int_{E_t}^{\infty} \sigma(E) f(E) dE ,$$

where f is the fraction of the fission neutron flux between E and E + dE. When the cross section curve as a function of energy for a threshold reaction is known, then $\bar{\sigma}_{f.s.}$ can be calculated by graphical integration of

$$\bar{\sigma}_{f.s.} \approx \sum_{E_t}^{\infty} \sigma F \, \Delta E , \qquad (1)$$

where σ and F are respectively the average cross section and fraction of the fission flux in an energy interval ΔE. Fission neutron cross sections obtained in this way provide absolute monitors for measuring fission neutron fluxes or the unmoderated fission component of a

reactor flux. They can be used to check those obtained experimentally with reactor neutrons.

1.3 Estimation of Interference

In order to calculate threshold reaction interference in activation analysis, two neutron fluxes have to be determined. First the reactor thermal flux, nv_o, which when multiplied by the effective cross section, $\hat{\sigma}_{n,\gamma}$, gives the equilibrium rate of the (n,γ) reaction, and second, the fission component of the reactor flux which when multiplied by the fission neutron cross section of the threshold reaction gives its equilibrium rate. The former is measured by determining the rate of a suitable (n,γ) reaction with and without a cadmium cover; the latter by measuring the rate of a threshold reaction.

As sample irradiations are done usually in only a few specified positions in a reactor, it is convenient to relate the fission component of the neutron spectrum to the reactor thermal flux, nv_o, at a particular position. Only a thermal flux monitor is then required with each irradiation in order to determine the threshold reaction interference. This of course assumes that the ratio of the two fluxes remains constant with possible variations in the thermal flux. It has been our experience that it does in the reactor core. If we use the term 'k' to define this ratio, then

$$\bar{\sigma}_{f.s.} = \frac{R}{k \ nv_o} \quad , \tag{2}$$

where R is the equilibrium rate of the threshold reaction in the irradiation position.

In analytical work it is more meaningful to express interference in terms of apparent concentration rather than as a reaction rate. The apparent concentration of an impurity resulting from the

threshold reaction can then be subtracted from the total concentration to give the true concentration of the impurity. The apparent concentration of the impurity will be that which would give the same activity by the (n, γ) reaction as that which is given by the threshold reaction on the target. Thus,

$$dN/dt_{(n, \gamma)} = N_i \, \hat{\sigma}_{n, \gamma} \, nv_o$$

and $$dN/dt_{(thresh.)} = N_t \, \tilde{\sigma}_{f.s.} \, k \, nv_o$$

where $N_{i, t}$ are the numbers of atoms of impurity isotope and target isotope respectively. The apparent concentration of impurity, i, in grams per gram of target element is then

$$\frac{\tilde{\sigma}_{f.s.} \, k \, At \, (At \, Wt)_i}{\hat{\sigma}_{n, \gamma} \quad A_i \, (At \, Wt)_t}$$

$A_{i, t}$ are the fractional abundances of isotopes i and t and $(At \, Wt)_{i, t}$ are the atomic weights of the respective elements.

1.4 Measurement of Fission Neutron Cross Sections

The fission neutron cross sections of many threshold reactions have been determined by several groups with reactor neutrons using one of the $\tilde{\sigma}_{f.s.}$ values given by HUGHES (3) as a flux monitor. A tabulation of results by ROCHLIN (5) in 1959 showed wide discrepancies but recent detailed comparisons of a few cross sections from the several groups of workers by PASSELL et al. (6), MELLISH (7) and ROY et al. (8) have shown these discrepancies to be mainly due to differences in values of $\tilde{\sigma}_{f.s.}$ used for the reference standards. If, for example, the value of 30 mb for the S-32 (n,p) P-32 given by HUGHES (3) is adjusted to 60 mb, which is the value obtained from the cross section curve using equation 1, then closer agreement is obtained.

The reaction U-238 (n,f) has been used in this study to determine the fission neutron component of the reactor flux in an empty fuel rod irradiation position of the D_2O moderated reactor N.R.X. The cross section of this reaction from its threshold at about 0.5 MeV up to 14 MeV has been accurately measured (9) and the fission yield of Ba-139, which is the fission product that was determined, is not sensitive to the energy of the neutrons causing fission. If highly depleted U can be obtained, this reaction is ideal for determining fission neutron flux. The value of k obtained in this way was used in conjunction with the reactor thermal flux to transform reaction rates of several threshold reactions to fission neutron cross sections using equation 2.

2. EXPERIMENTAL

2.1 Outline of Method

Irradiations in the N.R.X. reactor were carried out using the pneumatic carrier facility (10). The irradiation position is an empty fuel rod near the centre of the moderator tank. With the reactor operating at 40 MW, the reactor thermal flux, nv_o, averages 6.5×10^{13} n cm^{-2} sec^{-1}. From 1 to 100 mg of metal foil, wire or turnings were used, the weight depending on the expected reaction rate. The capsules used for the irradiations were lined with 0.76 mm cadmium in order to decrease the rate of the (n,γ) reaction on any impurity which might lead to the same end product. Where the product of the threshold reaction could not be produced by an (n,γ) reaction, e.g. Ni-58 (n,p) Co-58, some irradiations were done without the cadmium cover.

The convention of WESTCOTT (11) was used to describe the reactor thermal neutron flux, nv_0. It was determined by irradiating either a dilute Au-Al alloy (0.73 wt % Au) monitor or a similar Co-Al alloy monitor (0.976 wt % Co) with the sample, under cadmium. A similar monitor was then irradiated immediately following the sample irradiation, without the cadmium cover. The cadmium-covered reaction rates of the dilute alloys have been found by EASTWOOD et al. (12,13) to require small self-shielding corrections. The cadmium ratio and the uncovered rate were then used to determine nv_0 in the manner outlined in a previous publication (14).

The activity of the product nuclide of a threshold reaction was measured by γ-ray spectroscopy using a 3" x 3" NaI crystal and 100 channel Chalk River pulse analyser. The efficiency of the scintillator was determined in some cases using sources of the nuclide to be measured which were standardized by a $4\pi\,\beta\text{-}\gamma$ coincidence method (15). In other measurements the efficiency for the particular γ-ray energy was taken from a curve obtained by counting standardized sources of nuclides with known decay schemes in the range 0.16 to 1.3 MeV. Information on the decay scheme and conversion coefficients of the nuclide being measured was obtained from the Nuclear Data Sheets (16) in order to convert the measured γ-ray activities to the nuclear disintegration rates. Obviously the first method is more accurate.

2.2 Experimental Details

U-238 (n,f)

Target: Depleted uranium containing 12 ppm U-235 in the form of a 20% alloy with aluminum.

Chemical Separation: Ba-139 separated by precipitating carrier

BaCl$_2$ with conc. HCl - ether. Purified by Fe(OH)$_3$ scavenge

and further precipitation with HCl - ether with La hold-back

carrier. Final precipitation as BaSO$_4$ for counting.

Counting: 0.166 MeV γ-photopeak; Fission yield 5.7%;

Scintillator standardized with Ba-139.

Ni-58 (n,p) Co-58

Target: Ni wire, International Nickel Co., high purity.

No chemical separation.

Counting: 0.81 MeV γ-photopeak; 1 γ/dis.

Ni-60 (n,p) Co-60

Target: Bell Telephone Labs., zone refined Ni. Co content 0.5 ppm

contributed, under Cd, less than 5% to reaction rate by

Co-59 (n,γ) reaction.

No chemical separation.

Counting: 2.5 MeV sum peak; Scintillator standardized with Co-60.

Co-59 (n,p) Fe-59

Target: Co wire, Johnson-Matthey spec. pure.

Chemical Separation: Fe carrier extracted with di-isopropyl ketone

from 7N HCl, backwashed with H$_2$O, acidified, Co and Mn

hold-back carriers added and Fe extracted again. Cycle re-

peated then Fe precipitated with NH$_4$OH and burned-off to

Fe$_2$O$_3$ for counting.

Counting: 1.10 and 1.29 MeV γ-photopeaks; Scintillator standardized

with Fe-59.

Fe-54 (n,p) Mn-54

Target: Ferrovac E high purity Fe turnings.

Chemical Separation: Fe dissolved in dil. HNO_3 with Mn^{+2} carrier

added. Conc. HNO_3 added, boiled and $KClO_3$ added to

precipitate MnO_2. Cycle repeated with Fe hold-back carrier,

MnO_2 counted.

Counting: 0.84 MeV γ-photopeak; Scintillator standardized with Mn-54.

Fe-56 (n,p) Mn-56

Target: As above. No chemical separation.

Counting: 0.84 MeV γ-photopeak; 1 γ/dis.

Ti-46 (n,p) Sc-46; Ti-47 (n,p) Sc-47; Ti-48 (n,p) Sc-48

Target: Titanium turnings, commercially pure.

Chemical Separation: Part of one sample dissolved in HCl, Sc carrier

added and extracted with T.B.P. The γ-spectrum was identical

with that of irradiated metal therefore measurements were

made directly on samples.

Counting: Sc-46, 1.12 MeV γ-photopeak; 1 γ/dis.

Sc-48, 1.32 MeV γ-photopeak, 1 γ/dis.

Sc-47, 0.160 MeV γ-photopeak; Scintillator standardized

with Sc-47.

Al-27 (n,α) Na-24

Target: High-purity Al foil. No chemical separation.

Counting: 2.75 MeV γ-photopeak; Scintillator standardized with Na-24.

Zn-64 (n,p) Cu-64, Zn-67 (n,p) Cu-67

Target: Cominco high purity zinc metal.

Chemical Separation: Dissolved in HCl in presence of Cu^{+2} carrier,

almost neutralized, SO_2 bubbled through and NH_4CNS added to

ppt CuCNS. Dissolved in HCl and scavenged with $Fe(OH)_3$.

Final ppt of CuCNS.

Counting: <u>Cu-64</u> 0.51 MeV anihilation photopeak; 2 x 0.19 γ/dis.

        <u>Cu-67</u> 0.182 MeV γ-photopeak; 0.45 γ/dis.

<u>Pb-204 (n,2n) Pb-203, Pb-204 (n,n') Pb-204m</u>

<u>Target</u>: Cominco high purity Pb metal.

<u>Chemical Separation</u>: Dissolved in HNO_3 with In^{+3} hold-back carrier

    and pptd. as $PbCl_2$. Dissolved, more In carrier added and pptd.

    finally as $PbCrO_4$.

<u>Counting</u>: <u>Pb-203</u> 0.28 MeV photopeak; Standardized with Hg-203 1 γ/dis.

    <u>Pb-204</u> 0.9 MeV photopeak (doublet). 2 γ/dis.

3. RESULTS

3.1 Experimental Fission Neutron Cross Sections

The reactions studied are shown in Table I. Included for completeness is an earlier reported value (14) for S-32 (n,p) P-32 adjusted to the U-238 (n,f) value of 310 mb. The last column contains values of fission neutron cross sections for which there is good agreement between calculated and experimental values. For the remainder either no result has been reported or the reported results are widely scattered.

Under the column headed 'experimental $\bar{\sigma}_{f.s.}$' are the values that we have obtained using the calculated fission neutron cross section of the U-238 (n,f) reaction to determine k. Its value was found to be 0.0274 in an empty fuel rod position with a precision of $\pm 5\%$. The total error in the value of k, which includes the uncertainties in $\bar{\sigma}_{f.s.}$ for the U-238 (n,f) reaction and the fission yield, is estimated to be $\pm 10\%$. This error is reflected in the fission neutron cross sections for which we estimate a total error of $\pm 15\%$.

The calculation of the $\bar{\sigma}_{f.s.}$ values assumes that the reactor neutron spectrum has the characteristic fission shape above 0.5 MeV. This assumption is only justified if the experimental cross sections of reactions with differing threshold energies agree with accepted values of their fission neutron cross sections. In Figure 1 the average fission neutron cross sections per 0.5 MeV interval are plotted for the reactions U-238 (n,f) and Al-27 (n,α) Na-24 (17,18). It is clear that the most probable energy for the maximum rate of the U-238 (n,f) reaction is about 2 MeV while for the Al-27 (n,α) reaction it is about 8 MeV. From the area under the curve, $\bar{\sigma}_{f.s.}$ for the Al-27 (n,α) reaction is 0.61 mb and the preferred experimental value is in good agreement with this. The value of 0.85 mb obtained in this work based on 310 mb for the U-238 (n,f) reaction however is high. Similarly the Fe-56 (n,p) Mn-56 reaction, with a maximum rate at about the same energy as the Al-27 (n,α) reaction, appears to have a high cross section in N.R.X. The inference to be drawn from this is that the neutron spectrum above about 0.5 MeV in an empty fuel rod position in N.R.X. is not a pure fission spectrum but is hardened, i.e., there is a higher flux of higher energy neutrons. As the fission neutrons reaching this position from the nearest fuel rods have to traverse about 6" of D_2O this might be expected. The strength of this argument is diminished however by the fact that the exoergic reaction Zn-67 (n,p) Cu-67 shows a high value. Although the cross section curve is not known the maximum rate would be expected to occur at low energy.

3.2 Interferences in N.R.X.

Apparent concentrations of impurities caused by threshold reactions on the target element are shown in Table II. They have

been calculated from the experimental fission neutron cross sections of Table I and the value of 0.0274 for k using equation 2. As these are experimental values they are only meaningful for activation analyses carried out in the N.R.X. reactor.

4. DISCUSSION

4.1 Monitoring Fission Neutron Flux

In order to predict the interference from target element threshold reactions in other reactors, the fission neutron component of the reactor is usually obtained by irradiating a monitor element for which $\bar{\sigma}_{f.s.}$ is reasonably well known. Nickel is very useful for this purpose as the (n,γ) product Ni-65 has a short half-life and the others are long lived and do not emit γ-rays. No cadmium cover is required since Co-58 is not produced by an (n,γ) reaction. PASSELL et al. (6) have pointed out that Co-58 has a high thermal cross section, 1650 barns, which diminishes the usefulness of Ni as a fission neutron monitor. However for short irradiations this is unimportant; with a thermal flux (nv_0) of 6.5×10^{13} n cm^{-2} sec^{-1} the burn-out of Co-58 is only 1.5% at three days.

Unfortunately the full cross section curve for the Ni-58 (n,p) reaction has not yet been determined so that the energy at which the maximum reaction rate occurs in a fission flux is not known. However the value of 97 mb for $\bar{\sigma}_{f.s.}$ that we have obtained suggests that this energy is low as this value is in reasonable agreement with the accepted fission neutron cross section. If now the interfering threshold reaction is known to have a high threshold then monitors such as Al or Fe should be used to determine the

appropriate value of k. In this way possible error due to hardening of the fission spectrum is avoided.

4.2 Analysis by Means of Threshold Reactions

The presence of high energy neutrons in a reactor spectrum is not a total loss to activation analysis as some threshold reactions can be used to advantage. For example, in the determination of lead the isotope Pb-208 with an abundance of 52.3% has a thermal cross section of only 0.6 mb. The product nuclide, 3.3 hr Pb-209, emits β-particles only. This makes for unreliable counting due to the large self-absorption corrections necessary because of the high Z of the source. By making use of the (n,2n) reaction on Pb-204, 1.48% abundance, γ-spectroscopy can be used to measure the activity of the 52 hr Pb-203 source thus obviating self-absorption errors. This reaction has been used by REED et al. (19) to determine the Pb-204/208 ratio in meteorites using an irradiation facility inside an enriched fuel rod.

However, our value of 5 mb for the fission neutron cross section means that in N.R.X. the detection limit for lead using this method is about 200 times poorer than using the Pb-208 (n,γ) reaction, even though the precision of a determination is far greater. This detection limit for lead based on Pb-204 can be bettered by a factor of ten by counting the metastable 67 min. Pb-204m produced by inelastic scattering. An irradiation of 20 μg lead for 1 hour in N.R.X. core gives an activity equal to background in our counting system after 1 hour decay. This is our definition of detection limit. The (n,n') reactions are being studied as a means of determining the fast neutron distribution in the reactor because of their well defined thresholds. Lead is useful in this

regard as the Pb-204 (n,n') threshold is 2.18 MeV and the (n,2n) threshold 8.94 MeV. The rates of both these reactions can be determined simultaneously so that only one monitor is required to detect distortions of the fission neutron spectrum.

5. CONCLUSION

The estimation of interferences in activation analysis, using reactor neutrons, by threshold reactions on the target element can now be made with reasonable confidence. Sufficient consistent values of fission neutron cross sections appear in the literature to choose several monitors with maximum reaction rates at different energies in order to determine the effective fission flux in the reactor and its possible hardening. One can also make an estimate of the sensitivity of the (n,2n) or (n,n') reaction for radioactivation of the element in question when the (n,γ) reaction is not suitable.

ACKNOWLEDGEMENTS

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TABLE I

EXPERIMENTAL FISSION NEUTRON CROSS SECTIONS
IN AN EMPTY N.R.X. FUEL ROD POSITION

Reaction	Q Value MeV	Experimental Values of $\overline{\sigma}_{f.s.}$ mb.	Preferred Lit. Value $\overline{\sigma}_{f.s.}$ mb.
U-238(n,f)			310
Al-27(n,α)Na-24	-3.14	0.85	0.61
S-32(n,p)P-32	-0.926	58	60
Ti-46(n,p)Sc-46	-1.58	10	-
Ti-47(n,p)Sc-47	0.183	18	-
Ti-48(n,p)Sc-48	-3.21	0.53	-
Fe-54(n,p)Mn-54	0.094	59	52
Fe-56(n,p)Mn-56	-2.93	1.2	0.85
Co-59(n,p)Fe-59	-0.780	1.4	-
Ni-58(n,p)Co-58	0.399	97	90
Ni-60(n,p)Co-60	-2.03	3.2	-
Zn-64(n,p)Cu-64	0.209	31	30
Zn-67(n,p)Cu-67	0.211	0.88	0.55
Pb-204(n,2n) Pb-203	-8.94	5.0	-
Pb-204(n,n') Pb-204m	-2.18	22	-

TABLE II

SPECIFIC INTERFERENCES PRODUCED

IN THE N.R.X. REACTOR

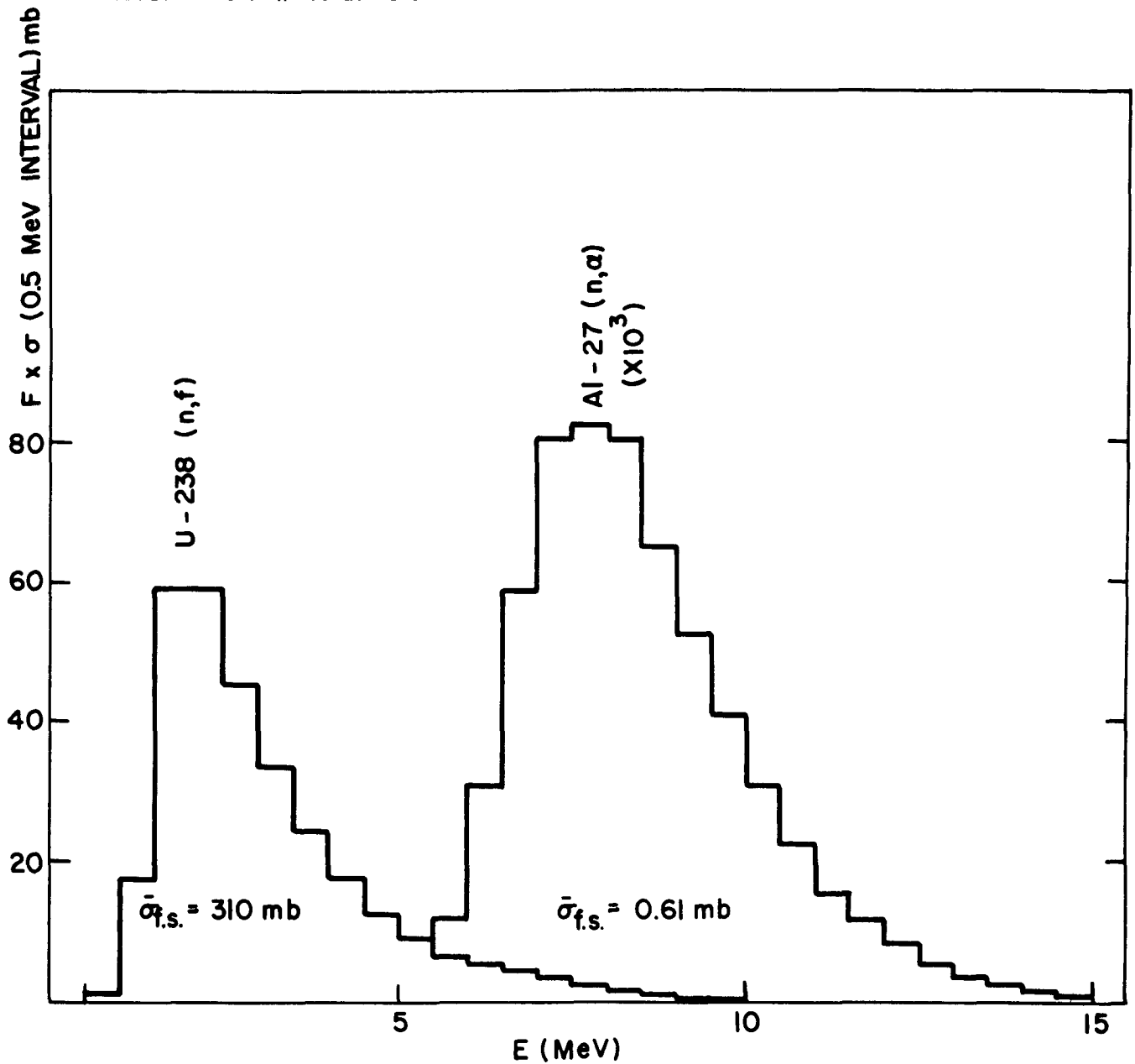| Impurity	Analysis Target	Apparent Concentration
Fe	Co	1.14%
P	S	0.78%
Cu	Zn	136 ppm
Na	Al	35 ppm
Mn	Fe	2.15 ppm
Sc	Ti	0.94 ppm
Co	Ni	0.63 ppm

FIGURE 1. Average Fission Neutron Cross Section per
0.5 MeV interval for U-238 (n,f) and Al-27
(n,α) Reactions.