2

BNL 29707
CONF-810682--8

ACTIVATION OF Tl, Pb, AND Bi BY 10-160-MEV NEUTRONS: POSSIBLE APPLICATION TO THE ANALYSIS OF Bi

P. P. Parekh* and H. L. Finston**

*Brookhaven National Laboratory, Upton, New York, U.S.A.

**City University of New York, Brooklyn College, Brooklyn, New York, U.S.A.

The medium energy intense neutrons (MEIN) available at the Brookhaven Chemistry Linac Irradiation Facility have an energy distribution up to ~ 160 MeV and an effective neutron flux of ~ 1.3 x 10^{11} cm^{-2} s^{-1}. The present work explores the feasibility of using this facility for the analysis of Tl, Pb and Bi by activation with MEIN. The most sensitive reactions, from a practical standpoint, were found to be Tl (n, xn) ^{200}Tl (x = 4, 6), Pb (n, xn) ^{204m}Pb (x = 0, 3, 4, 5) and ^{209}Bi (n, 6n) ^{204}Bi. The absolute sensitivities attainable with these reactions are 0.1, 0.05 and 0.08 μg of Tl, Pb and Bi respectively, for 1 h irradiation at 1.3 x 10^{11} n cm^{-2} s^{-1} with samples counted 2 h after the end of irradiation. The advantages of the method over thermal neutron activation analysis are that all three elements can be assayed at the sub-microgram concentration levels by γ-spectrometry with the help of a simple radiochemical purification and the analytical results can be verified by cross checking via the multiple (n, xn) reaction products. However, interference from Bi in the determination of Pb and from Pb and Bi in the determination of Tl limits its usefulness to the analysis of Bi.

Introduction

The state-of-the-art in neutron activation analysis can best be described as sample irradiation followed by non-destructive high-resolution Ge(Li)-spectrometry at judiciously selected time intervals. Elaborate radiochemical separations of individual elements have become obsolete and group separations are found adequate for unfavorable cases. In this manner most elements can, and have been determined utilizing either reactor neutrons, 14 MeV neutrons or photons. However, the last three stable elements, Tl, Pb

and Bi are among the few exceptions. Table 1 gives the nuclear data pertinent to the activation of these elements with reactor and 14 MeV neutrons. The product nuclides of the only sensitive (n, γ) reactions on these elements are pure β^- emitters; hence careful radiochemical purifications are required and there are the concomitant difficulties of β^- counting which limit the application of the method.

The medium energy intense neutrons (MEIN) available at the Chemistry Linac Irradiation Facility (CLIF) of Brookhaven National Laboratory have an almost flat energy distribution in the 30-160 MeV region and an effective neutron flux of $\sim 1.0 \times 10^{11}$ n cm^{-2} s^{-1}.[1] Thus far, these neutrons have been applied for the synthesis of new neutron-rich isotopes and for study of decay schemes[2-8]. The present work explores the feasibility of using this facility for the analysis of the aforementioned three elements by activation with MEIN.

Experimental

Figure 1 gives a schematic diagram of the MEIN facility and the CLIF Laboratory. The 200 MeV proton beam ($\sim$ 80 μA) from the Brookhaven linear accelerator is stopped in a water-cooled copper disc (21.6 cm diameter and 4.76 cm thick) to produce a medium energy intense neutron source (MEIN). The energy distribution of these secondary neutrons[1] (calculated for an incident 200 MeV protons stopping in a Cu target and averaged over the angular intervals 0^o-30^o) is given in the inset to Fig. 1. As mentioned earlier, these neutrons have an almost flat energy distribution in the 30-160 MeV region and a flux of $\sim 1.0 \times 10^{11}$ n cm^{-2} s^{-1}.

For sample irradiation, a pneumatic carrier facility is installed in the CLIF laboratory $\approx$ 8 m above the spur tunnel. It is powered by a simple household vacuum system. The pneumatic tube transports a rabbit from the

laboratory to a position 9 cm from the end of the copper beam stop. The transit time is ∿ 2 sec. A layer of boron is inserted in the space between the beam stop and the rabbit to filter out slow neutrons. Both beryllium and plastic rabbits (inner dimensions: 3.41 cm x 1.75 cm) were used in the work although the former was preferred because of lesser induced radioactivity. Details of the MEIN facility are described by KATCOFF et al.[1]

About 0.1 g each of high-purity Tl, Pb and Bi metal beads (Six-9 grade) were weighed accurately, paced in a polythene capsule (15 mm long and 4 mm outer diameter) and then heat-sealed. A piece of 0.05 mm thick Al foil (10 mm x 10 mm) was used as a flux monitor. The foil was placed on the outside of the capsule covering the sample and held in position with tape. Also about 0.2 g Bi $(NO_3)_3 . 5\ H_2O$ and 0.1 g Pb $(NO_3)_2$ (Johnson Mathey's specpure grade) were weighed accurately and packed along with Al monitors in the manner described above.

The samples were irradiated for 6.0 min at a MEIN flux of ∿ 1.0×10^{11} n cm^{-2} s^{-1}. The irradiated metal beads of Tl, Pb and Bi were γ-counted ∿ 1 h after the irradiation using a high-resolution Ge(Li) detector coupled to a computerized 4096-channel analyzer. The γ-spectra were recorded at different time intervals for about a month and the data were stored on magnetic tapes. Energy and efficiency calibrations were performed with National Bureau of Standards γ-ray sources. γ-spectra were analyzed using the INTRAL program[9] for energies and intensities and the CLSQ program[10] for decay curve fitting.

From these measurements, the reaction yields for the (n, xn) product nuclides of the 3 targets were evaluated. Since Bi is mono-isotopic, it was

possible to calculate the effective crossection (σ_{eff}) for the various targets (n, xn) reaction. The σ_{eff} for Tl and Pb could not be evaluated because of their polyisotopic nature.

In the determination of Tl and Pb via (n, xn) reactions, the magnitudes of the Bi (n, pxn) interference in the determination of Pb, and the Pb (n, pxn) and Bi (n, αxn) interferences in the determination of Tl had to be evaluated. For this purpose radiochemical separations of Pb from the irradiated Bi metal and of Tl from the irradiated salts of Pb and Bi were carried out using the procedure outlined in Figures 2a) and 2b), respectively.

Results and Discussion

Table 2 and Fig. 3 give the σ_{eff} for the (n, xn) reactions on ^{209}Bi for x = 4 through 10. These cross sections are calculated relative to σ_{eff} of 40 mb for the ^{27}Al (n, α) ^{24}Na reaction[1]. For comparison the σ_{eff} reported for several targets[1] have also been included in Fig. 3. Note that σ_{eff} decreases as x increases and the slopes become steeper as Z decreases. For example, the σ_{eff} for the (n, 4n) reaction increases from 21.7 mb[1] for a light target ($_{23}V$) to 98 mb[1] for an intermediate target ($_{41}Nb$) to as high as 258 mb for the heavy $_{83}Bi$. From the standpoint of neutron activation analysis, the (n, xn) reaction should yield the highest sensitivity for heavy elements like Tl, Pb and Bi. Although σ_{eff} for Tl and Pb were not evaluated for the reason mentioned earlier, some broad conclusions can be drawn from the systematics on σ_{eff} made by KATCOFF et al.[1]. These authors observed that for a given value of x, σ_{eff} for the even Z targets $_{28}Ni$ and $_{30}Zn$ are considerably lower than for neighboring odd Z targets $_{27}Co$ and $_{29}Cu$. If this observation is extra-

polated to the three targets under study, then for a given value of x the σ_{eff} for $_{83}Bi$ and $_{81}Tl$ are expected to be higher than for $_{82}Pb$. Again from the general trend in Fig. 3 it seems the σ_{eff} should be higher for Bi than for Tl and perhaps the highest that can be expected for a stable element.

Table 3 gives the specific activity of the various (n, xn) reaction products of Tl, Pb and Bi. The specific activity is expressed in terms of peak intensity (in cpm) of the most useful γ line per µg of the element and corresponds to 1 h bombardment at a flux of 1.3×10^{11} n cm^{-2} s^{-1} and counted 2 h from the end of bombardment on the face of the Ge(Li) detector. Although unconventional, this is a more practical way of expressing specific activity. In the case of Tl, the reactions Tl (n, xn) ^{198m}Tl ($T_{1/2}$ = 1.9 h; x = 6, 8) and Tl (n, xn) ^{200}Tl ($T_{1/2}$ = 26.1 h; x = 4, 6) offer approximately equal sensitivities. However, the latter is recommended because of its convenient long half-life. It is clear that ^{209}Bi (n, 6n) ^{204}Bi ($T_{1/2}$ = 11.3 h) and Pb (n, xn) ^{204}Pb ($T_{1/2}$ = 66.9 m, x = 0, 3, 4, 5) are the most sensitive reactions for the determination of these elements. The practical sensitivity (absolute) is calculated only for the most useful reaction (underlined in the table). It is defined as that amount of element which gives net peak intensity of 1 cpm under irradiation and counting conditions specified above. The absolute sensitivities attainable are 0.13, 0.05 and 0.08 µg of Tl, Pb and Bi respectively. The magnitude of interference was calculated for the most useful reaction under conditions identical to those used in the evaluation of practical sensitivity. On a weight for weight basis the interference of Bi (n, p5n) reaction in the determination of Pb is ∿ 50%. Since the 11.3 h ^{204}Bi does not decay via the metastable state of ^{204m}Pb, interference

is strictly from a conflicting nuclear reaction. In the determination of Tl via ^{200}Tl the interference of ∿ 14% and ∿ 2% is the gross interference from the interfering nuclear reactions shown in Table 3 and the in-growth of ^{200}Tl from the decay of ^{200}Pb and ^{200}Bi-^{200}Pb. The actual interference from the nuclear reactions is therefore lower than indicated.

The salient features of the method are 1) all three elements can be assayed at the submicrogram concentration levels by γ-spectrometry after a simple radiochemical purification like that shown in Figure 2. 2) since σ_{eff} of all types of reactions induced by MEIN are in the range of few hundred millibarns and less[1] the radioactivity induced in the samples are expected to be much lower than that encountered typically in reactor irradiation and 3) the analytical results can be verified by crosschecking through the multiple reaction products (see Table 3). The disadvantages of the method are 1) it is not so versatile for the simple reason that MEIN is almost the only facility of its kind and 2) nuclear interference from Bi in the determination of Pb and from Pb and Bi in the determination of Tl narrows down its usefulness to the analysis of Bi.

Acknowledgment

The authors wish to thank Seymour Katcoff for his helpful suggestions and encouragement. Research was carried out, in part, under contract with the U. S. Department of Energy and supported by its Office of Basic Energy Sciences.

* Present Address: New York State Department of Health
Division of Laboratories and Research
Albany, NY 12201 USA

References

1. S. Katcoff, J. B. Cumming, J. Godel, V. J. Buchanan, H. Susskind and C. J. Hsu, Nuclear Inst. & Methods, 129 (1975) 473.
2. E-M. Franz, S. Katcoff, H. A. Smith, Jr. and T. E. Ward, Phys. Rev. C12 (1975) 616.
3. P. E. Haustein, E-M. Franz, S. Katcoff, N. A. Morcos, H. A. Smith, Jr. and T. E. Ward, Phys. Rev. C14 (1976) 645.
4. P. E. Haustein, E-M. Franz, R. F. Petry and J. C. Hill, Phys. Rev. C16 (1977) 1559.
5. J. Gilat and S. Katcoff, J. Inorg. Nucl. Chem. 40 (1978) 369.
6. P. E. Haustein, H-C. Hseuh, R. L. Klobuchar, E-M. Franz, S. Katcoff and L. K. Peker, Phys. Rev. C19 (1979) 2332.
7. E-M. Franz, S. Katcoff, P. P. Parekh and L. K. Peker, Phys. Rev. C (submitted).
8. P. P. Parekh, L. K. Peker, S. Katcoff and E-M. Franz, Phys. Rev. C (submitted).
9. J. B. Cumming (unpublished): Modification of program by R. Gunninck, H. B. Levy and J. B. Niday, Univ. of Cal. Radiat. Lab. Report No. UCID-15140 (unpublished).
10. J. B. Cumming, NAS-NRC Nuclear Sci. Ser. Report #NAS-NS-3107 (1962) (unpublished).

Table 1

Activation Analysis of Tl, Pb and Bi with Reactor--and 14 MeV Neutrons

Element	Reaction	Mode of Decay	Practical Sensitivity (μg)	
			Reactor	14 MeV
Tl	$^{203}Tl(n,\gamma)^{204}Tl$ (3.8 y)	β^-,no γ	0.01	--
	$^{203}Tl(n,2n)^{202}Tl$ (12.2 d)	E.C.,γ(440 KeV)	3	--
Pb	$^{208}Pb(n,\gamma)^{209}Pb$ (3.3 h)	β^-,no γ	0.04	--
	$^{204}Pb(n,2n)^{203}Pb$ (52.3 h)	E.C.,γ(279 KeV)	8	100
	$^{204}Pb(n,n')^{204m}Pb$ (66.9 m)	IT,γ(374 KeV)	0.9	11
Bi	$^{209}Bi(n,\gamma)^{210}Bi$ (5.0 d)	β^-,no γ	0.005	--
	$^{209}Bi(n,p)^{209}Pb$ (3.3 h)	β^-,no γ	140	--

*Based on 10 cpm for β^- and 1 cpm peak intensity for γ,counted 2 h from the end of irradiation.

$\phi_{(th)} = 10^{13} ncm^{-2}s^{-1}$, $\phi_{(f)} = 10^{12} ncm^{-2}s^{-1}$, $\phi_{(14\ MeV)} = 10^{9} ncm^{-2}s^{-1}$

Irradiation Time: 1.0 d for reactor--and 1.0 h for 14 MeV neutrons

Reactions yielding poor sensitivities (> 200 μg) not considered.

Table 2

Effective Cross Sections for the $^{209}Bi(n, xn)$ Reactions

Product Nuclide	$T_{1/2}$	Reaction	σ eff mb
^{200}Bi	36.4 m	(n,10n)	28.8
^{201}Bi	1.77 h	(n,9n)	35.1
^{202}Bi	1.67 h	(n,8n)	79.6
^{203}Bi	11.8 h	(n,7n)	130
^{204}Bi	11.3 h	(n,6n)	164
^{205}Bi	15.3 d	(n,5n)	201
^{206}Bi	6.2 d	(n,4n)	258

Table 3

Specific activity of the various (n, xn) reaction products of Tl, Pb and Bi sensitivity of the most useful reaction and magnitude of nuclear interference

Element	Product nuclide and half-life	E_γ* KeV	Specific activity peak intensity cpm/µg @	Absolute sensitivity** µg	Nuclear Interference	
					Reaction	Magnitude*** %
Tl	32.8m Tl-194m	749	0.6	——		
	2.8h Tl-197	426	1.4	——		
	1.9h Tl-198m	587	8.3	——		
	7.4h Tl-199	208	2.6	——		
	26.1h Tl-200	368	7.6	0.13	Pb(n,pxn)	∿14
					Bi(n,α 6n)	∿ 2
	73h Tl-201	167	0.4	——		
	12.2d Tl-202	440	1.0	——		
Pb	42m Pb-197m	385	2.4	——		
	2.4h Pb-198	290	1.2	——		
	1.5h Pb-199	353	1.2	——		
	21.5h Pb-200	148	0.8	——		
	9.4h Pb-201	331	9.6	——		
	3.6h Pb-202m	422	6.3	——		
	52.1h Pb-203	279	3.5	——		
	66.9m Pb-204m	375	19.6	0.05	Bi(n,p5n)	∿50
Bi	36.4m Bi-200	462	3.0	——		
	1.77h Bi-201	629	1.7	——		
	1.67h Bi-202	961	7.8	——		
	11.8h Bi-203	820	1.4	——		
	11.3h Bi-204	375	12.6	0.08	None	——
	15.3d Bi-205	703	0.1	——		
	6.24d Bi-206	803	0.9	——		

Irradiation Time: 1 h; Flux: 1.3×10^{11} n cm^{-2} s^{-1}

*Most useful γ-line considered, @ counted 2 h from the end of irradiation on the face of a Ge(Li) detector (efficiency 20% relative to a 3" x 3" NaI(Tl) detector)

**Calculated for the most useful nuclear reaction

***Weight for weight basis

Figure captions:

Fig. 1. Schematic diagram of the Medium Energy Intense Neutron (MEIN) Facility and the Chemistry Linac Irradiation Facility (CLIF). The calculated MEIN energy spectrum is shown in the inset.

Fig. 2. Flow diagrams showing the radiochemical procedures for Pb and Tl.

Fig. 3. Effective cross sections σ_{eff} for the (n, xn) reactions on several targets: 200 MeV primary proton beam. Open points: Katcoff et al. (Ref. 1). Closed points: This work.

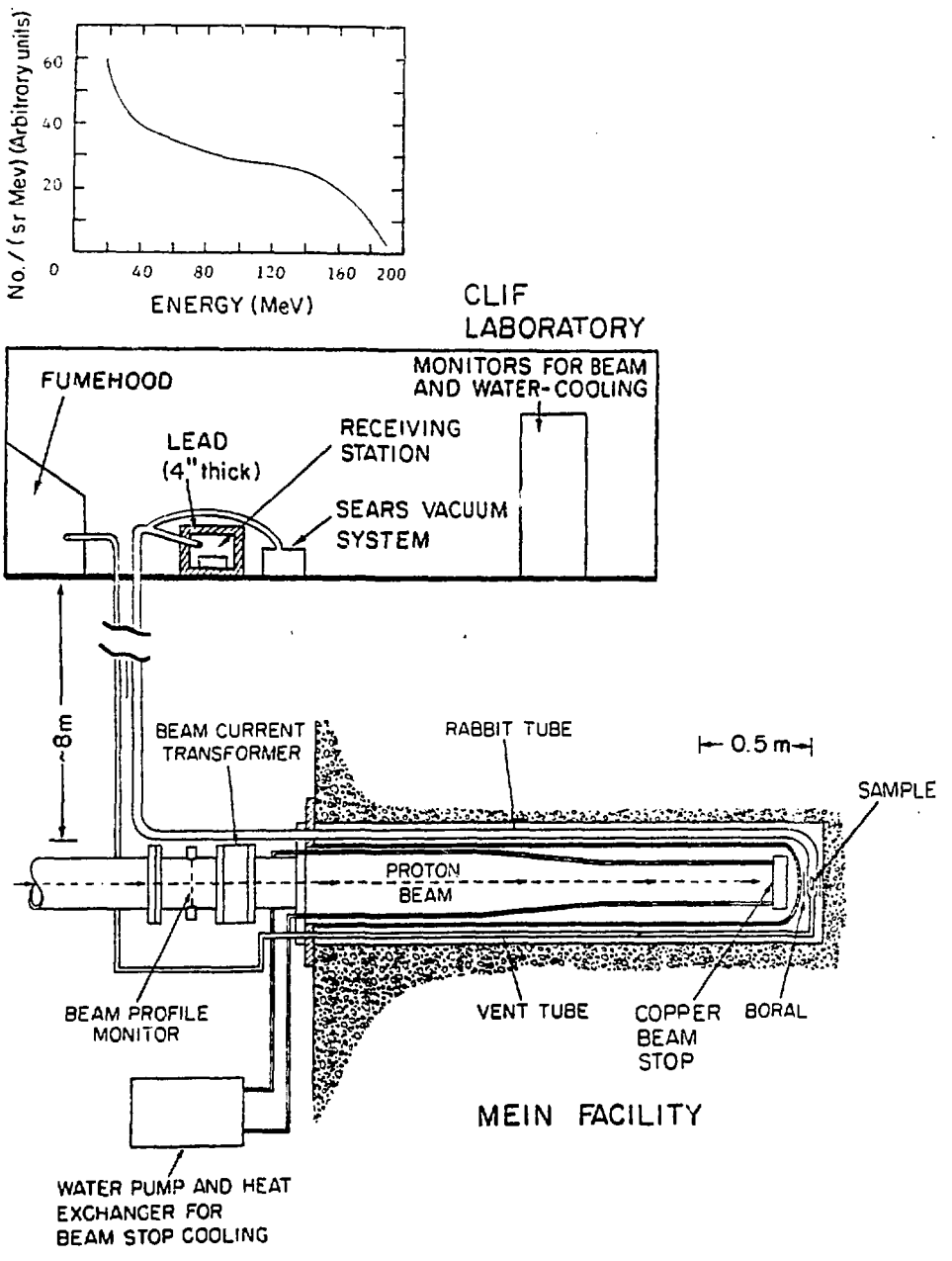
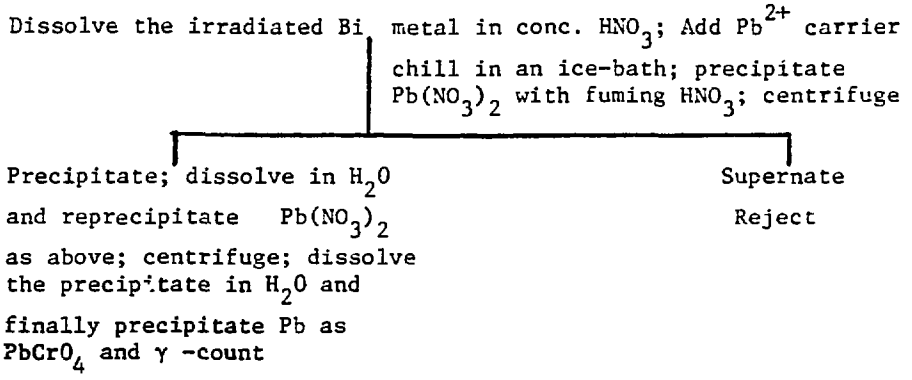

No./(sr Mev) (Arbitrary units)
60
40
20
0
40
80
120
160
200
ENERGY (MeV)
CLIF
LABORATORY
FUMEHOOD
MONITORS FOR BEAM
AND WATER-COOLING
LEAD
(4" thick)
RECEIVING
STATION
SEARS VACUUM
SYSTEM
~8m
BEAM CURRENT
TRANSFORMER
RABBIT TUBE
0.5 m
SAMPLE
PROTON
BEAM
BEAM PROFILE
MONITOR
VENT TUBE
COPPER
BEAM
STOP
BORAL
MEIN FACILITY
WATER PUMP AND HEAT
EXCHANGER FOR
BEAM STOP COOLING

Fig. 1

a) Radiochemical Separations of Pb from Bi Target



b) Radiochemical Separation of Tl from Pb and Bi Targets

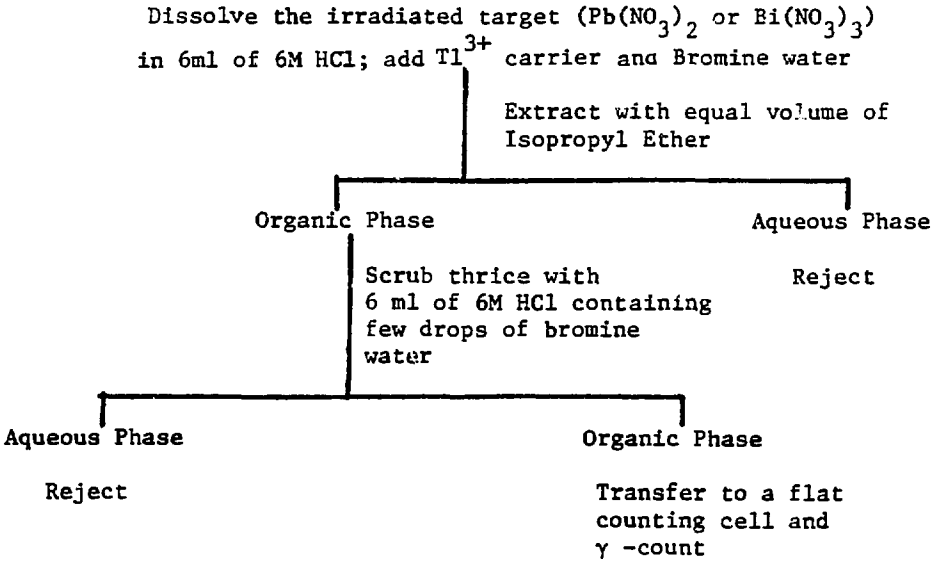


Figure 2

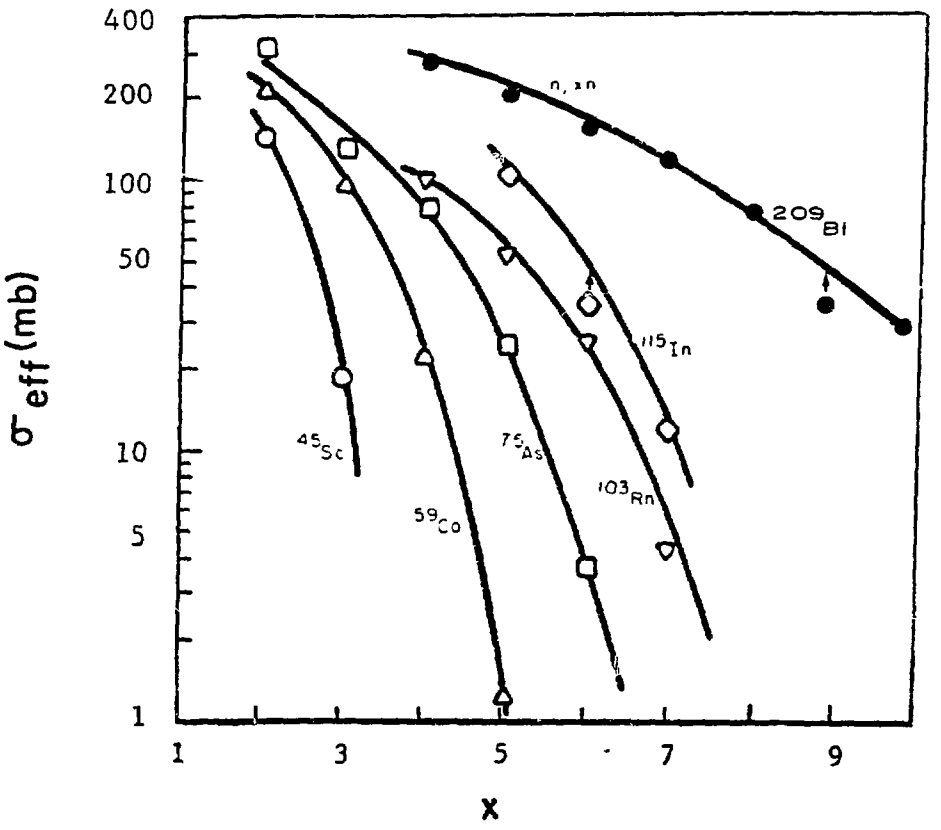

400
200
100
50
10
5
1
σ_{eff} (mb)
1
3
5
7
9
X
^{209}Bi
^{115}In
^{103}Rh
^{75}As
^{59}Co
^{45}Sc

Fig. 3