

ACTIVATION ANALYSIS OF HIGH-PURITY SILICON

III. MULTI-ELEMENT ACTIVATION ANALYSIS: APPLICATION OF THE TRIPLE COMPARATOR METHOD

F. DE CORTE,* A. SPEECKE, J. HOSTE

Institute for Nuclear Sciences, University of Ghent, Ghent (Belgium)

(Received March 25, 1971)

The triple comparator method is used for the analysis of impurities of high purity silicon by neutron activation. The ratios of the specific photopeak activities of the isotopes investigated to the specific photopeak activities of the gold, indium and cobalt comparators were determined. The triple comparator method avoids some tedious problems in the multi-element activation analysis and it is very well suited for the determination of 'non-expected' elements.

In a previous paper¹ a separation scheme was described for the simultaneous determination, by neutron activation analysis, of 21 elements in high purity silicon: Au, Sb, Ga, Fe, Tl, Na, K, Sc, Cr, Sm, Eu, La, As, Co, In, Zn, Cu, W, Mo, Sn and Ta.

As a multi-element activation analysis causes many problems with respect to the standard, a triple comparator method was proposed, using ⁶⁰Co, ^{114m}In and ¹⁹⁸Au.² In this technique the *k* ratios of the elements to be analysed, i.e. the ratios of the specific photopeak activities of the isotopes investigated to the specific photopeak activities of the comparator isotopes, are adapted for each new ratio of thermal to epithermal reactor neutron flux, using the relation

$$k_x = k_s \frac{S_x D_x S_s^* D_s^*}{S_s D_s S_x^* D_x^*} \frac{\left[\frac{(\Phi_{th})_x}{(\Phi_{epi})_x} + \frac{I}{\sigma_{th}} \right] \left[\frac{(\Phi_{th})_s}{(\Phi_{epi})_s} + \frac{I^*}{\sigma_{th}^*} \right]}{\left[\frac{(\Phi_{th})_x}{(\Phi_{epi})_x} + \frac{I^*}{\sigma_{th}^*} \right] \left[\frac{(\Phi_{th})_s}{(\Phi_{epi})_s} + \frac{I}{\sigma_{th}} \right]} \quad (1)$$

where *S* – saturation factor = $1 - e^{-\lambda t}$, *t* – irradiation time, λ – decay constant,

D – decay factor = $e^{-\lambda T}$, *T* – decay time,

Φ_{th} – thermal reactor neutron flux,

Φ_{epi} – epithermal reactor neutron flux,

σ_{th} – thermal activation cross-section,

I – resonance integral,

* Research associate of the N. F. W. O.

and where the asterisks (*) refer to a comparator, and the indices x and s denote the 'activation' and 'reference' irradiation sites, respectively.

The flux ratios $(\Phi_{th})_x/(\Phi_{epi})_x$ from Eq. (1) can be calculated from Eq. (2)

$$A_{sp} = \frac{\theta N_A S E \alpha D}{M} (\sigma_{th} \Phi_{th} + I \Phi_{epi}) \quad (2)$$

where A_{sp} – specific photopeak activity,
 θ – isotopic abundance of the target nuclide,
 N_A – Avogadro's number,
 S – saturation factor,
 E – efficiency of the detector for the γ -ray measured,
 α – γ -ray abundance in the decay scheme of the radioisotope,
 D – decay factor,
 M – atomic weight of the irradiated element.

When irradiating and counting the three comparators, for which all the parameters of the first half of Eq. (2) are known, a system of three equations with unknowns (Φ_{th} and Φ_{epi}) arises, so that three sets of Φ_{th} and Φ_{epi} , and next of Φ_{th}/Φ_{epi} can be calculated.

The triple comparator method avoids some tedious problems in a multi-element activation analysis, such as the treatment of the standards and the need for space in the irradiation capsule. Moreover, this technique is very well suited for the determination of 'non-expected' elements, as the k values can be evaluated afterwards. On the other hand, it should be noted that during the whole set of experiments the measurement parameters must be kept rigorously constant.

As the knowledge of the I/σ_{th} values of the isotopes measured is required for the calculation of the k values (see Eq. 1), eight resonance integrals not available in the literature had to be determined. This was the case for ^{50}Cr , ^{58}Fe , ^{151}Eu , ^{139}La , ^{68}Zn , ^{186}W , ^{98}Mo and ^{116}Sn . In a previous paper the determination of the σ_{th} and I values of the reaction $^{113}\text{In}(n, \gamma)^{114m}\text{In}$ was described.

Silicon of five different purity levels was analysed, combining the above mentioned separation scheme and the triple comparator method.

Experimental

Nuclear data

The values of σ_{th} and I , as well as the I/σ_{th} ratios of the comparators and the isotopes under investigation, are listed in Table 1. Most of these data were taken from GOLDMAN and ROESSER³ and from DRAKE.⁴ It should be noted that I is defined according to the HÖGDAHL convention.⁵ The values between brackets

Table 1
 σ_{th} , I and I/σ_{th} values

Isotope formed	σ_{th} , barn	I , barn	I/σ_{th}
^{46}Sc	23	10.2	0.44
^{51}Cr	17.0	8.30*	0.49*
^{59}Fe	1.2	0.66*	0.55*
^{152m}Eu	2800	2014*	0.71*
^{42}K	1.1	0.98*	0.89*
^{64}Cu	4.5	4.2	0.93
^{24}Na	0.53	0.517	0.98
^{140}La	8.9	11.0*	1.24*
^{60}Co	37	75	2.03
^{69m}Zn	0.1	0.31*	3.1*
^{72}Ga	5.2	21.6	4.15
^{187}W	40	290*	7.25*
^{76}As	4.5	40.3	8.96
^{99}Mo	0.51	4.72*	9.25*
^{153}Sm	210	3163	15.1
^{198}Au	98.8	1550	15.7
^{122}Sb	6.06	143	23.6
^{114m}In	9.45 (Ref. ¹)	258 (Ref. ¹)	27.3 (Ref. ¹)
^{182}Ta	21.07	578	27.4
^{117m}Sn	0.006	0.4*	72*

* Values were determined in this work.

were experimentally determined in this work by measuring the cadmium ratios (R_{Cd})

$$\frac{I}{\sigma_{th}} = \frac{\Phi_{th}/\Phi_{epi}}{R_{Cd} - 1} \quad (3)$$

where $R_{Cd} = \frac{A_{sp} \text{ after irradiation without Cd cover}}{A_{sp} \text{ after irradiation with Cd cover}}$.

The activity measurements were carried out γ -spectrometrically on a NaI(Tl) detector, except in the case of ^{117m}Sn , where a Ge(Li) detector was used.

Reference and 'activation' irradiation sites

Channel 3 of the Thetis reactor was chosen as reference irradiation site for the determination of the k_s values. $(\Phi_{th})_s$ and $(\Phi_{epi})_s$ at this place were experimentally determined from the usual Co and Au flux monitors, irradiated with and without

Cd cover during 5 hrs, and found to be $7.42 \cdot 10^{10}$ and $3.31 \cdot 10^9 \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$, respectively, so that $(\Phi_{\text{th}})/(\Phi_{\text{epi}}) = 23.7$.

The irradiations for the activation analyses were performed at the BR-2 reactor in Mol during 15-hr periods. The values of thermal and epithermal neutron fluxes were calculated from the comparator activities according to Eq. (2).

Treatment of comparators and standards

Working at the Thetis reactor, the comparators were prepared as follows. The gold comparator was irradiated after evaporating a solution, containing 10.52 μg of gold, in a small plastic tube. Indium was irradiated as a mixture of about 1 mg specpure In_2O_3 with 1 g specpure Al_2O_3 . The cobalt comparator was irradiated as a Co-Al wire, containing 2% cobalt. For the determination of the k_s values, the standards were irradiated as specpure or a.g. products, taking care to avoid self-shielding effects caused by high absorption cross-sections.

For the analyses at the BR-2 reactor in Mol, the comparators were prepared as follows: 100 μl of Au or In solutions, containing 1.501 μg Au and 1.511 μg In, respectively, were spotted in silica tubes and evaporated under an infrared lamp. Cobalt was irradiated as 1–2 mg of a Co-Al wire containing 2% Co.

After irradiation, the Au and In comparators were dissolved in aqua regia and 6N HCl solution, respectively. When irradiating an In_2O_3 - Al_2O_3 mixture, the Al_2O_3 was filtered off, whereby no adsorption effects of In occurred. After surface etching of the Co-Al alloy in diluted HCl medium, it was dissolved in 6N HCl. The irradiated standards were dissolved in the appropriate solutions. When standardizing tin, the removal of ^{125}Sb is necessary as has already been pointed out in an earlier paper.² Use was made of the spontaneous deposition of Sb on an Fe foil, as described by KLEEMANN and HERRMANN.⁶ The deposition velocity and yield were investigated as a function of stirring time, temperature, acid, Sb and Sn concentrations. During these experiments the following parameters were kept constant: speed of stirring, liquid volume (50 ml) and surface area of the Fe foil (42.4 cm^2). The results of the experiments are shown in Fig. 1. From the data so obtained the following conditions were chosen for the removal of the ^{125}Sb daughter from the mixture of the Sn isotopes: stirring time: 1 hr; temperature: 40 °C; HCl concentration: 3N; no addition of Sb carrier. In these circumstances the deposition yield amounted to 98%. Ge(Li) γ -spectrometric control revealed that no Sn was co-deposited.

Counting conditions

After irradiation, the comparators were dissolved in 20-ml glass tubes and measured in a 25-ml well-type NaI(Tl) scintillation counter coupled to a 400 channel analyser. The counting efficiency of the detector [E_α value of Eq. (2)

amounted to 0.0960 for ^{114m}In (192 keV), 0.300 for ^{198}Au (412 keV) and 0.175 for ^{60}Co (1173 + 1332 keV). In order to allow the decay of the short-lived radioisotopes, the comparator activities were measured at the earliest 1–2 weeks after irradiation.

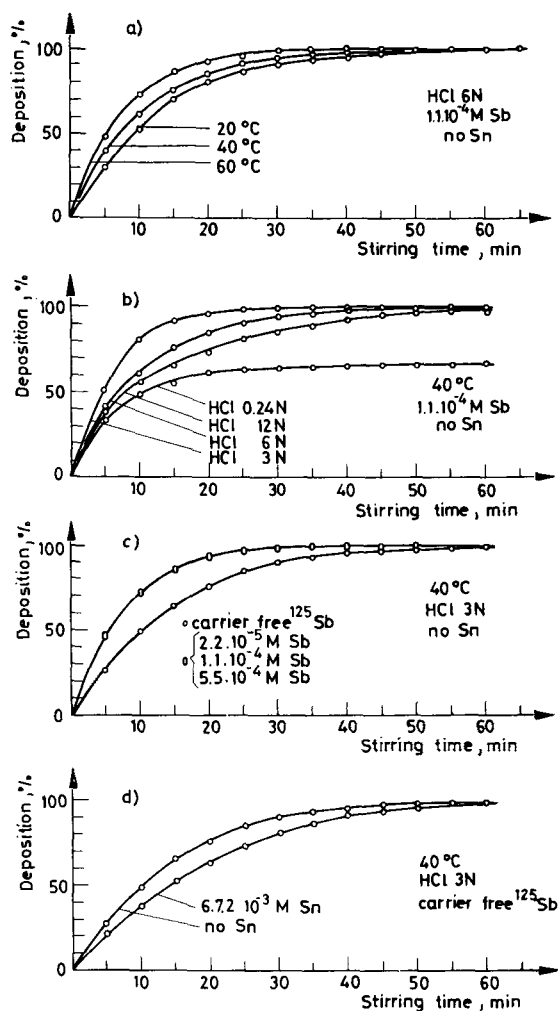


Fig. 1. Spontaneous deposition of Sb on a Fe foil

From the separation scheme discussed in an earlier paper,² it was obvious that the different fractions resulting from the separation procedures can be subdivided into three counting groups. The brackets refer to a group of isotopes simultaneously measured by mixed γ -spectrometry. Consequently, the k_s values were determined using the same counting conditions.

- Group 1: (^{198}Au , ^{122}Sb , ^{72}Ga , ^{59}Fe), ^{51}Cr , ^{42}K , $^{99}\text{Mo}/^{99m}\text{Tc}$, ^{117m}Sn ;
40 ml solutions in glass counting tubes;
NaI(Tl) well-type detector + 400-channel analyser.
- Group 2: (a) (^{60}Co , ^{76}As), ^{114m}In , ^{69m}Zn , ^{64}Cu ;
35 ml solutions in 50-ml plastic vessels;
(b) ^{187}W , ^{182}Ta ;
70 ml solutions in 125-ml plastic vessels;
(a) + (b) NaI(Tl) flat detector + 400-channel analyser.
- Group 3: (^{24}Na , ^{46}Sc , ^{140}La , ^{152m}Eu , ^{153}Sm);
70 ml solutions in 150-ml Erlenmeyer flasks;
Ge(Li) detector + 4096-channel analyser.

Determination of the k_s values

The experimentally determined k_s ratios vs. the three comparators are listed in Table 2. The values given take into account a decay of 24 hrs. The reproduci-

Table 2
 k_s values (irradiation time 5 hrs; decay time 24 hrs)

Isotope	Photopeaks measured, keV	k_s vs.		
		^{60}Co comparator	^{114m}In comparator	^{198}Au comparator
^{24}Na	1368	0.162	0.679	$1.42 \cdot 10^{-4}$
	2754	$5.52 \cdot 10^{-2}$	0.231	$4.84 \cdot 10^{-5}$
^{42}K	1525	0.137	0.572	$1.20 \cdot 10^{-4}$
^{46}Sc	889	0.141	0.589	$1.23 \cdot 10^{-4}$
	1120	0.106	0.446	$9.32 \cdot 10^{-5}$
^{51}Cr	320	0.192	0.802	$1.68 \cdot 10^{-4}$
^{59}Fe	1 099 + 1 291	$1.71 \cdot 10^{-3}$	$7.16 \cdot 10^{-3}$	$1.50 \cdot 10^{-6}$
^{60}Co	1 173 + 1 332	0.417	1.75	$3.65 \cdot 10^{-4}$
^{64}Cu	511	10.4	43.8	$9.18 \cdot 10^{-3}$
^{69m}Zn	439	0.177	0.740	$1.55 \cdot 10^{-4}$
^{72}Ga	834	21.6	90.5	$1.89 \cdot 10^{-2}$
^{76}As	559	22.3	93.7	$1.96 \cdot 10^{-2}$
$^{99}\text{Mo}/^{99m}\text{Tc}$	141	2.33	9.77	$2.04 \cdot 10^{-3}$
^{114m}In	190	$7.07 \cdot 10^{-2}$	0.296	$6.19 \cdot 10^{-5}$
^{117m}Sn	158	$1.86 \cdot 10^{-2}$	$7.78 \cdot 10^{-2}$	$1.63 \cdot 10^{-5}$
^{122}Sb	564	30.9	130	$2.72 \cdot 10^{-2}$
^{140}La	487	0.724	3.03	$6.35 \cdot 10^{-4}$
	1 595	0.320	1.34	$2.81 \cdot 10^{-4}$
^{153}Sm	103	8.20	34.8	$7.15 \cdot 10^{-2}$
^{152m}Eu	842	11.2	47.2	$9.89 \cdot 10^{-3}$
	963	7.63	31.9	$6.68 \cdot 10^{-3}$
^{182}Ta	68	4.12	17.2	$3.61 \cdot 10^{-3}$
^{187}W	60	63.3	265.4	$5.55 \cdot 10^{-2}$
^{198}Au	412	733	3 069	0.642

bility of the determinations amounted to about 5%. For practical reasons the k_s values were plotted as a function of decay after irradiation.

Activation analysis results

Results of the triple comparator method. For the analysis of the silicon samples, three irradiations were performed. The results of the flux determinations using the triple comparator method are summarized in Table 3. With the aid of the

Table 3
Flux determinations in BR-2

Comparator system	Si samples	Φ_{th} $n \cdot cm^{-2} \cdot sec^{-1}$	Φ_{epi} $n \cdot cm^{-2} \cdot sec^{-1}$	Φ_{th}/Φ_{epi}
Co—Au	D 1	$1.12 \cdot 10^{14}$	$3.13 \cdot 10^{12}$	36.0
Co—In		$1.12 \cdot 10^{14}$	$3.28 \cdot 10^{12}$	34.0
Au—In		$1.07 \cdot 10^{14}$	$3.46 \cdot 10^{12}$	30.9
Average		$1.10 \cdot 10^{14}$	$3.29 \cdot 10^{12}$	33.6
Co—Au	D 3—C 3	$1.00 \cdot 10^{14}$	$3.24 \cdot 10^{12}$	30.9
Co—In		$0.99 \cdot 10^{14}$	$3.42 \cdot 10^{12}$	28.9
Au—In		$0.93 \cdot 10^{14}$	$3.63 \cdot 10^{12}$	25.6
Average		$0.97 \cdot 10^{14}$	$3.43 \cdot 10^{12}$	28.5
Co—Au	B 3—A 3	$1.04 \cdot 10^{14}$	$5.40 \cdot 10^{12}$	19.2
Co—In		$1.03 \cdot 10^{14}$	$5.70 \cdot 10^{12}$	18.1
Au—In		$0.94 \cdot 10^{14}$	$6.07 \cdot 10^{12}$	15.4
Average		$1.00 \cdot 10^{14}$	$5.72 \cdot 10^{12}$	17.6

flux ratios thus determined, the k_s values from Table 2 were converted to the k_x ratios according to Eq. (1). Finally, from these k_x ratios vs. the three comparators and from the comparator activities, the standard activities A_s were calculated. A typical example of such a conversion is given in Table 4 for the analysis of Si D 1. From the results it is obvious that the A_s values computed from the three comparators are in good agreement with each other.

Impurity concentrations. The results for five semiconductor grade silicon samples are shown in Table 5. The upper concentration limits were calculated according to the method of CURRIE.⁷

It is striking that only a few of the elements under investigation were present in the analysed silicon samples. Moreover, the concentrations of the elements detected were quite low, in the ppb range or less. Na was detected in all the samples. Gold too, with its very low detection limit, was found in almost all silicon samples. The other impurities, Sb, Ta, Sc, As and Cu seem to be present accidentally.

Table 4
Calculation of the standard activities (Si D1)

Isotope	Decay time, hr	k_x vs. Au comparator (I)	k_x vs. Co comparator (II)	k_x vs. In comparator (III)	As from (I), cpm/ng	As from (II), cpm/ng	As from (III), cpm/ng	As, average value, cpm/ng
¹⁹⁸ Au	76.25	0.642	363	1 784	36 710	38 485	35 919	37 038
¹²⁵ Sb	76.25	$2.72 \cdot 10^{-2}$	15.0	74.0	1 550	1 590	1 490	1 545
⁷² Ga	76.25	$2.28 \cdot 10^{-3}$	1.26	6.60	130.4	133.6	132.9	132.3
⁵⁹ Fe	76.25	$2.98 \cdot 10^{-6}$	$1.67 \cdot 10^{-3}$	$8.37 \cdot 10^{-3}$	0.170	0.177	0.169	0.172
⁵¹ Cr	64.5	$2.94 \cdot 10^{-4}$	0.185	0.928	19.1	19.6	18.7	19.1
⁴² K	68.0	$1.49 \cdot 10^{-5}$	$9.25 \cdot 10^{-3}$	$4.55 \cdot 10^{-2}$	0.931	0.981	0.916	0.943
⁷⁶ As	62.0	$1.05 \cdot 10^{-2}$	6.85	33.5	700	726	674	700
⁶⁰ Co	62.0	$6.52 \cdot 10^{-4}$	0.417	2.12	43.4	44.2	42.7	43.5
^{114m} In	84.0	$1.14 \cdot 10^{-4}$	$5.86 \cdot 10^{-2}$	0.296	6.00	7.21	5.96	6.39
^{69m} Zn	65.5	$2.97 \cdot 10^{-5}$	$2.07 \cdot 10^{-2}$	$9.09 \cdot 10^{-2}$	1.90	2.20	1.83	1.98
⁶⁴ Cu	63.75	$1.52 \cdot 10^{-3}$	0.966	4.88	99.3	102.4	98.3	100.0
¹⁸⁷ W	67.5	$2.44 \cdot 10^{-2}$	14.9	74.4	1 533	1 580	1 498	1 537
⁹⁹ Mo/ ^{99m} Tc	108.5	$2.19 \cdot 10^{-3}$	0.840	4.47	88.6	89.1	90.1	89.3
^{117m} Sn	99.5	$2.88 \cdot 10^{-5}$	$1.28 \cdot 10^{-2}$	6.43 $\cdot 10^{-2}$	1.29	1.35	1.30	1.31
¹⁸² Ta	99.25	$7.70 \cdot 10^{-3}$	3.35	16.9	344	355	340	346
²⁴ Na(1)	69.0	$2.75 \cdot 10^{-5}$	$1.64 \cdot 10^{-2}$	$8.26 \cdot 10^{-2}$	1.70	1.74	1.66	1.70
(2)	69.0	$9.28 \cdot 10^{-6}$	$5.64 \cdot 10^{-3}$	$2.83 \cdot 10^{-2}$	0.574	0.598	0.570	0.581
^{152m} Eu(3)	69.0	$4.96 \cdot 10^{-4}$	0.290	1.45	30.7	30.7	29.2	30.2
(4)	69.0	$3.31 \cdot 10^{-4}$	0.197	0.976	20.5	20.9	19.6	20.3
¹⁴⁰ La(5)	69.0	$5.20 \cdot 10^{-4}$	0.308	1.54	32.1	32.7	31.0	31.9
(6)	69.0	$2.27 \cdot 10^{-4}$	0.137	0.678	14.0	14.5	13.7	14.1
¹⁵³ Sm	69.0	$5.83 \cdot 10^{-3}$	3.55	17.5	366	376	352	365
⁴⁶ Sc(7)	69.0	$2.80 \cdot 10^{-4}$	0.141	0.707	14.4	14.9	14.2	14.5
(8)	69.0	$2.14 \cdot 10^{-4}$	0.105	0.523	11.0	11.1	10.5	10.9

(1) 1368 keV; (2) 2754 keV; (3) 842 keV; (4) 963 keV; (5) 487 keV; (6) 1595 keV; (7) 889 keV; (8) 1120 keV.

Table 5
Analysis results of semiconductor grade Si, ppb

B content, ppb Si-type Specific resistance	Si D1	Si D3	Si C3	Si B3	Si A3
	<1 p >250 $\Omega \cdot \text{cm}$	<1 n >25 $\Omega \cdot \text{cm}$	<0.5 n >50 $\Omega \cdot \text{cm}$	<0.25 n >150 $\Omega \cdot \text{cm}$	<0.12 n >200 $\Omega \cdot \text{cm}$
Au	0.00074	0.00028	$<10^{-4}$	0.00017	0.00048
Sb	0.0093	0.0032	<0.003	<0.002	<0.006
Ga	<0.03	<0.003	<0.003	<0.004	<0.01
Fe	<20	<30	<40	<40	<100
K	<5	<1	<1	<2	<5
Cr	<0.5	<0.4	<0.6	<0.5	<1
Mo	<0.2	<0.06	<0.08	<0.07	<0.2
Sn	<9	<6	<8	<7	<20
As	<0.02	0.81	<0.008	0.007	<0.02
Co	<0.2	<0.2	<0.2	<0.2	<0.6
In	<3	<2	<3	<2	<7
Zn	<6	<3	<3	<3	<9
Cu	<0.1	<0.06	<0.07	2.62	<0.56
W	<0.01	<0.005	<0.006	<0.005	<0.02
Ta	1.6	<0.03	<0.04	<0.03	<0.09
Na	0.30	1.53	0.34	0.24	0.51
Eu	<0.01	<0.006	<0.002	<0.008	<0.02
Sm	<0.003	<0.002	<0.002	<0.002	<0.006
La	<0.01	<0.01	<0.01	<0.01	<0.04
Sc	0.15	<0.02	<0.04	<0.03	<0.09
Tl	<2	<2	<2	<2	<9

Table 5 gives a clear idea of the sensitivity of the proposed method using 1-g samples. The detection limits varied from 10^{-4} ppb for Au to 20 ppb for Fe. It should be noted that the different detection limits for one element are due to the different delays between irradiation and measurement.

*

Grateful acknowledgment is made to the 'National Fonds voor Wetenschappelijk Onderzoek' for financial support. Thanks are also due to Mr. J. DE RUDDER for technical assistance.

References

1. F. DE CORTE, A. SPEECKE, J. HOSTE, *J. Radioanal. Chem.*, 8 (1971) 287.
2. F. DE CORTE, A. SPEECKE, J. HOSTE, *J. Radioanal. Chem.*, 3 (1969) 205.
3. D. T. GOLDMAN, J. R. ROESSER, Chart of the Nuclides, General Electric Co., Schenectady, N. Y., 1966.
4. M. K. DRAKE, *Nucleonics*, 24 (1966) 188.
5. O. T. HØGDAHL, Proc. IAEA Symp. on Radiochemical Methods of Analysis, Vol. I, Vienna, 1965.
6. E. KLEEMANN, G. HERRMANN, *Intern. J. Appl. Radiation Isotopes*, 7 (1959) 149.
7. L. A. CURRIE, *Anal. Chem.*, 40 (1968) 587.