

REPORT

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THE PREPARATION OF SYNTHETIC STANDARDS
FOR USE IN INSTRUMENTAL NEUTRON-
ACTIVATION ANALYSIS

by

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NATIONAL INSTITUTE FOR METALLURGY

ANALYTICAL CHEMISTRY DIVISION

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SYNOPSIS

An account is given of the formulation and preparation of synthetic standards suitable for the routine analysis of minerals, ores, and ore concentrates by instrumental neutron activation. Fifteen standards were prepared, each containing from one to seven elements. The standards contain forty-four elements that produce isotopes with half-lives longer than 12 hours. An evaluation of the accuracy and precision of the method of preparation is given.

SAMEVATTING

Die formulering en bereiding van sintetiese standaarde wat geskik is vir die roetineontleding van minerale, ertse en ertskonsentrasies deur instrumentele neutronaktivering word beskryf. Daar is vyftien standaarde berei wat elkeen van een tot sewe elemente bevat. Die standaarde bevat vier en veertig elemente wat isotope met 'n vervaltyd van langer as 12 uur gee. Die akkuraatheid en presisie van die bereidingsmetode word geëvalueer.

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1. INTRODUCTION

Many investigators engaged in instrumental neutron-activation analysis (INAA) make use of international reference materials^{1,2} for calibration purposes. However, the use of these materials for routine calibrations has two disadvantages: the number of elements for which certified values are available is limited, and the concentrations of the elements in the standards may not be those most suitable for INAA. The preparation and analysis of auxiliary in-house standards for routine calibration purposes, based on international reference materials, are time-consuming. As INAA is far less susceptible to matrix effects than most other techniques, synthetically prepared standards are often to be preferred, and are widely used³⁻⁵. Fairly complex procedures for their preparation — including absorption onto resins and coprecipitation — have been developed in order to overcome the problems of long-term storage of solutions and homogeneity of bulk synthetic standards.

Inaccuracies due to inhomogeneity of solid synthetic standards can be overcome by the use of solutions, but the deterioration of dilute solutions during lengthy storage can also lead to inaccuracies. In many instances, the use of synthetically prepared standards implies the use of single-element standards, which is a disadvantage for a multi-element technique such as INAA, because there are many vials to be irradiated and counted. For this reason, one of the principal aims of this study was the formulation and preparation of a small number of multi-element standards to cover the 44 elements most often determined by this method. Problems due to the instability and incompatibility of multi-element standard solutions in different solvents can be avoided by the preparation, in irradiation vials, of a large suite of standards from freshly prepared solutions of each of the elements added individually to the vials.

Each solution can be dried on a selected substrate before the next solution is added. Although this approach is time-consuming, it has distinct advantages in the long term. Drying conditions can be tailored for each element so that the probability of loss (e.g., of volatile elements) is minimized, and the problems associated with the lack of long-term stability are avoided.

Experience gained at the National Institute for Metallurgy (NIM) over the past few years has indicated that it is possible for synthetic standards to be used in the great majority of routine analyses. International reference materials could then be reserved for use in limited quantities for control purposes.

2. EXPERIMENTAL METHODS

A number of factors require consideration before it can be decided which elements can be combined in a single standard. Of these, mutual peak interference is obviously the most important, and could have been assessed by the use of a computer programme and a computerized library of isotopes. Account must also be taken of other factors including peak distortions due to Compton edges, the introduction of impurities from other chemical compounds, from the quartz vial, and from the silica substrate, and the total activity of the irradiated standard at the required decay times. These requirements can best be met by irradiation of each of the chemical compounds to be used so that the decision can be based on the spectra obtained. Requests are often received at NIM for the analysis of particular groups of elements, and it was therefore necessary for such groupings to be taken into account in this investigation so that the number of standards used for a particular analysis could be reduced.

2.1. Selection of Chemicals and Materials

The selection of the compounds to be used in the preparation of standards was not difficult, because stoichiometric compounds of most elements are readily available.

Where stoichiometric compounds were not available, the compound used instead was analysed for the relevant element by a standard analytical method. The compounds selected for the preparation of the standards discussed in this report, together with their grades and brand names, are listed in Table 1. In view of the high quality of most chemicals, alternative brands of equivalent grade could probably be used.

Ultra-pure chemicals are desirable but, because their use can considerably increase the cost, chemicals of Analar and Specpure grade were used in the preparation of the standards. A comprehensive quantitative analysis of each chemical was not necessary. The compounds were irradiated, and the spectra obtained were compared so that interferences with the analytical peaks of the various elements to be combined in the same standard could be minimized. Thus, the presence of interfering peaks and Compton edges was avoided.

This initial combination of elements was evaluated further by careful examination of the computer printout of the spectra for the presence of small peaks that would cause interference and were not apparent from a visual examination of the initial spectra. The combination was modified when impurities or interferences were observed that would affect the accuracy of the preparation of another element in the initial combination. Such modifications were necessary in only a few instances, since the spectra plotted

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TABLE 1

Concentrations and combinations of elements

Sad no.	Element	Concn in vials μg	Source of element	Dissolution (solvent or method)	Grade and supplier	Minimum concn %
I	As	25	As_2O_3	NaOH soln, 10%	Resublimed powder. Hopkins & Williams. Specpure. Johnson Matthey. '99999'. Engelhard. 'Baker analysed' reagent. J.T. Baker. Specpure. Johnson Matthey. A.R. Riedel de Haën. A.R. Protea Lab. Services.	99,5
	Co	30	Sponge	Aqua regia		99,999
	Au	5	Pure wire	Aqua regia, 20%		99,9
	Zn	700	Metal	HCl, 20%		
	Ni	2 000	Metal	Aqua regia, 20%		
	W	75	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	H_2O		
	Cr	500	$\text{K}_2\text{Cr}_2\text{O}_7$	HCl, 10%		
II	Ga	1 000	Metal	Aqua regia, 20%	Specpure. Johnson Matthey. Specpure. Johnson Matthey. A.R. Merck. '99999'. Polymetals. '99999'. Polymetals.	99,5
	Cd	400	Metal	H_2O_2 , 10%		
	Sb	75	$\text{K}(\text{SbO})\text{C}_2\text{H}_3\text{O}_4 \cdot 5\text{H}_2\text{O}$	HCl, 10% (a few drops of NH_4OH are added to the vial before drying)		
	Se	200	Pure metal	Aqua regia, not heated		
Te	1 500	Pure metal	Aqua regia, not heated			
III	Zr	4 000	Metal	HF soln, 10%	Reactor-grade Zr. NIM. Specpure. Johnson Matthey. Specpure rod. Johnson Matthey.	99,8
	Hf	90	HfO_2	HF soln, 10%		
	Fe	9 000	Metal	Aqua regia		
IV	Th	40	$\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$	Distilled H_2O (determined gravimetrically as ThO_2)	'R'. May and Baker. A.R. Merck. A.R. Hopkins & Williams.	- 99,5 99,9
	Mo	3 000	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	H_2O		
	Ag	1 000	AgNO_3	HNO_3 , 10%		
V	Rb	500	RbCl	H_2O	Suprapur. Merck. Suprapur. Merck. Specpure. Johnson Matthey. Specpure. Johnson Matthey. Specpure. Johnson Matthey.	- - - - -
	Cs	50	CsCl	H_2O		
	Lu	50	Lu_2O_3	HNO_3 , 20%		
	Ho	50	Ho_2O_3	HNO_3 , 20%		
	Nd	500	Nd_2O_3	HNO_3 , 20%		
VI	Tb	50	Tb_2O_3	HNO_3 , 20%	Specpure. Johnson Matthey. Specpure. Johnson Matthey. Specpure. Johnson Matthey.	- - -
	Sm	20	Sm_2O_3	HNO_3 , 20%		
	La	50	La_2O_3	HNO_3 , 20%		
VII	Ta	50	Ta_2O_5	Fusion with $\text{K}_2\text{S}_2\text{O}_7$, leaching with 10% tartaric acid	Specpure. Johnson Matthey. '99999'. Engelhard.	- 99,999
	Ir	5	Pure metal	Standardized solution ⁷		
VIII	Na	800	NaCl	H_2O	A.R. Protea Lab. Services. A.R. Merck. Specpure. Johnson Matthey.	99,5
	Ce	500	$(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	HNO_3 , 50%		
	Tm	500	Tm_2O_3	HNO_3 , 50%		
IX	Br	200	KBr	H_2O	A.R. Merck. Specpure. Johnson Matthey.	99,6
	Yb	50	Yb_2O_3	HNO_3 , 50%		
X	Ru	200	Pure metal	Standard solution ⁷	'99999'. Engelhard. Specpure. Johnson Matthey.	99,999
	Os	50	$(\text{NH}_4)_2\text{OsCl}_6$	HCl, 5% (a few drops of NH_4OH are added to the vial before drying)		
XI	Hg	1 000	HgCl	Individual mass measured into each vial	A.R. Merck. Specpure. Johnson Matthey.	- -
	Re	100	KReO_4	H_2O		
XII	Pt	1 000	Pure metal	Standardized solution ⁷	'99999'. Engelhard. '99999'. Engelhard.	99,999 99,999
	Pd	500	Pure metal	Standardized solution ⁷		
XIII	Sc	100*	Sc_2O_3	Dry-mixed in a rotary mill, dilution with pure SiO_2	Specpure. Johnson Matthey. A.R. B.D.H.	- 99,0
	Ba	700	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$			
XIV	Eu	50	Eu_2O_3	HNO_3 , 50%	Specpure. Johnson Matthey.	
XV	K	10 000	KCl	H_2O	G.R. Cica Kanto Chemicals. High-purity U_3O_8 , NIM.	99,8
	U	25	U_3O_8	HNO_3 , 10%		

* The concentration was found to be too high; 20 μg would probably be better for the type of sample on which Sc analysis is normally required.

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previously revealed nearly all the significant interfering peaks. This procedure was found to be easier and less time-consuming than that requiring detailed analysis of each chemical prior to the selection of combinations of elements.

The high-purity quartz tubing in which the standards were prepared was obtained from the British American Optical Co. Ltd. The coarse silica used for the support on which the solutions were dried was obtained from a vein of pure quartz. The quartz had previously been used as an internal reference material at NIM, and was found to contain no impurities that could affect the accuracy of analysis of the prepared standards. The following elements were determined in the quartz: zinc (0,2 p.p.m.), iron (4,5 p.p.m.), potassium (14 p.p.m.), sodium (15 p.p.m.), nickel (0,1 p.p.m.), and chromium (0,1 p.p.m.). Qualitative analysis of the quartz showed that no element of interest was present in significant concentration. Blank samples were prepared to correspond to each of the standards and were then analysed, with the standards, by INAA.

It was not possible for interferences from every source to be eliminated by variation of the combinations of elements. However, there were few residual impurities affecting the concentrations of the elements in the standards, and their effects were limited. The following corrections had to be made to the calculated concentrations of the prepared standards: arsenic (0,02 per cent), barium (0,71 per cent), chromium (0,22 per cent), potassium (0,14 per cent), sodium (2,8 per cent), antimony (0,25 per cent), samarium (0,02 per cent), and tungsten (0,14 per cent). Spectra of the standards irradiated and counted under the conditions discussed in Section 2.3 are shown in Figures 1 to 15. The selected analytical energies are listed, with other nuclear data⁸, in Table 2. Some of the interferences that would be encountered in the analysis of samples are also tabulated.

2.2. Preparation of Synthetic Standards

Known masses of the elements in solution were added to pure silica in quartz irradiation vials. After the solution had been dried, the vials were heat-sealed.

Blank standards were prepared in vials for analysis. These standards consisted of the same amount of pure silica and solvent as each of the synthetic standards.

The concentration of each of the elements in the standards was such that, in most cases, counting statistics of better than 2 per cent could be obtained when the standards were irradiated and counted under the same conditions as were typical samples of minerals, ores, and ore concentrates. (A lower concentration of the element in the standards would be more appropriate when trace elements are to be analysed after a radiochemical separation procedure.)

2.2.1. Standard Solutions

Approximately 50 ml of each solution of an element was prepared individually for immediate use, 100 μ l being added to the vial to give the required mass of the element. All the standard solutions were prepared according to mass, i.e. concentrations were determined as mass of element per unit mass of solution. All the measurements of mass were made on a five-figure decimal-point balance.

(1) Standard Solutions in Water

The required amounts of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Th}(\text{NO}_3)_4 \cdot n\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, RbCl , CsCl , NaCl , KBr , KReO_4 , and KCl were accurately measured and dissolved in freshly boiled distilled water. The solution of thorium that was prepared was fifty times more concentrated than necessary so that the amount of thorium could be determined accurately. For this determination, a measured mass of the solution was placed in a platinum dish, and the solution was evaporated to dryness. The residue was then carefully heated in a furnace at 950°C, and the thorium content of the original solution was determined from the resulting mass of ThO_2 . The confidence limit (95 per cent) for this determination was 1,2 per cent. Each of the three results was within 0,7 per cent of their mean.

(2) Standard Solutions in Nitric Acid

The required amounts of AgNO_3 , Lu_2O_3 , Ho_2O_3 , Nd_2O_3 , Tb_4O_7 , Sm_2O_3 , La_2O_3 , $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, Tm_2O_3 , Yb_2O_3 , Eu_2O_3 , and U_3O_8 were dissolved by being heated in a 70 per cent (v/v) nitric acid solution, and diluted with water to the required concentration. Cadmium metal was dissolved by gentle heating in a 15 per cent (v/v) nitric acid solution, and diluted to volume with dilute nitric acid.

(3) Standard Solutions in Hydrochloric Acid

Accurately measured amounts of Zn , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 0,5\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{OsCl}_6$ were dissolved in hydrochloric acid, and diluted with distilled water.

TABLE 2

Nuclear data

Isotope	Half-life d	Thermal cross-section b	Main energies of isotope keV*	Interfering isotope	Energy of interference keV	Energy used for correction of interference keV
^{110m} Ag	253	3,2	658, 884, <u>937</u> , <u>1384</u> , 764	^{110m} Ag	658	1384
⁷⁶ As	1,10	4,3	<u>559</u> , <u>657</u> , 1216			
¹⁹⁸ Au	2,69	98,8	412			
¹⁹⁹ Au(Pt)	3,15	25800	158, 208			
¹³¹ Ba	12,0	13,5	<u>496</u> , 124, <u>216</u> , 373	¹⁶⁰ Tb	216	879
⁸² Br	1,48	3,26	<u>776</u> , 554, <u>1044</u> , 1317, 828	⁹⁹ Mo	778	140
¹¹³ Cd	2,25	0,30	<u>528</u> , <u>335</u> , 492	¹²⁴ Sb	1045	1691
¹⁴¹ Ce	33	0,54	145	⁵⁹ Fe	335	1099
⁶⁰ Co	1916	37	<u>1332</u> , <u>1173</u>	⁵⁹ Fe	142	1099
⁵⁸ Co(Ni)	71,3		<u>811</u>	²³³ Pa	145	312
⁵¹ Cr	27,8	16	<u>320</u>	¹⁵² Eu	811	1408
¹³⁴ Cs	748	30	<u>796</u> , <u>605</u> , 569, 475, 802, 563	¹²⁴ Sb	603	1691
¹⁵² Eu	4526	5700	122, 344, <u>1408</u> , 244	¹⁸² Ir	604	317
¹⁵⁴ Eu	5840	390	123, <u>1274</u> , <u>723</u> , 1005	¹⁸² Ta	1410	1221
⁵⁹ Fe	45	1,23	<u>1099</u> , <u>1292</u> , 192	¹⁸² Ta	1274	1221
⁷² Ga	0,583	5,0	<u>834</u> , 2201, <u>630</u> , 2507	¹⁶⁰ Tb	1272	879
¹⁸¹ Hf	42,5	12,6	<u>482</u> , 133, <u>346</u>	¹⁸² Ta	1289	1221
²⁰³ Hg	46,6	4,9	<u>279</u>	⁵⁴ Mn	835	835†
¹⁶⁶ Ho	1,11	63	<u>1379</u> , <u>1582</u> , <u>1662</u>	⁷⁵ Se	280	265
¹⁸² Ir	74	910	<u>317</u> , <u>468</u> , <u>308</u> , 296	⁵¹ Cr	320	None
⁴² K	0,521	1,3	<u>1525</u>	¹²⁴ Sb	1526	1691
¹⁴⁰ La	1,68	9,55	<u>1596</u> , <u>487</u> , 816, 329	²³⁹ Np	210	278
¹⁷⁷ Lu	6,7	2100	<u>208</u> , <u>113</u>	⁵⁹ Fe	142	1099
⁹⁹ Mo	2,78	0,51	<u>140</u> , <u>739</u> , 181, 366	¹⁵² Sm	531	103
²⁴ Na	0,625	0,53	<u>1368</u> , 2754	¹¹³ Cd	528	336
¹⁴⁷ Nd	11,0	1,30	<u>91</u> , <u>531</u> , 319, 398	¹⁸² Ta	229	1221
²³⁹ Np(U)	2,35		<u>106</u> , <u>278</u> , <u>228</u>	¹⁸⁰ Tb	310	879
¹⁹¹ Os	15	12,5	<u>129</u> , 82, 50	²³¹ Pa	87	312
²³³ Pa(Th)	27,4		<u>312</u> , 300, <u>341</u> , 399, 416	¹⁵² Sm	90	103
¹⁰⁶ Pd	0,567	12,3	<u>88</u>	⁵⁹ Fe	192	1099
¹⁹⁷ Pt	0,75	0,96	<u>191</u> , 77	⁷⁵ Se	136	265
¹⁸⁶ Rb	18,7	0,91	<u>1076</u>	¹⁸¹ Hf	136	482
¹⁸⁶ Re	3,75	105	<u>137</u>	¹⁸⁷ W	136	685
¹⁰³ Ru	39,6	1,23	498, 610, 40	¹³¹ Ba	137	496
				¹³¹ Ba	496	124

¹⁶⁴ Ho	1,11	63	<u>1379, 1582, 1662</u>	⁵¹ Cr	320	None
¹⁶⁷ Tm	74	910	<u>317, 468, 308, 296</u>	¹²⁴ Sb	1526	1691
⁴² K	0,521	1,3	<u>1525</u>			
¹⁴⁰ La	1,68	9,55	<u>1596, 487, 816, 329</u>	²³⁹ Np	210	278
¹⁷⁷ Lu	6,7	2100	<u>208, 113</u>	⁵⁸ Fe	142	1099
⁹⁹ Mo	2,78	0,51	<u>140, 739, 181, 366</u>			
²⁴ Na	0,625	0,53	<u>1368, 2754</u>	¹⁵³ Sm	531	103
¹⁴⁷ Nd	11,0	1,30	<u>91, 531, 319, 398</u>	¹¹⁵ Cd	528	336
				¹⁸² Ta	229	1221
²³⁵ Np(U)	2,35		<u>106, 278, 228</u>			
¹⁹¹ Os	15	12,5	<u>129, 82, 50</u>	¹⁵⁹ Tb	310	879
²³³ Pa(Th)	27,4		<u>312, 300, 341, 399, 416</u>	²³³ Pa	87	312
¹⁰⁶ Pd	0,567	12,3	<u>88</u>	¹⁵³ Sm	90	103
				⁵⁴ Fe	192	1099
¹⁹⁵ Pt	0,75	0,96	<u>191, 77</u>			
¹⁸⁷ Rb	18,7	0,91	<u>1076</u>	⁷⁵ Se	136	265
¹⁸⁵ Re	3,75	105	<u>137</u>	¹⁸¹ Hf	136	482
				¹⁸⁷ W	136	685
¹⁰¹ Ru	39,6	1,23	<u>498, 610, 40</u>	¹³¹ Ba	137	496
¹²⁴ Sb	60,3	3,45	<u>603, 1691, 723</u>	¹³¹ Ba	496	124
¹²² Sb	2,8	6,2	<u>564, 693, 1140, 1257</u>			
				⁷⁶ As	563	559
⁴⁶ Sc	84	23	<u>889, 1121</u>	¹³⁴ Cs	563	796
⁷⁴ Se	120	30	<u>265, 136, 280, 121</u>	¹³⁴ Cs	563	796
¹⁵³ Sm	1,96	210	<u>103, 70</u>	¹⁸² Ta	264	1221
				¹⁸¹ Hf	137	482
¹⁸² Ta	115	21	<u>1121, 68, 1221, 1189, 1231</u>	²³³ Pa	104	312
¹⁶⁰ Tb	72,1	30	<u>879, 966, 299, 1272</u>	²³⁹ Np	106	278
				⁴⁶ Sc	1121	889
^{123m} Te	117	1,1	<u>159, 89</u>	¹⁸² Ta	1274	1221
				¹⁵⁴ Eu	1275	724
¹⁷⁰ Tm	129	106	<u>84</u>	^{117m} Sn	159	None
				⁴⁶ Sc	159	889
¹⁸⁷ W	0,99	38	<u>686, 480, 71, 134, 618</u>	¹⁸⁰ Tb	87	879
¹⁸³ Yb	32	3200	<u>64, 198, 177, 110, 131</u>	¹⁸² Ta	85	1221
				²³³ Pa	87	312
⁶⁵ Zn	244	0,82	<u>1116</u>	^{110m} Ag	687	1385
				¹⁸¹ Hf	482	346
⁹⁰ Zr	65,5	0,075	<u>757, 724</u>	¹⁸⁰ Tb	197	879
				¹⁸² Ta	198	1221
				¹⁸² Ta	177	1221
				¹⁵² Eu	1112	1408
				¹⁸² Ta	1113	1221
				¹⁸⁰ Tb	1115	879
				¹²⁴ Sb	723	1691
				¹⁵⁴ Eu	723	1275

SECTION 2

* Underlined energies are those used for analysis.
 † Correction made by the determination of the contribution of ⁵⁴Mn at a long decay time.

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(4) *Standard Solutions in Hydrofluoric Acid*

Accurately measured amounts of zirconium (with a maximum hafnium concentration of 200 p.p.m.) and hafnium oxide were dissolved in hydrofluoric acid in a clean Teflon beaker. The solution was refluxed slowly on a sand-bath for a few hours to ensure its dissolution. The solutions were diluted to the required concentrations in clean plastic bottles. The correction that was applied to the hafnium concentration in the standard — necessitated by the hafnium in the zirconium — was found to be 131 p.p.m.

(5) *Standard Solutions in Aqua Regia*

Although other acids could be used for the dissolution of some of the metals, aqua regia was found to be the most effective. Accurately measured amounts of cobalt, gold, nickel, iron, gallium, selenium, and tellurium were dissolved in aqua regia. The solutions of the elements were heated, but no heat was applied to the solutions containing selenium and tellurium. The solutions were diluted to the required mass with water.

(6) *Solutions in Other Solvents*

Arsenous oxide was dissolved, without heating, in a solution (10 to 15 ml) containing 5 g of sodium hydroxide. Tantalum oxide was fused with 5 g of potassium pyrosulphate and heated with a hot 10 per cent solution of tartaric acid. This solution was diluted to the required mass with 10 per cent tartaric acid. The dissolution and standardization of iridium, ruthenium, platinum, and palladium are described in detail elsewhere⁷. Scandium and barium standards were prepared by mixing of the selected compounds with pure silica in a rotary mill.

2.2.2. *Standards in Quartz Vials*

The quartz tubing, which has an inner diameter of 4 mm and an outer diameter of 6 mm, was cut into 50 mm sections. The tubes were cleaned in a 5 per cent solution of nitric acid in an ultrasonic bath, boiled in a 1:1 solution of nitric acid and then in distilled water, and washed with acetone and dried in an oven. After being cleaned, the vials were handled with plastic gloves until they had been sealed. One end of each vial was heat-sealed, and 0.4 g of pure, coarsely ground silica was added. To each vial, 100 μ l of the appropriate standard solution was added. The amount added was determined by mass measurements on a balance weighing to five decimal figures. The quartz vials containing the solution were then centrifuged to ensure that none of the solution dried on the top half of the quartz vial. This precaution is particularly necessary for the volatile elements, which could otherwise be lost in the heat-sealing of the vials. After each solution containing a single element was added, the vials were dried in a heated desiccator at 80°C (for the non-volatile elements) or 40°C (for the potentially volatile elements: arsenic, antimony, selenium, tellurium, bromine, and osmium). Non-volatile elements in standards containing volatile elements were added and dried before the volatile elements. A few drops of ammonium hydroxide were added to precipitate the solutions containing osmium and antimony.

After all the elements had been added to a particular set of vials, the vials were heat-sealed. A jet of water was sprayed onto the lower two-thirds of each of the vials that contained volatile elements to prevent volatilization.

Mercury was added as solid mercurous chloride to each vial since it was considered that it could be lost if it was added in solution.

The quantity of each standard prepared varied from 40 vials of standard XIV to 120 vials of standard I in anticipation of the expected usage.

2.3. *Spectra and Total Activity of Standards*

The standards were irradiated for 3 hours in the core of the SAFARI I reactor at Pelindaba in a thermal flux of approximately 1.9×10^{13} n/cm²/s, and an epithermal flux of approximately 1×10^{12} n/cm²/s. The standards were counted at decay times of 3 days or longer. The counting system consisted of a lithium-drifted germanium (GeLi) detector (Table 3) connected to an Intertechnique Didac 4000 multichannel analyser equipped with an automatic sample changer. Corrections for dead-time were made by use of a fixed-frequency pulser to determine the loss of pulses in the spectrum. Spectra were collected on a magnetic tape⁹ and processed by the use of a modified version of the Hevesy programme¹⁰. Spectra for the standards counted at the main decay times are shown in Figures 1 to 15.

The total activity of each standard was determined by the integration of all counts between 0 and 2000 keV. The minimum distances at which a count-rate of 5200 count/s would not be exceeded (a dead time of approximately 20 per cent) on the counting system used (see Table 3) are listed in Table 4. Standard X could not be counted at short decay times because of the activities of ^{181m}Os, ¹⁸³Os, ⁹⁷Ru, and ¹⁰⁶Ru, which

TABLE 3

Characteristics of the GeLi detector

Relative efficiency* for ⁶⁰ Co at 1,332 MeV	Resolution	Peak-to-Compton ratio†
	1. At full width, one-half maximum 2. At full width, one-tenth maximum	
9,3%	1. 1,95 2. 3,79	35,1

* Relative to a 7,5 cm by 7,5 cm thallium-activated sodium iodide detector. Determined by use of a 10 μ Ci source calibrated by the U.S. National Bureau of Standards at 25 cm from the detector.

† The Compton intensity is normalized to 1.

have relatively short half-lives. It was not intended that these particular isotopes should be used for analysis, but, if they are to be used, then concentrations lower than those described in this Section are necessary.

2.4. Precision of the Preparation

Although precautions were taken against errors arising from the preparation and addition of standard solutions, and during the sealing of the vials, a check was carried out on the reproducibility of the procedure for the preparation of the samples, as follows.

Five vials of each standard were selected at random. Because of the high gradient of the flux across the vials during irradiation, monitoring of the flux was necessary. The errors relating to such monitoring can be reduced to a minimum only if use is made of the same isotope that is being determined. The monitoring was done by irradiation of the vials, round each of which had been wound a coil of stainless-steel wire (containing iron, nickel, chromium, and tantalum) to the height of the sample in the vial. This created nearly ideal conditions for monitoring of the flux to be carried out for the isotopes produced by these elements. The monitoring wire was removed and counted apart from the samples. The appropriate counts obtained from the monitoring wire were then divided into the counts obtained from the samples to normalize for variations in the flux. The reproducibility of the method of preparation, as obtained from five separate samples counted once and one sample counted five times, and from the calculated counting statistics of the isotopes in the monitoring wire, are listed in Table 5. As can be seen, the reproducibility of the method used for the preparation of the samples is good. The precision for the measurement of five separate samples ranges from 0,8 per cent for chromium to 2,7 per cent for iron. The precision calculated from the counting data on a single sample and for the flux monitor agree closely with the precision calculated for the separate samples. It can therefore be deduced that the error in the preparation steps is small. The magnitude of the error cannot be determined with confidence because of the limited amount of data available.

2.5. Time and Cost of the Preparation

The cost was based on the forty-seven eight-hour man-days taken for the preparation of 1000 vials of the standards, the average time taken for the preparation of one vial being 22 minutes. At R113 per man-day, the cost is R5,30 per vial. The preparation of the quartz vial took approximately one-third of the time.

The average cost of a good reference material certified for a few elements is in the region of R1 to R2 per gram.

2.6. Analysis of Selected Reference Materials

The prepared standards were used for the analysis of selected reference materials. As suitable materials to cover the whole range of elements under consideration were not available, the choice was confined, wherever possible, to reference materials of minerals and ores. The irradiation and counting conditions were the same as those discussed in Section 2.3. The values obtained for these analyses were then compared with the certified values for the reference materials as a check on whether the standards had been correctly prepared (see Table 6).

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TABLE 4
Total activity of the prepared standards

Standard no.	Decay time d	Distance corresponding to 5200 count/s cm
I	3,7	23
	12,8	6
	31	3
II	3,7	24
	12,8	7
	31	4
III	3,7	9
	12,8	5
	31	4
IV	3,7	18
	12,8	10
	31	8
V	1,9	25
	8,0	10
	29	5
VI	1,9	29
	7,9	11
	29	6
VII	8,2	12
	28	10
	29	7
VIII	2,6	25
	8,2	8
	29	7
IX	2,6	30
	8,1	10
	29	3
X	9,8	4
	29	2
XI	3,0	30
	9,9	12
	29	3
XII	0,9	19
	3,1	20
	10,1	15
XIII	29	12
	3,1	25
	10,2	8
XIV	29	8
	3,2	15
	10,3	4

3. DISCUSSION

Although it is possible for many different combinations of elements to be used, it was shown that the combinations described in this report are appropriate for the analysis of minerals and ores.

It was found that the first four of the standards listed in Table 1, which contain 18 elements, are the most useful. The combination of elements in each standard makes it possible for peak ratios to be determined that are used in the correction of those interferences most commonly encountered in the analysis of samples. The recommended concentrations are such that the standards can be irradiated and counted under the same conditions as most of the minerals, ores, and ore concentrates for which the standards are intended.

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TABLE 5

Precision of measurement of isotopes monitored under ideal conditions (same isotope in standard monitor)

Element	R.S.D. of counting procedures			
	Fe	Cr	Te	Ni
Determined precision of replicate counting, σ_{RC} (1 sample counted 5 times)	1,7	0,72	0,39	0,84
Calculated counting statistics of element in monitor wire ⁹ , σ_{MC}	1,2	0,12	1,5	1,8
Determined precision of 5 separate samples	2,7	0,77	1,9	1,6
Calculated precision for counting of 5 separate samples, $\sqrt{\sigma_{RC}^2 + \sigma_{MC}^2}$	2,1	0,8	1,65	1,96

R.S.D. Relative standard deviation.

The standards have been found to be more radioactive than most geological samples when the latter are irradiated and counted under comparable conditions. The reproducibility of the method of preparation is good for the four elements for which ideal monitoring of the flux was possible. The same level of reproducibility probably holds good for at least the non-volatile elements, since the only significant errors would be those made by the operator when measuring the solutions into the vials. A simple method for monitoring of the flux, which may give improved results for all isotopes, is being investigated. Preliminary results are given in the Appendix.

A comparison of the certified values for the reference materials with the values obtained by use of these synthetic standards (Table 6) confirms that the effects of the non-stoichiometry of chemicals, operator errors, and so on, are negligible. The results are within acceptable limits, generally within 5 per cent of the certified or recommended values quoted in percentages, and within 10 per cent for the results quoted in parts per million. As no suitable reference materials were available for the following elements, no comparisons could be made: gallium, selenium, tellurium, holmium, neodymium, samarium, lanthanum, iridium, thulium, bromine, ruthenium, osmium, mercury, rhenium, platinum, and palladium. This method is not entirely reliable as a check on the accuracy of the concentrations assigned to the standards because there are analytical errors associated with both of the values to be compared. However, it is much less time-consuming than is the analysis of a random selection of vials by alternative methods because some constituents, such as gold, silver, uranium, and the rare-earth elements, require special techniques, with a consequent increase in the time required for analysis and the consumption of additional sets of standard vials.

Although the preparation cost of synthetic standards is higher than that incurred when reference materials are bought, it should be noted that only a few reference standards are available that have 'usable' or recommended values for a large number of elements in any particular material.

4. CONCLUSIONS

The suite of fifteen standards prepared contain a total of 44 elements and include most of the elements that produce isotopes with half-lives longer than 12 hours and are suitable for INAA. The problem arising from the lengthy storage of synthetic standards in bulk is overcome by the direct preparation of standards in irradiation vials. Mutual interferences, peak distortion due to Compton edges, the total activity of each standard, and the fact that certain groups of elements are frequently analysed together are taken into account in the grouping of the elements in each standard. The reproducibility of the preparation procedure is shown to be adequate for the four elements for which corrections based on ideal monitoring of the flux could be made. An analysis of the reference materials and a comparison of the values obtained with the certified values showed the concentrations assigned to the standards to be free from gross errors. No such comparison was possible for gallium, selenium, tellurium, neodymium, samarium, lanthanum, iridium, thulium, bromine, ruthenium, arsenic, mercury, rhenium, platinum, and palladium.

The suite of standards prepared should considerably shorten the time spent on routine analyses, and reduce the amount of valuable international reference materials used. These materials can now be reserved for purposes of control.

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TABLE 6

Comparison between the certified values for selected reference materials and the values obtained with the prepared standards

Element	Reference material			Concentration determined by INAA*
	Name	Material	Certified concentration*	
Ag	ASK-3 ¹¹	Sulphide ore	19 R	21
	NBS-329 ¹²	Zinc conct.	91(1) C	93
	MP-1	Zn, Sn, Cu, Pb ore	59(4) C	63
As	NBS 1633 ¹³	Coal fly-ash	61(6) C	61
	MP-1 ¹⁴	Zn, Sn, Cu, Pb ore	0,79(4)% R	0,76%
Au	MA-1 ¹⁵	Siliceous Au ore	17,8±(±) R	17
Ba	NIM-S ^{16,17}	Syenite	2400(360) R	2485
Cd	NBS-329	Zinc conct.	0,14(1)% C	0,137%
	NBS-113a ¹²	Zinc conct.	0,78(1)% C	0,77%
Ce	NIM-G	Granite	198(26) R	196
Co	UM-1 ¹⁸	Ni, Cu, Co ore	0,035(1)% C	0,036%
	ASK-2 ¹¹	Schist	27 R	27
	ASK-3	Sulphide ore	88 R	85
Cr	BCS174/1 ¹⁹	Basic slag	0,18% C	0,175%
	NIMS	Syenite	12(3) P	14
	ASK-2	Schist	90 R	94
Cs	ASK-2	Schist	11 R	12,5
Eu	G-2 ^{20,21}	Granite	1,5 R	1,8
Fe	NBS-329	Zinc conct.	12,94(1)% C	13,0%
	NBS-113	Zinc conct.	2,08(1)% C	2,05%
	IGS-28 ²²	Ore	11,14(6)% R	11,06%
	BCS174/1	Basic slag	8,47% C	8,43%
Hf	IGS 35 ²²	Ore	1,16(6)% M	1,11%
K	NBS 1570 ²³	Spinach leaves	3,56% C	3,54%
	G2	Granite	3,74% R	3,9%
Lu	BCR-1 ²¹	Basalt	0,55 R	0,60
	NIM-G	Granite	2,2(5) M	2,1
Mo	MP-1	Zn, Sn, Cu, Pb ore	0,014(2)% R	0,0147%
	H, v-1 ²⁴	Cu, Mo, ore	0,058(±)% R	0,059%
Na	BCR-1	Basalt	2,43% R	2,4%
Ni	UM-1	Ni, Cu, Co, ore	0,88(1)% C	0,879%
	NBS-63 ²⁵	Phosphor bronze metal	0,32%	0,32%
	ASK-2	Schist	148 R	156
Rb	NIM-S	Syenite	530(58) R	551
	NIM-L ^{16,17}	Lujavrite	190(30) R	218
Sb	NBS-63	Phosphor bronze metal	0,49%	0,495%
Sc	IGS-28	Ore	0,14(±)% R	0,16%
	ASK-1	Larvikite	7,0 R	6,0
Ta	NBS-1570	Spinach leaves	0,16	0,17
	G-2	Granite	0,91 R	0,9
	NIM-G	Granite	4,6(7) M	4,2
Tb	NIM-G	Granite	2,8(6) M	2,9
Th	NIM-L	Lujavrite	65(9) R	61
	NIM-G	Granite	52(6) R	51
	BCR-1	Basalt	6,0 R	6,3
U	NBS-1633	Coal fly-ash	11,6(2) C	12,8
W	TLG-1 ²⁶	Tungsten ore	0,083(3)% R	0,085%
Zn	NBS-63	Phosphor bronze metal	0,61% C	0,62%
	NBS-329	Zinc conct.	45,5(1)% C	45,5%
	NBS113a	Zinc conct.	57,3(1)% C	57,5%
	MP-1	Zn, Sn, Cu, Pb ore	16,3(2)% R	16,2%
Zr	IGS 35	Ore	48,76(17) M	48,3%

* Values are given in parts per million except where otherwise indicated.

R Recommended result

C Certified result

M Mean result

() Figures in parentheses indicate that there is uncertainty regarding the last figure quoted. When two figures are quoted, e.g. (±), the limits are +1 to -2 in the last figure quoted.

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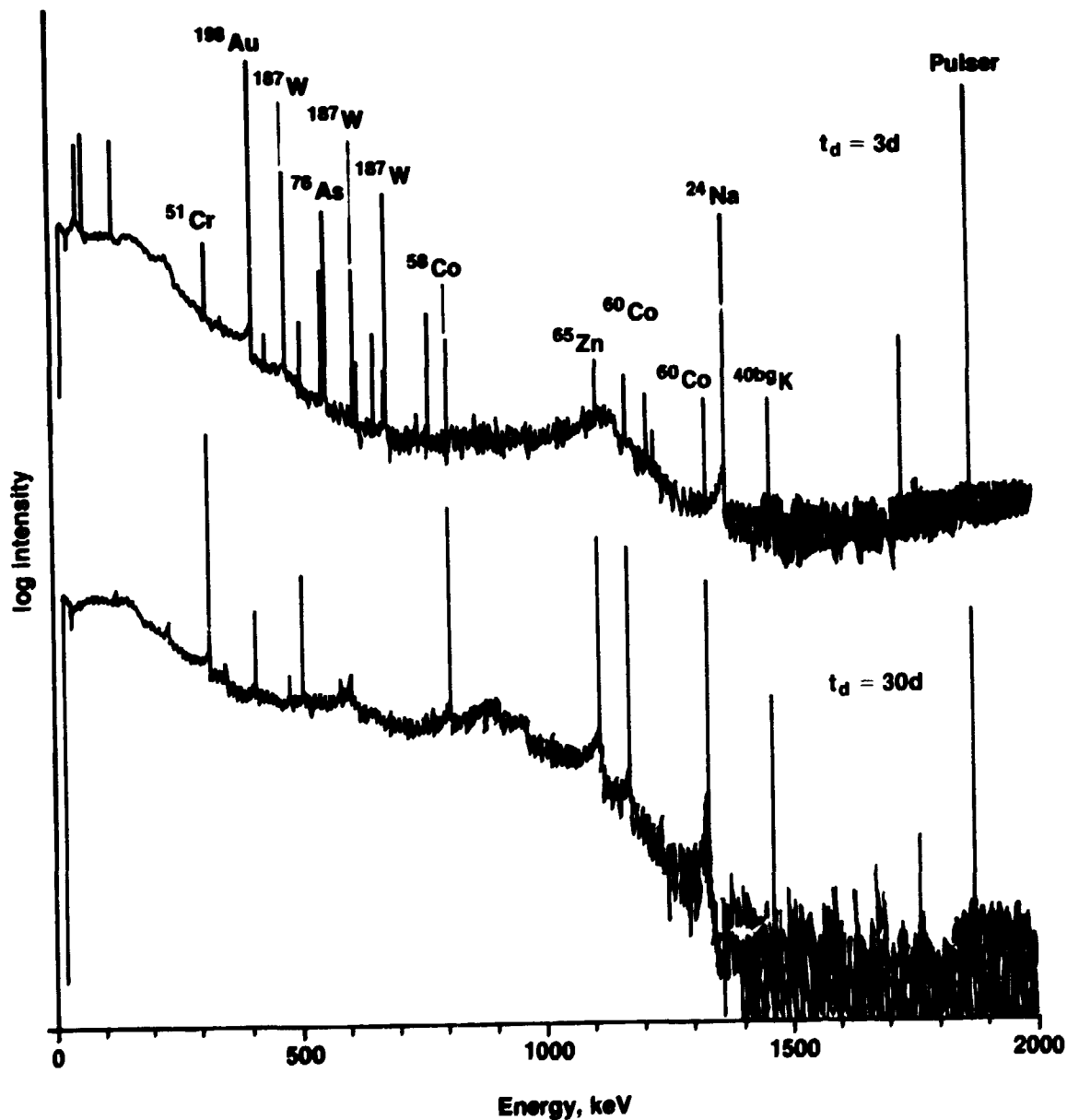


FIGURE 1. Spectra of Standard I at main decay times

SYNTHETIC STANDARDS FOR INAA

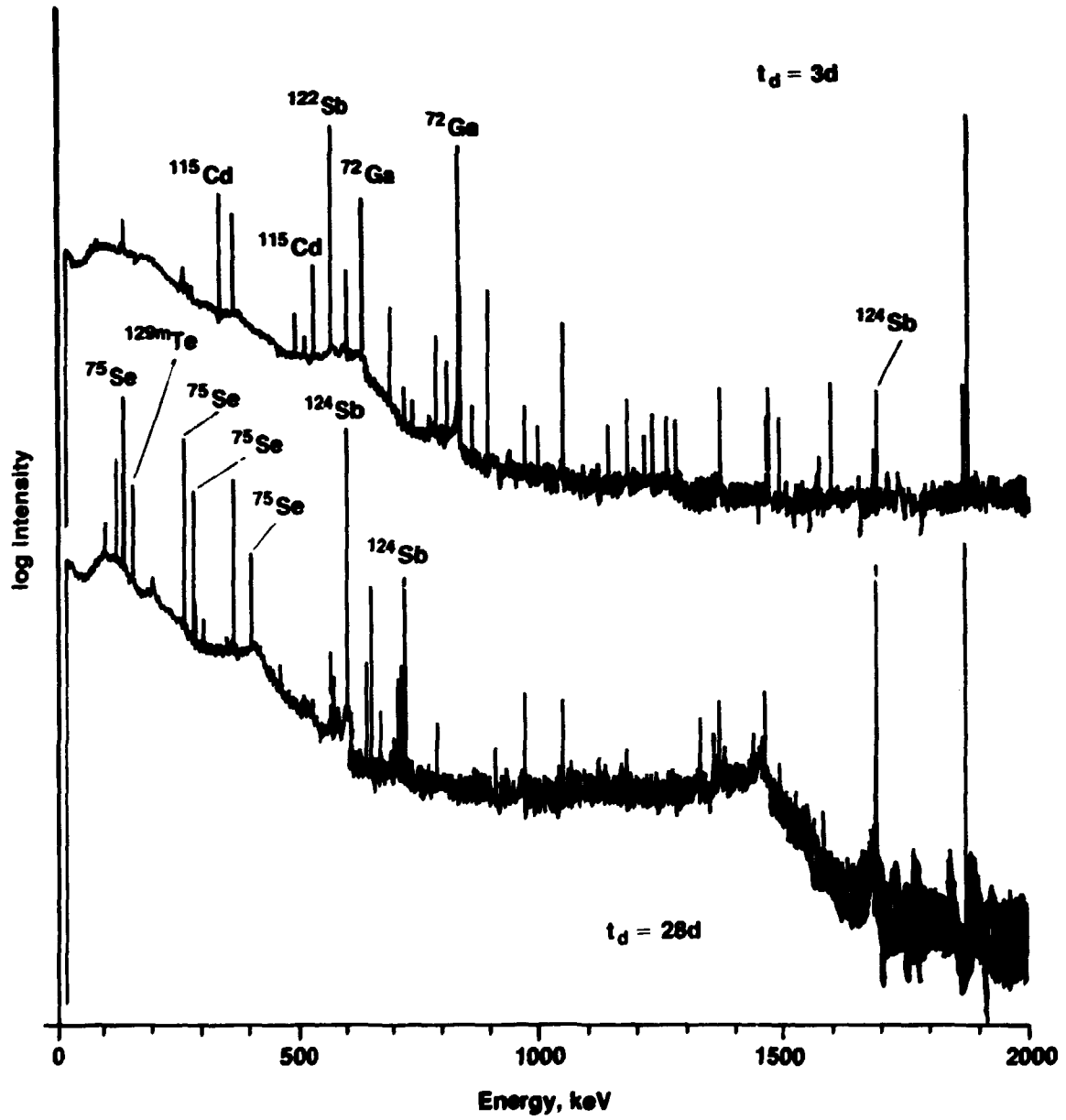


FIGURE 2. Spectra of Standard II at main decay times

SYNTHETIC STANDARDS FOR INAA

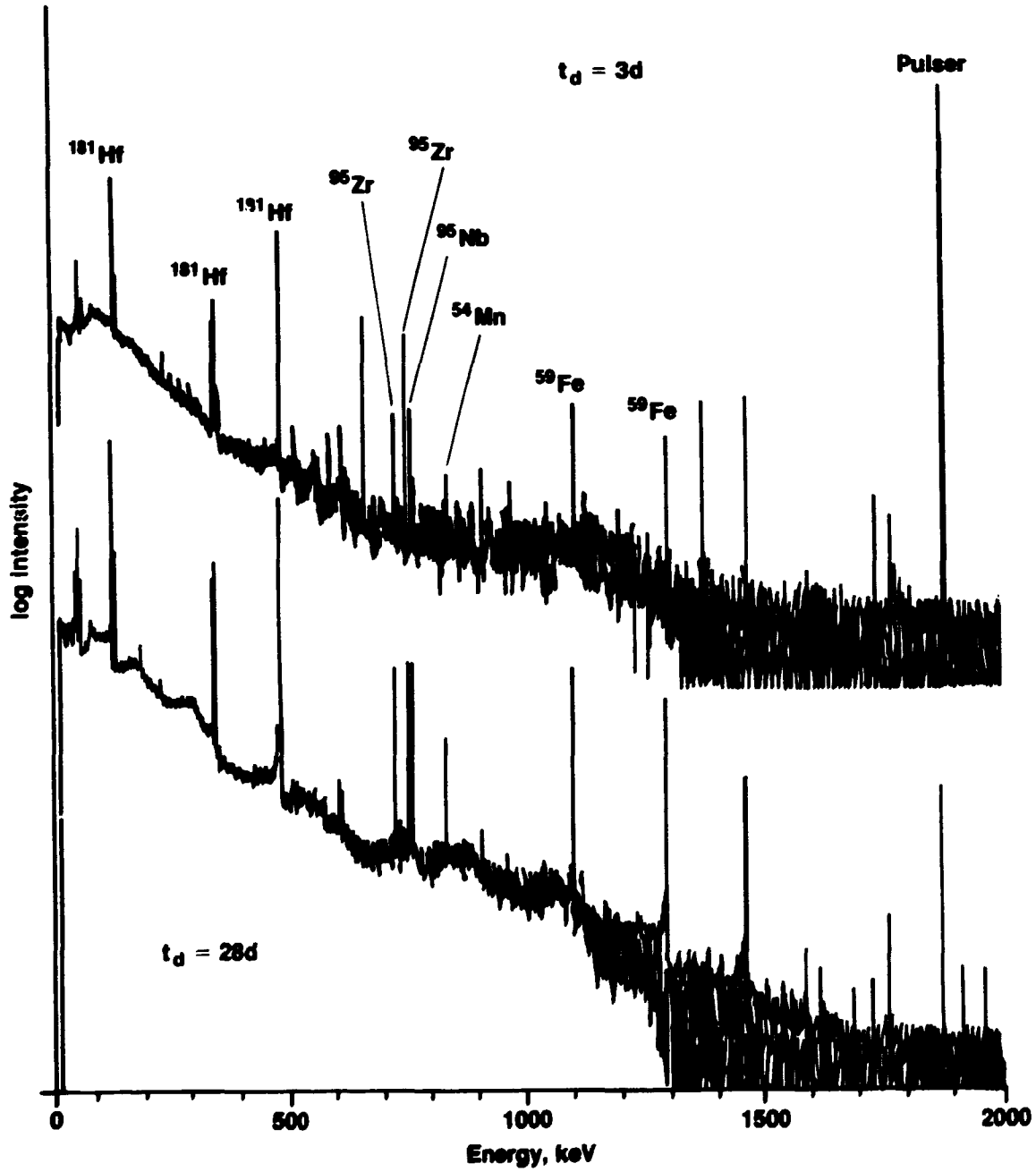


FIGURE 3. Spectra of Standard III at main decay times

SYNTHETIC STANDARDS FOR INAA

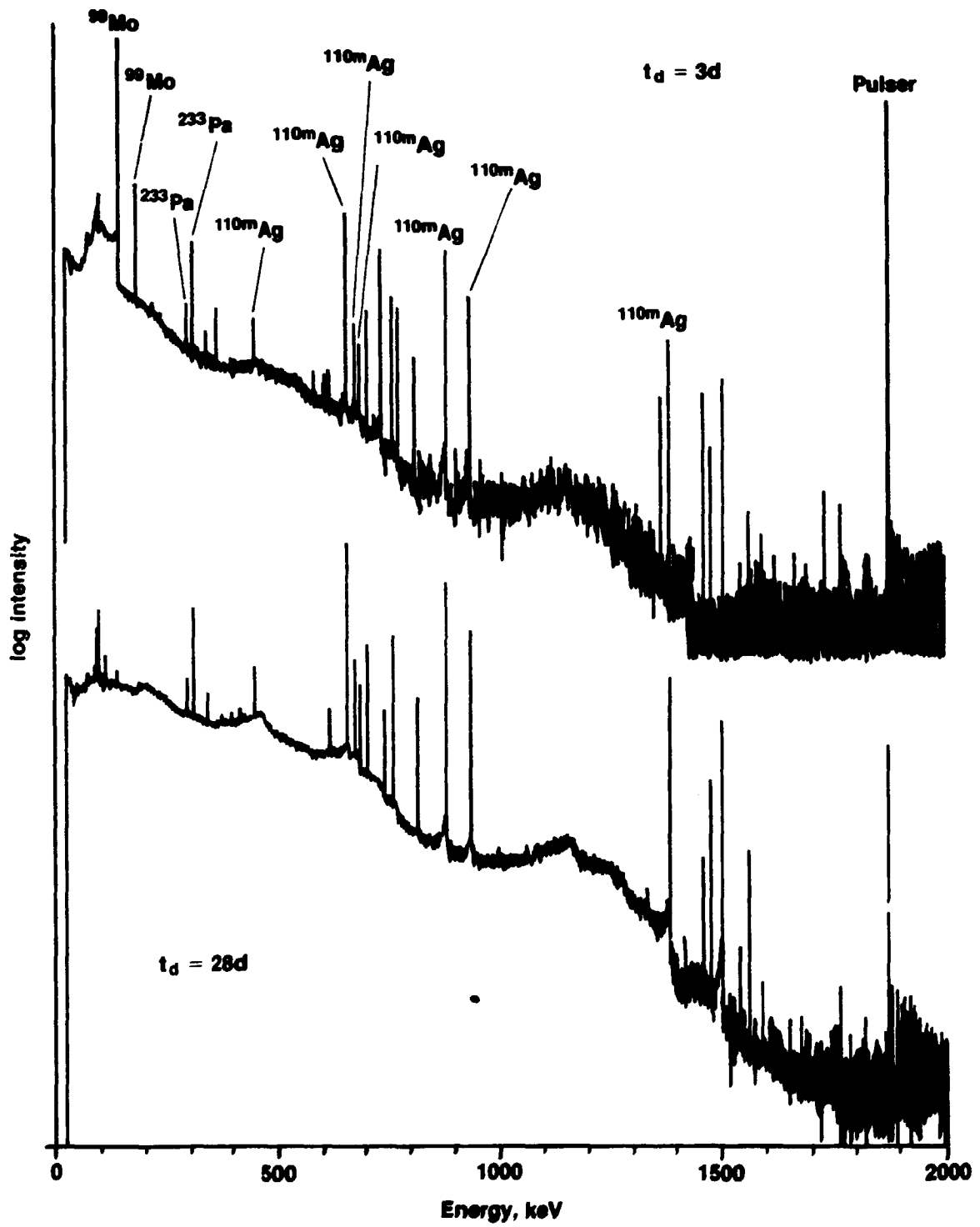


FIGURE 4. Spectra of Standard IV at main decay times

SYNTHETIC STANDARDS FOR INAA

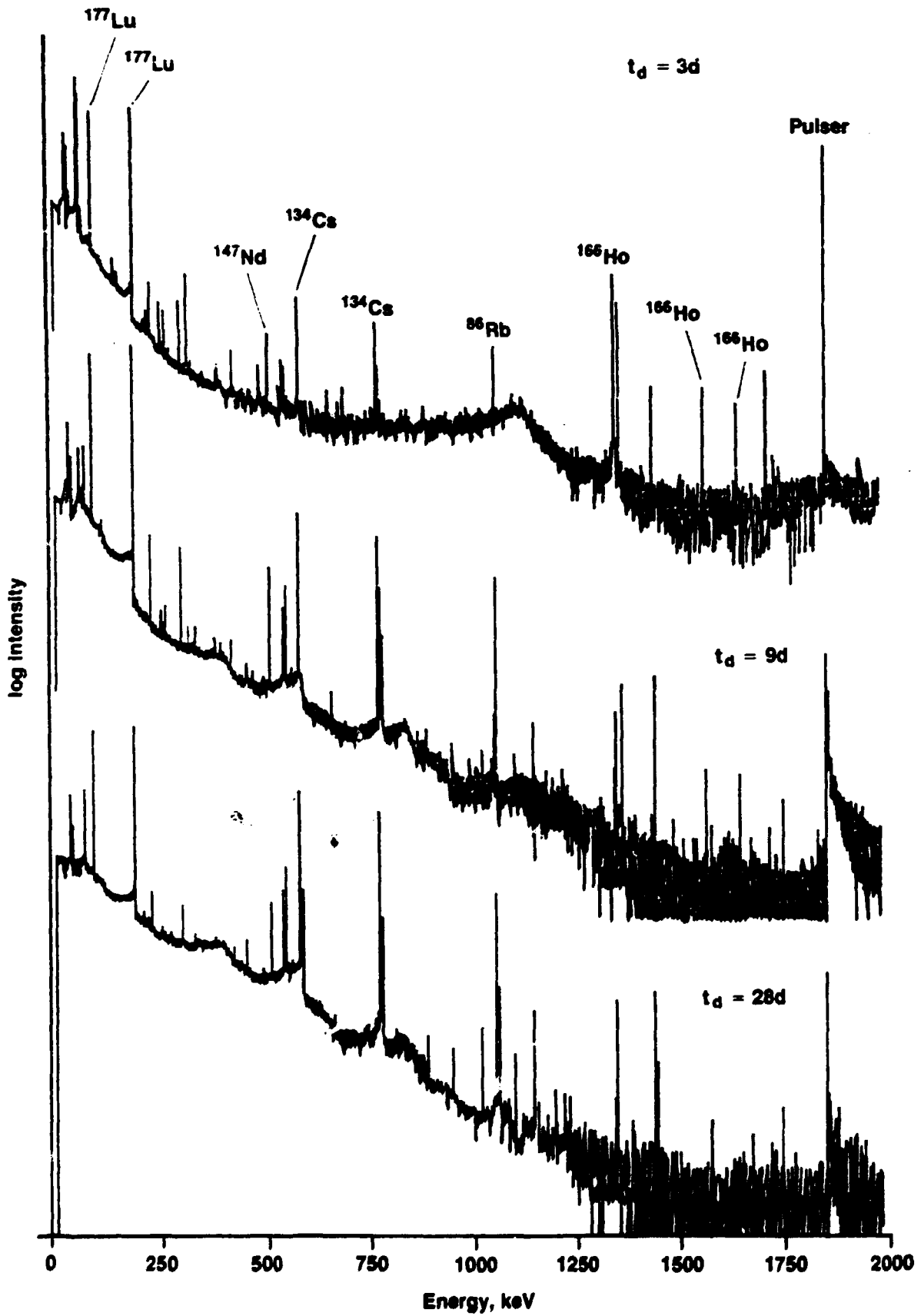


FIGURE 5. Spectra of Standard V at main decay times

SYNTHETIC STANDARDS FOR INAA

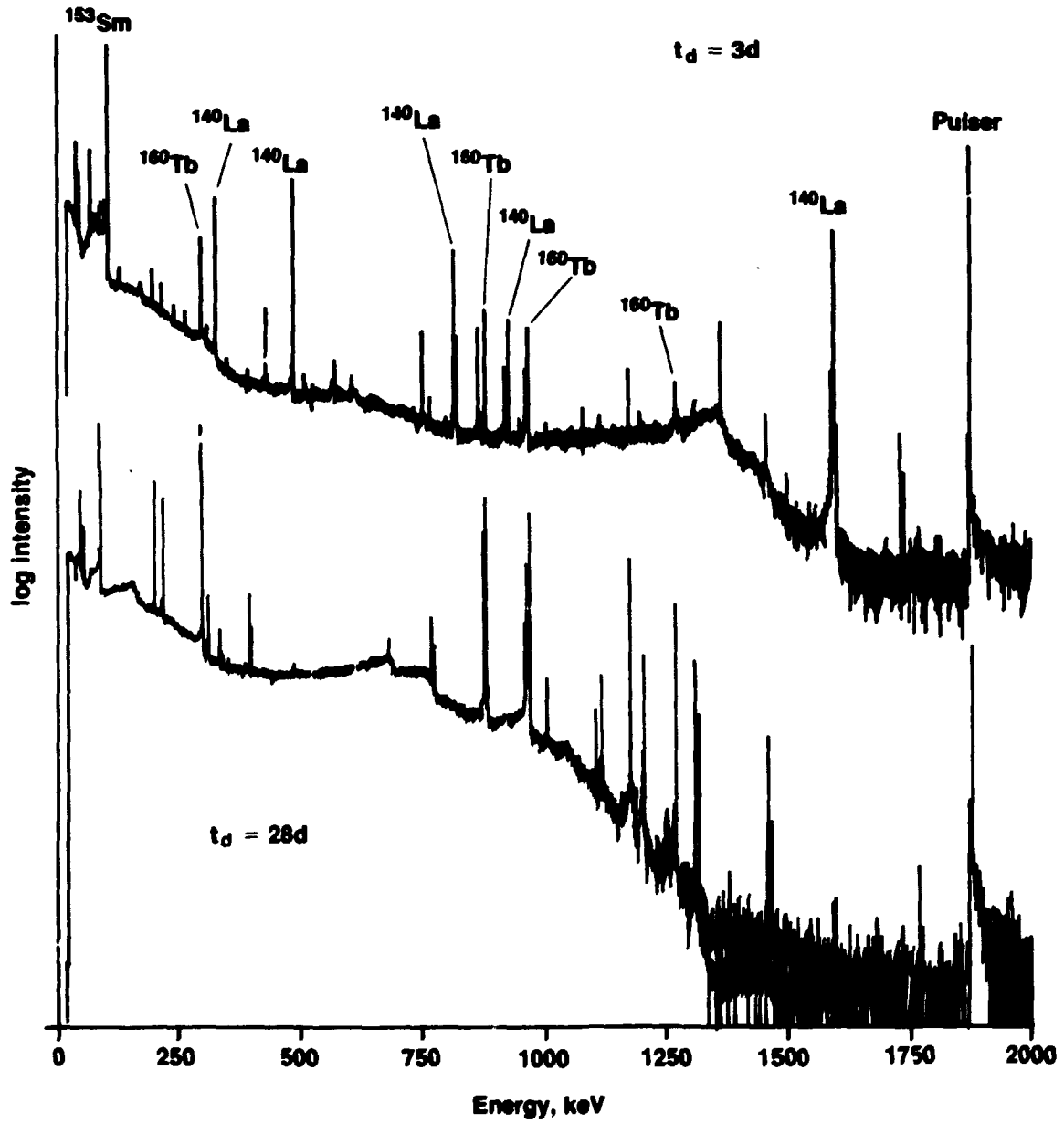


FIGURE 6. Spectra of Standard VI at main decay times

SYNTHETIC STANDARDS FOR INAA

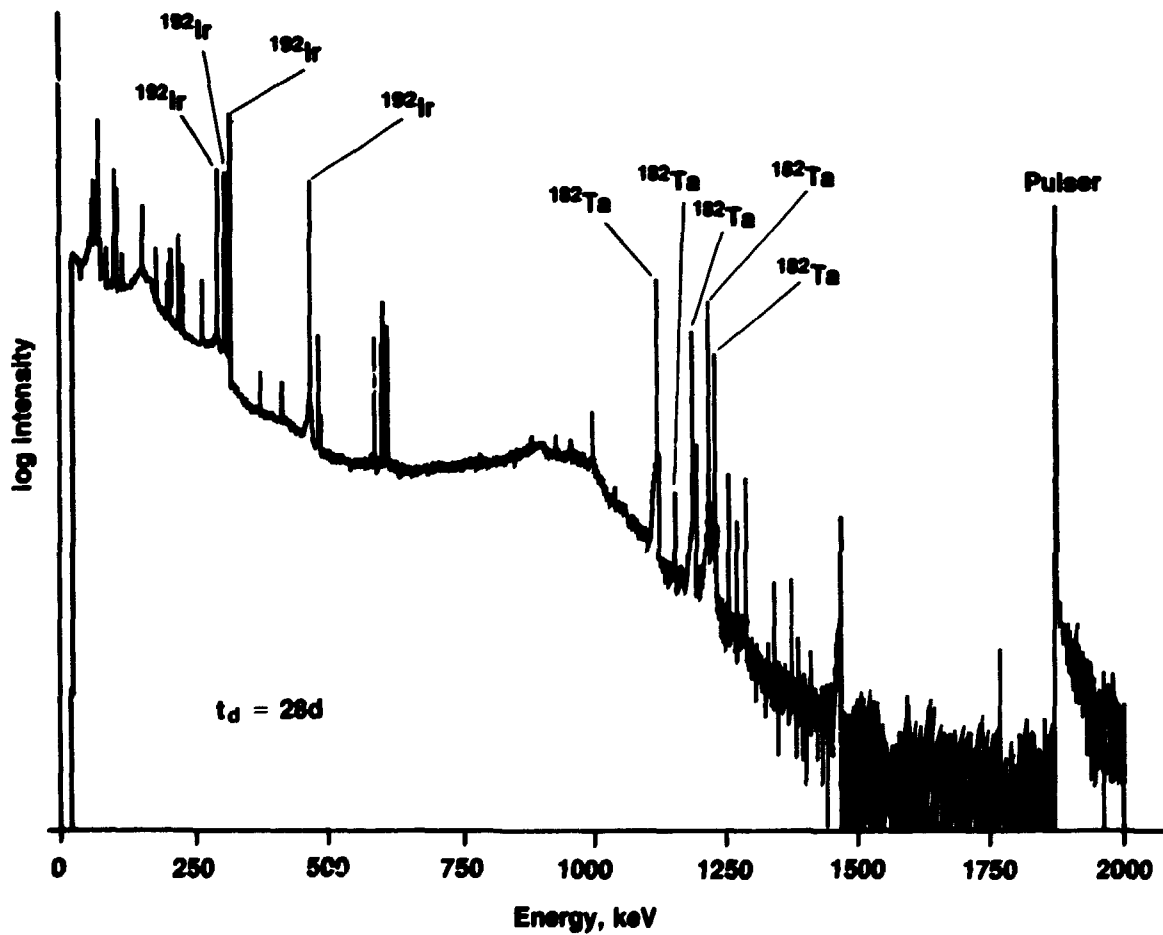


FIGURE 7. Spectrum of Standard VII at main decay times

SYNTHETIC STANDARDS FOR INAA

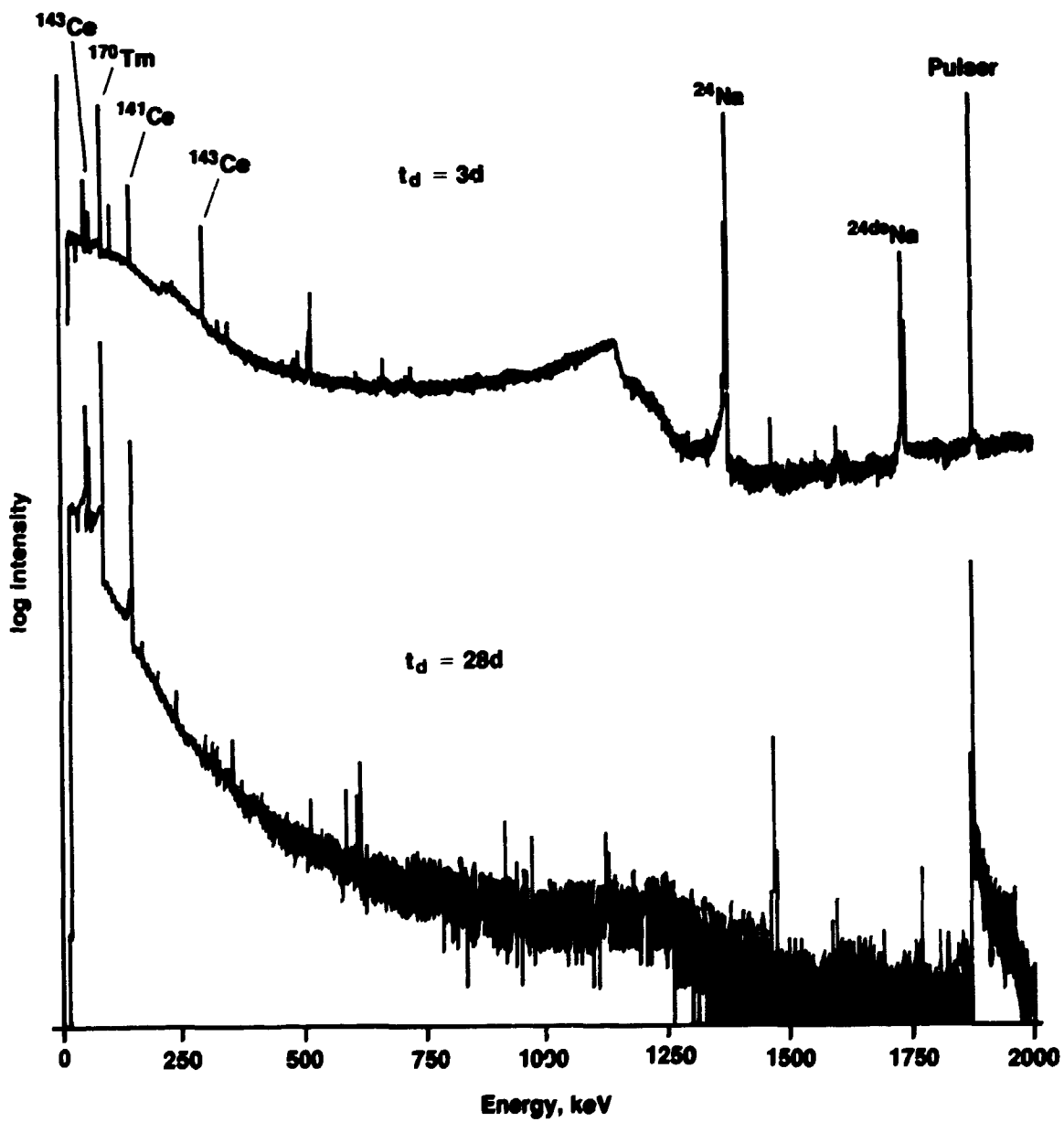


FIGURE 8. Spectra of Standard VIII at main decay times

SYNTHETIC STANDARDS FOR INAA

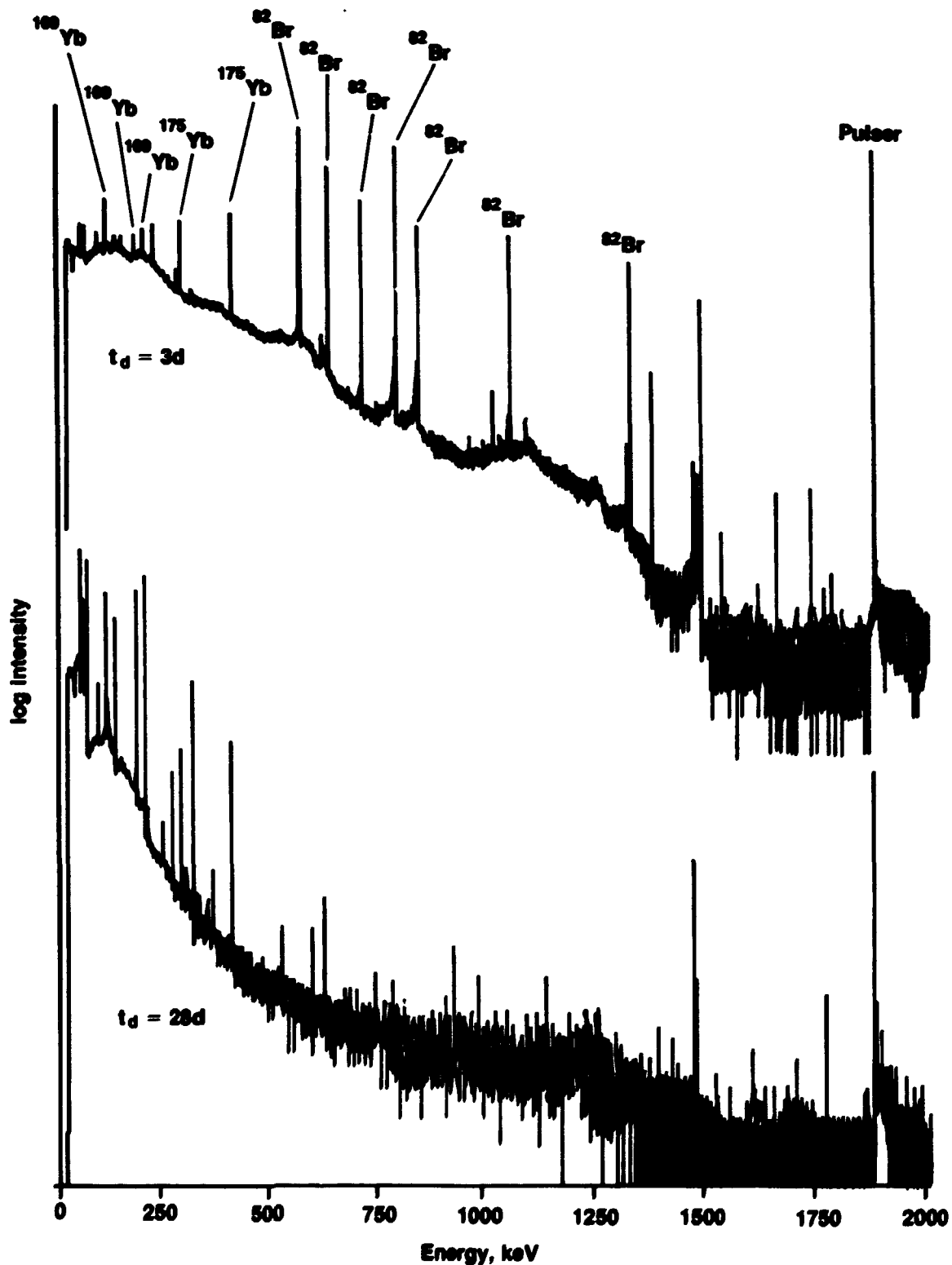


FIGURE 9. Spectra of Standard IX at main decay times

SYNTHETIC STANDARDS FOR INAA

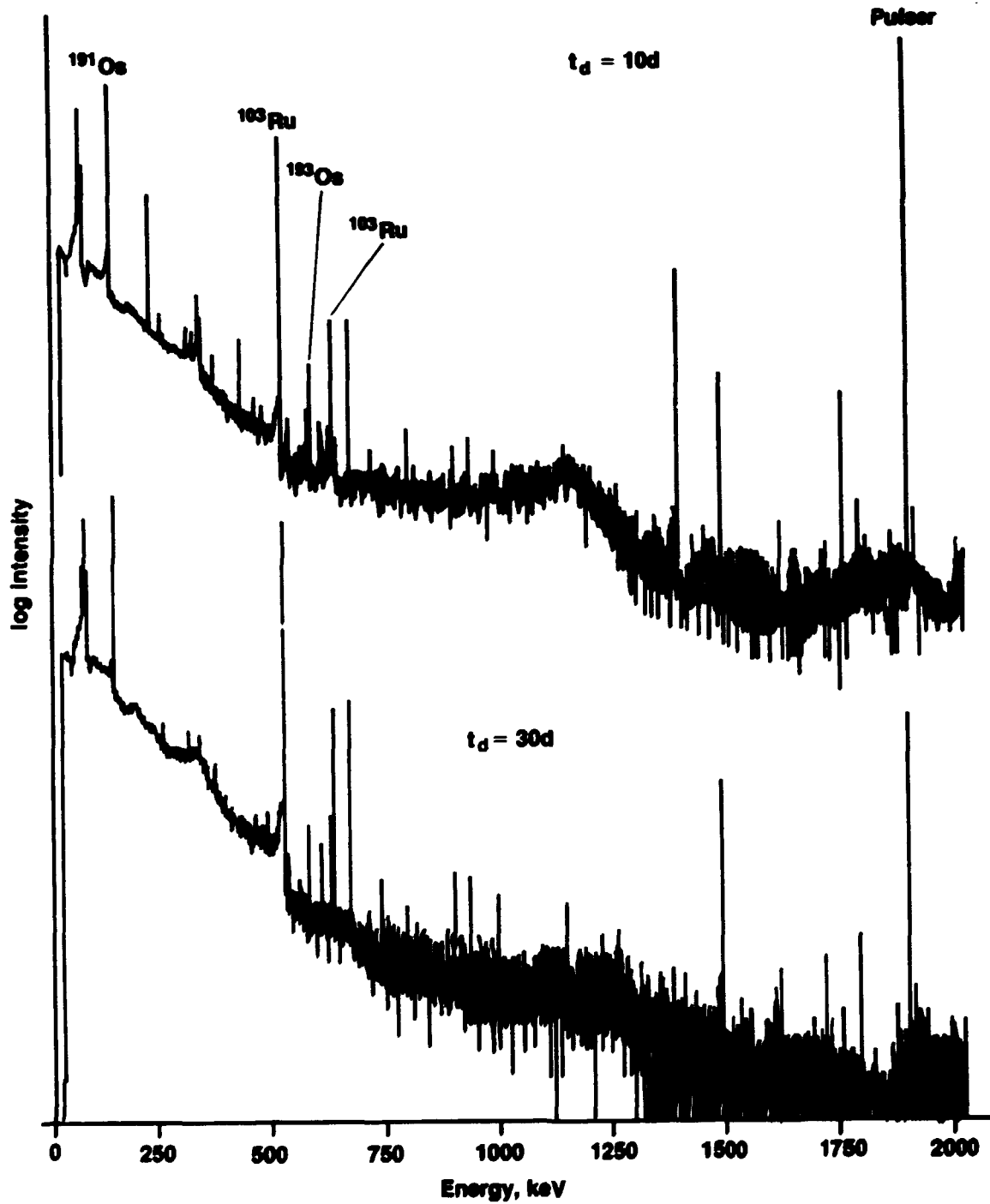


FIGURE 10. Spectra of Standard X at main decay times

SYNTHETIC STANDARDS FOR INAA

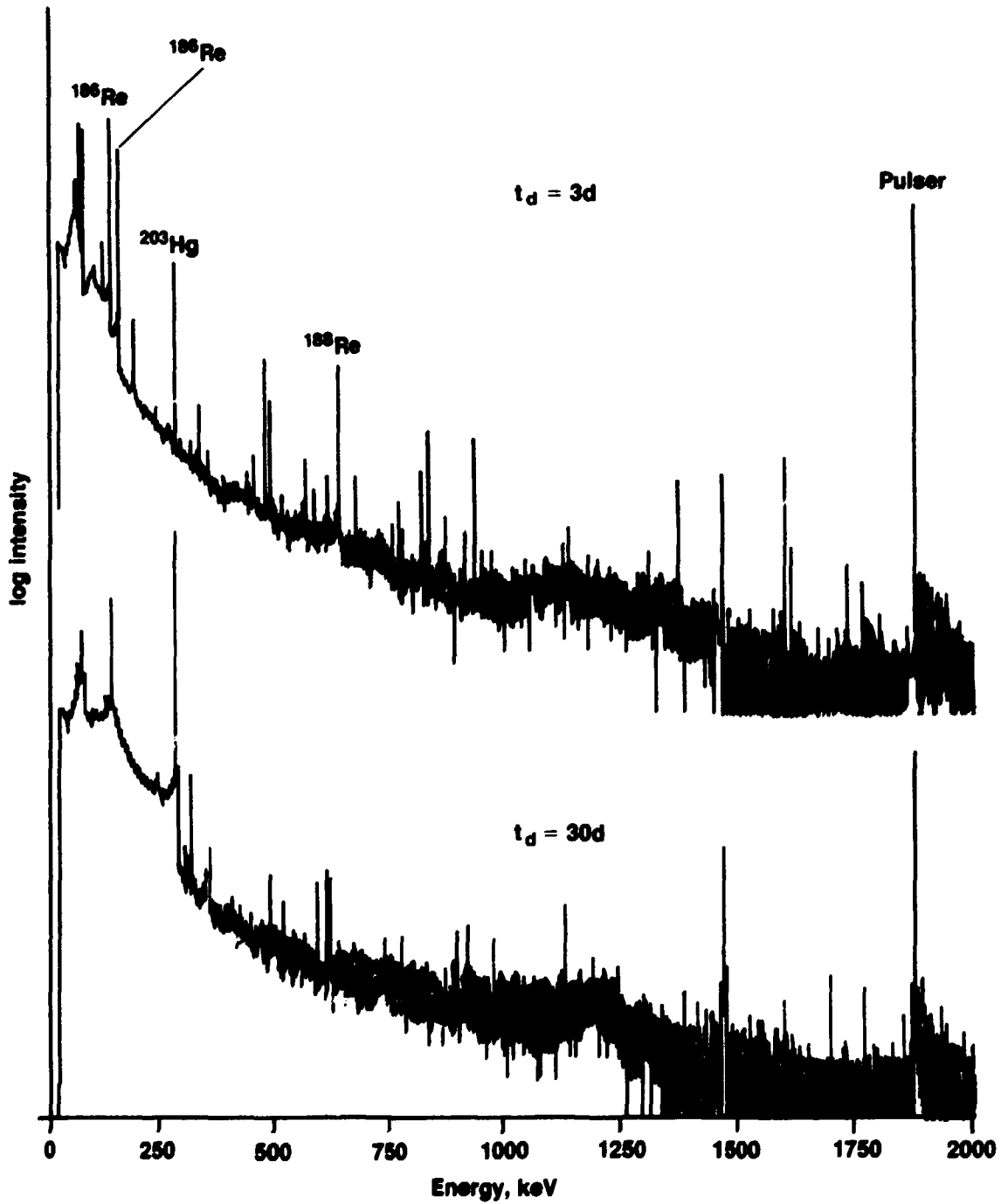


FIGURE 11. Spectra of Standard XI at main decay times

SYNTHETIC STANDARDS FOR INAA

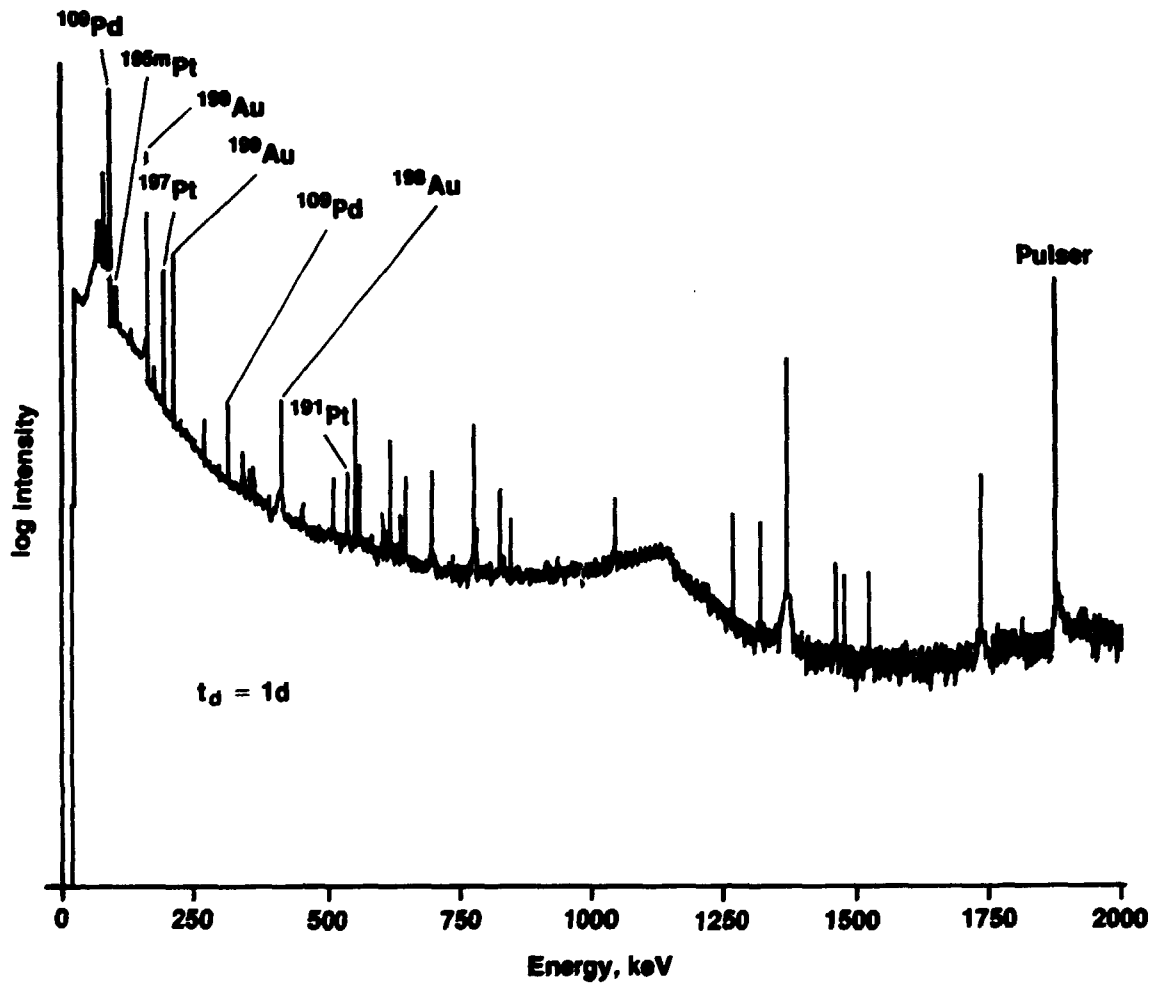


FIGURE 12. Spectrum of Standard XII at main decay times

SYNTHETIC STANDARDS FOR INAA

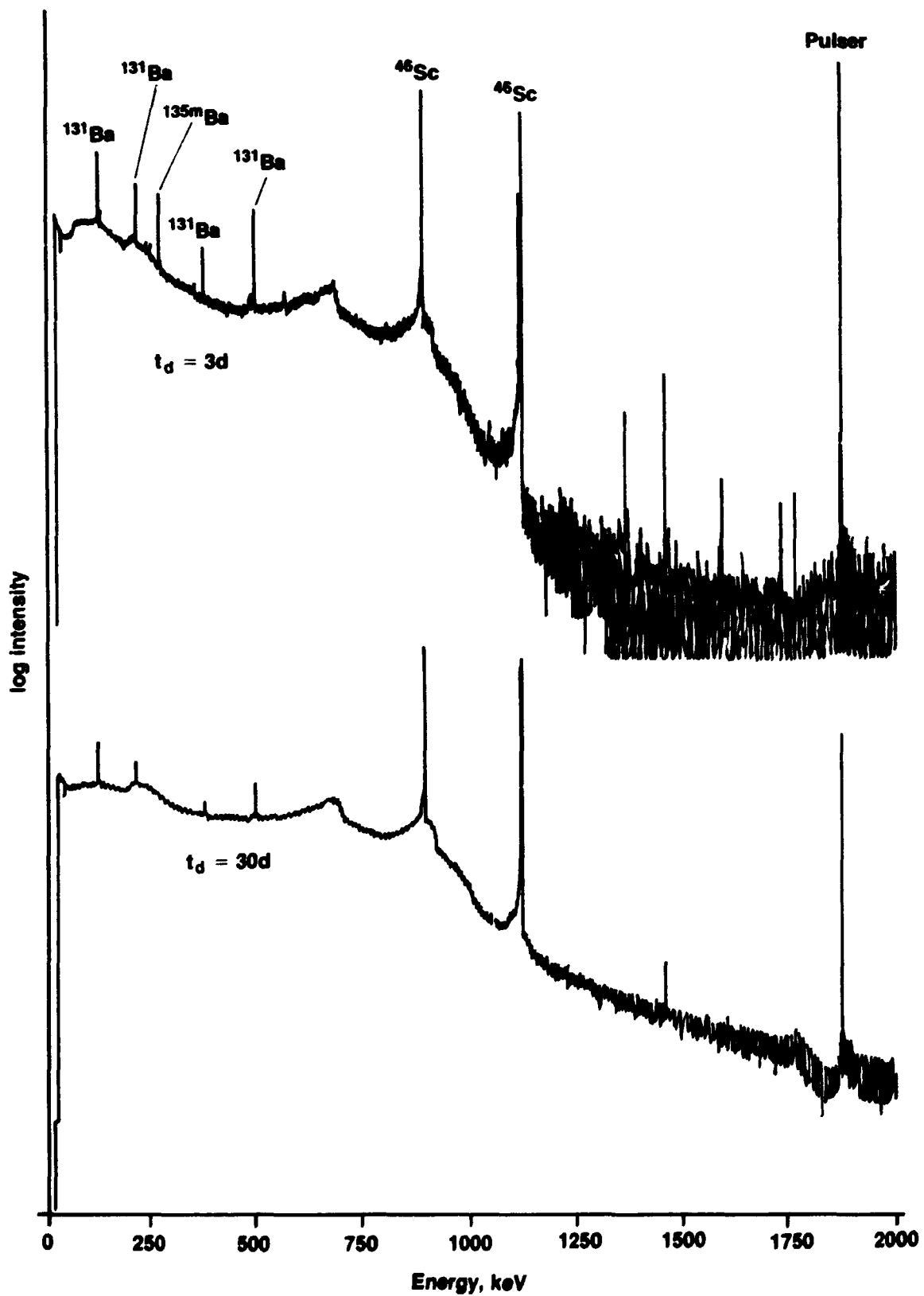


FIGURE 13. Spectra of Standard XIII at main decay times

SYNTHETIC STANDARDS FOR INAA

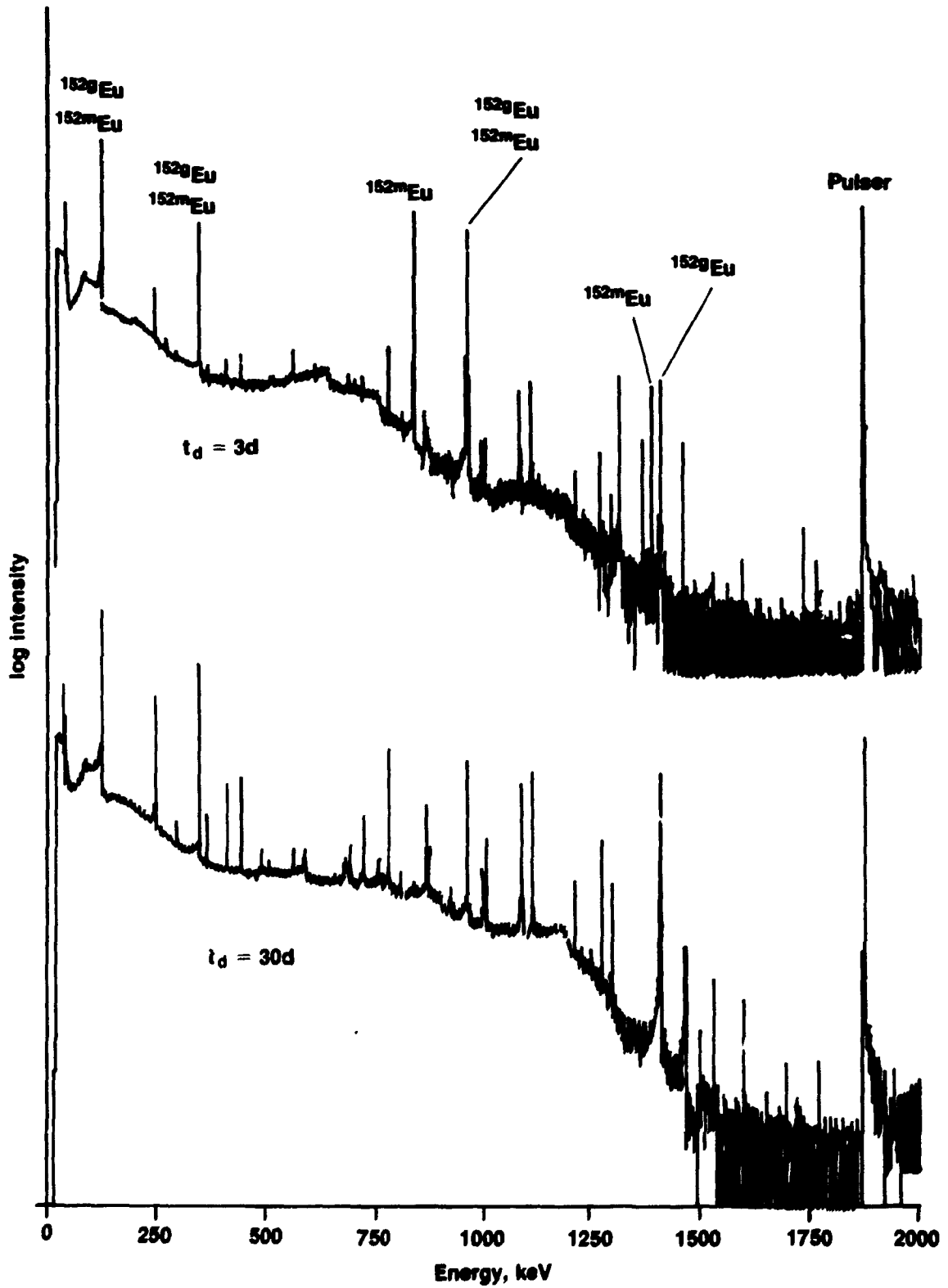


FIGURE 14. Spectra of Standard XIV at main decay times

SYNTHETIC STANDARDS FOR INAA

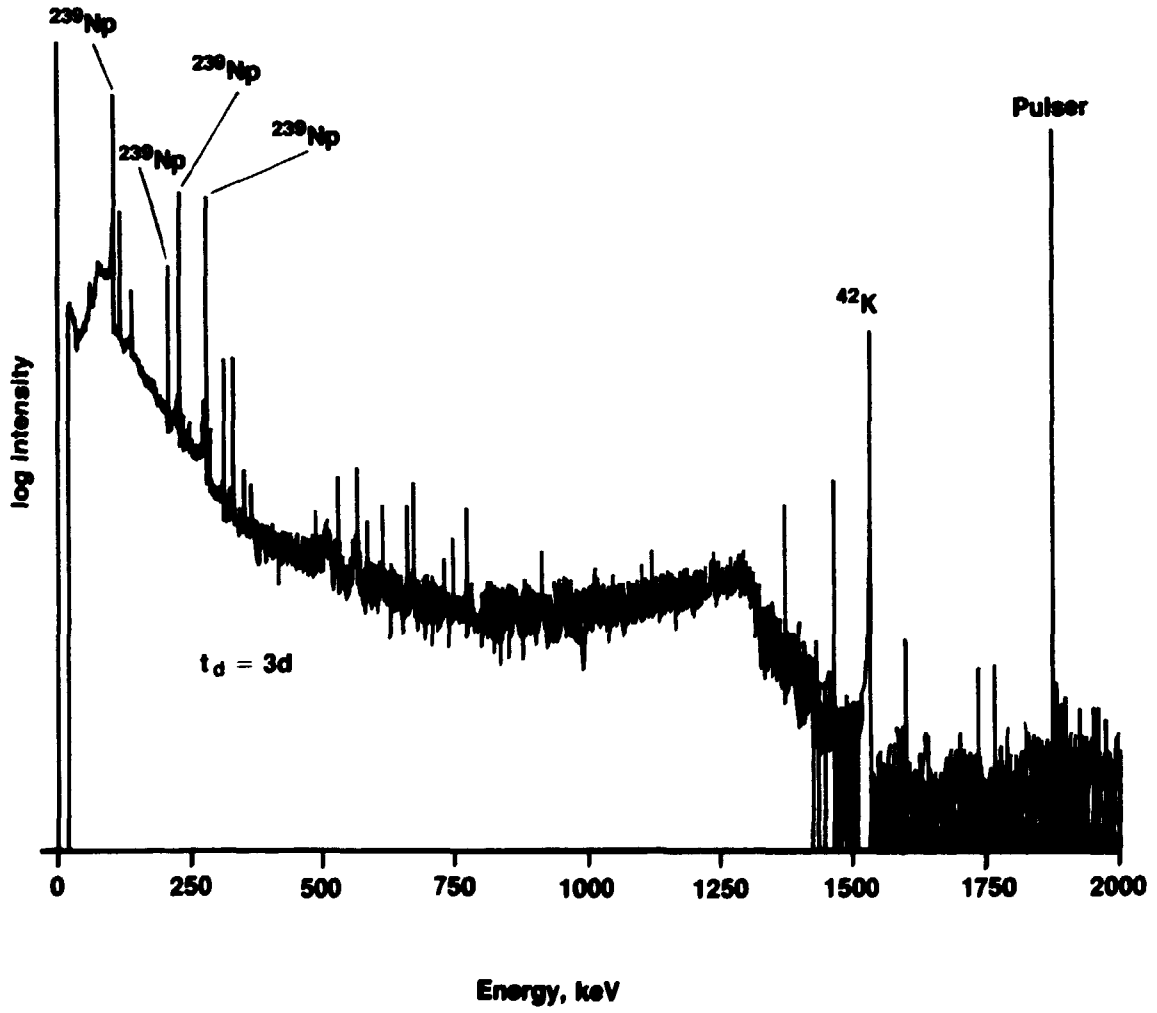


FIGURE 15. Spectrum of Standard XV at main decay times

APPENDIX

AN INVESTIGATION OF A DUAL-ISOTOPE FLUX-MONITORING SYSTEM

The precision of measurement of the isotope activity of each standard was determined by the irradiation, individually, of five vials of each standard, and by normalization of the counts thus obtained in terms of the counts obtained from a single isotope in the corresponding monitoring wire. The precisions obtained were worse than expected, except for those isotopes that were monitored by the same isotope in the monitoring wire. Further measurements of the precision, made by irradiation outside the reactor core, showed that the procedure used for monitoring of the flux was responsible for the error. Another flux-correction procedure was attempted in which use was made of the available data. The flux correction for each isotope is expressed in the following equation:

$$ax_1 + bx_2 = \text{flux correction,}$$

where x_1 is the number of normalized counts for ^{59}Fe or ^{51}Cr ,
 x_2 is the number of normalized counts for ^{182}Ta or ^{58}Co , and
 a and b are elements of $\{a; b \mid a + b = 1; 0 < a; b < 1\}$.

The values for a and b were determined for each isotope by optimization of the precision obtained from the five vials for each of the four standards in the combinations ^{59}Fe and ^{182}Ta , ^{59}Fe and ^{58}Co , ^{51}Cr and ^{182}Ta , and ^{51}Cr and ^{58}Co respectively.

The minimum relative standard deviation thus obtained, together with the relative standard deviation calculated from the relative intensities of ^{51}Cr , was used for the normalization of the flux. The precisions for one sample counted five times are given in Table I-1. The precisions listed in the third column are based on an inadequate number of results, and are therefore not necessarily indicative of the actual precision. The values for a and b would have to be determined from a larger number of samples.

The practicability of this flux-monitoring method will be investigated further. A method for the determination of the absolute thermal and epithermal fluxes based on the use of the thermal neutron cross-section and the resonance integral is also being investigated.

SYNTHETIC STANDARDS FOR INAA

TABLE I-1

Precision obtained with the dual-isotope method of flux monitoring

Isotope	Energy keV	Decay time	Distance cm	Precision		
				R.S.D. for 5 replicate counts on one vial	R.S.D. for single counts on 5 samples with ⁵¹ Cr as flux monitor	R.S.D. for single counts on 5 samples with the dual-isotope method as flux monitor
^{110m} Ag	937	28 to 30	10	0,38	1,7	1,6
⁷⁶ As	559	3 to 4	40	0,91	7,7	0,89
¹⁹⁸ Au	411	3 to 4	40	0,32	5,1	0,41
¹³¹ Ba	496	28 to 30	10	1,1	6,3	1,1
⁸² Br	776	3 to 4	40	0,59	7,1	2,4
¹¹⁵ Cd	336	3 to 4	40	2,27	7,9	3,6
¹⁴¹ Ce	145	28 to 30	10	1,9	7,3	2,4
⁶⁰ Co	1174	28 to 30	10	1,3	3,3	1,3
¹³⁴ Cs	605	28 to 30	10	0,67	7,3	3,1
¹⁵² Eu	1408	28 to 30	10	1,0	2,6	1,2
⁷² Ga	630	3 to 4	40	0,83	4,0	3,7
¹⁸¹ Hf	482	28 to 30	10	0,52	2,8	0,29
¹⁶⁶ Ho	1379	3 to 4	40	3,33	5,0	1,1
¹⁹² Ir	317	28 to 30	10	0,35	2,4	0,61
⁴² K	1526	3 to 4	40	2,4	2,4	1,1
¹⁷⁷ Lu	112	8 to 10	15	2,04	3,3	2,7
⁹⁹ Mo	141	3 to 4	40	1,5	3,2	1,3
¹⁴⁷ Nd	531	8 to 10	15	0,91	4,2	1,7
²³⁹ Np	278	3 to 4	40	0,38	7,8	1,3
¹⁹¹ Os	129	28 to 30	10	1,5	3,5	2,9
²³³ Pa	312	28 to 30	10	1,2	5,3	0,71
¹⁰⁹ Pd	88	1,0	20	0,23	1,2	0,37
¹⁹⁷ Pt	191	1,0	20	0,73	1,1	0,98
⁸⁶ Rb	1076	28 to 30	10	0,40	8,8	2,8
¹⁸⁶ Re	137	3 to 4	40	1,4	4,8	1,3
¹⁰³ Ru	497	28 to 30	10	0,82	2,9	1,6
¹²⁴ Sb	1691	28 to 30	10	0,80	6,0	1,9
¹²² Sb	564	3 to 4	40	0,59	7,4	4,0
⁴⁶ Sc	889	28 to 30	10	0,40	2,1	1,0
⁷⁵ Se	279	28 to 30	10	1,8	5,5	0,31
¹⁵³ Sm	103	3 to 4	40	0,63	5,4	0,98
¹⁶⁰ Tb	879	28 to 30	10	0,23	6,9	1,3
^{123m} Te	159	28 to 30	10	2,4	8,7	2,5
¹⁷⁰ Tm	84	28 to 30	10	1,8	10	3,9
¹⁸⁷ W	685	3 to 4	40	0,18	4,9	0,67
¹⁸⁸ Yb	177	28 to 30	10	0,46	6,5	0,86
⁶⁵ Zn	1115	28 to 30	10	1,02	1,9	0,85
⁹⁵ Zr	757	28 to 30	10	0,90	1,6	0,30

R.S.D. Relative standard deviation.