Journal of Radioanalytical Chemistry Vol. 3 (1969) 161—173

CONTRIBUTION TO 14 MeV NEUTRON ACTIVATION ANALYSIS USING HALF-LIVES BETWEEN 0.55 AND 873 MILLISECONDS*

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(Received November 26, 1968)

A study of the possibility of using half-lives between 0.55 and 873 msec in activation analysis with 14 MeV neutrons is presented here. The cyclic counting method is used: irradiation and detection are repeated several times and counts are memorised during all successive cycles until good final statistics are reached. The theoretical aspect of the cyclic counting method and the influence of neutron pulse shape on the activation results are discussed. The sample is activated and its activity measured in the same geometry: the sample and the scintillation detector are placed close to the target of the neutron generator. An electronic gating system is used to avoid photomultiplier gain fluctuations involved in neutron bombardment. Detection limits are measured for the following elements: Be, B, Al, Ca, As, Zr, In, Tl, Pb, Bi.

Introduction

The lower limit of half-lives used in activation analysis is generally of a few seconds' range.[1] The purpose of this work is to study the possibilities of using elements having half-lives less than one second in activation analysis with 14 MeV neutrons.

The technical difficulties arise mainly in the irradiation and sample transfer stages of analysis. (It should be pointed out that we consider chemical separations to be excluded in our case.) The first problem to be solved is due to the weak counting rate resulting from a single irradiation. For the neutron fluxes obtainable with pulsed 14 MeV neutron generators, the number of neutrons received by the irradiated sample becomes relatively small for the millisecond range irradiation time. In order to improve the final statistics, the cyclic counting method is used: irradiation and detection are repeated several times and counts are memorised during all successive cycles until good final statistics are reached.

Another difficulty lies in the activity loss during transfer of the irradiated sample to the detector when using classical transfer systems (pneumatic tube). We eliminate the transfer completely; the sample is activated and its activity measured without moving the sample; the sample is placed close to the target of the neutron generator and the detector close to the sample (Fig. 1). To eliminate photomultiplier gain fluctuations involved in neutron bombardment, a photomultiplier gating system is used and the dynode-chain current is increased.

* Work carried out at: Centre d'Etudes Nucleaires de Grenoble, France.

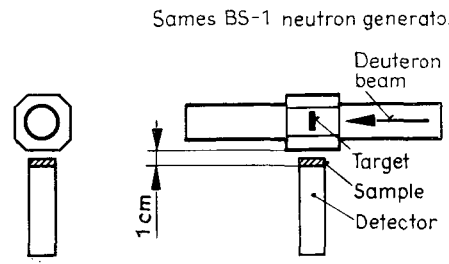

Fig. 1. Geometry of analysis

Cyclic counting method, theoretical remarks

General

It is interesting to study the theoretical results of cyclic counting as a function of the experimental parameters, in particular, the number of cycles.

Let us consider a cycle composed of four time delays:

- irradiation time t_1
- first cooling time t_2
- detection time t_3
- second cooling time t_4

The cycle length is thus equal to:

$$t_1 + t_2 + t_3 + t_4 = \tau$$

The cycle is repeated 1, 2, 3, ... k, ... $l-1$, l times. Let A_k be the activity of the sample at the end of irradiation number k.

$$A^k = N\sigma\Phi(1 - e^{-\lambda t_1}) \sum_{m=0}^{k-1} e^{-m\lambda\tau}$$

where $N = \dfrac{DPW}{M}$

D – Avogadro number;
P – isotopic abundance of the isotope studied;
W – weight of the irradiated element;
M – atomic mass of the irradiated element.

The number of disintegration occurring during the counting time t_3 of cycle number k is given by:

$$C_k = \int_{t_2}^{t_2+t_3} A_k e^{-\lambda t}\, dt = \frac{1}{\lambda} A_k e^{-\lambda t_2}(1 - e^{-\lambda t_3})$$

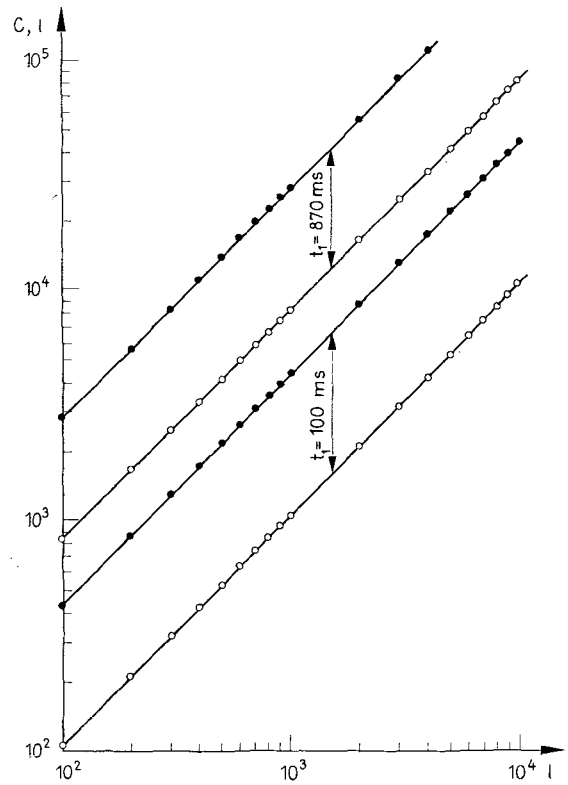

Fig. 2. Example of the theoretical results of cyclic counting as a function of the number of cycles and irradiation time. $C(l)$: number of counts memorised during l cycles in the 44 msec wide first channel of the 200-channel decay curve; $W_{Ca} = W_{O_2} = 0.1$ g; $\Phi = 10^8$ n$(4\pi)^{-1}$sec^{-1}; $\alpha = 0.1$; $t_2 = 150$ msec; ● ^{39}Ca(^{40}Ca(n,2n)^{39}Ca); ○ 7.3 sec ^{16}N background (^{16}O(n,p)^{16}N)

The total number of counts memorised during l successive cycles is thus equal to:

$$C(l) = \alpha \frac{N\sigma\Phi}{\lambda} e^{-\lambda t_2}(1 - e^{-\lambda t_1})(1 - e^{-m\lambda t_3}) \sum_{k|1}^{l} \sum_{m|0}^{k-1} e^{-m\lambda\tau}$$

where:

α — counting efficiency

$$\sum_{k|1}^{l} \sum_{m-0}^{k-1} e^{-m\lambda\tau} = \sum_{m|0}^{l-1} (l - m)\, e^{-m\lambda\tau}$$

We assume the neutron flux to be constant during all l cycles. In other words, we consider the neutron pulse form is rectangular and there is no amplitude change

from one pulse to another. Thus, $\Phi \times l = L$ is the total number of neutrons received by the sample.

We have then:

$$C(l) = \alpha\, WL \frac{\sigma}{\lambda} \frac{DP}{M} e^{-\lambda t_2}(1 - e^{-\lambda t_1})\ (1 - e^{-\lambda t_3}) \times \times \frac{1 - e^{-l\lambda\tau}}{1 - e^{\lambda\tau}} \left(1 - \frac{1}{l} \frac{1 - e^{-\lambda\tau}}{1 - e^{-l\lambda\tau}} \sum_{m/0}^{l-1} m e^{-m\lambda\tau}\right) \quad (1)$$

An example of the $C(l)$ function is illustrated in Fig. 2.

Influences of neutron pulse shape on the activation results

The particular geometry used in this work makes the simultaneous irradiation and measurement of standard and sample impossible. Two independent experiments are necessary. The question is whether the simple neutron monitoring usually used in activation analysis gives sufficient information for flux normalization. In fact, even if two experiments are characterized by the same number of neutrons received by the sample, the irradiation results may vary from one experiment to another. We noticed experimentally that two principal cases should be taken into consideration:

– the amplitude of the neutron pulses varies, but their form remains approximately rectangular (this may be the case just after the neutron generator is started because of increasing deuteron penetration into the ion source);

– the amplitude may be considered as reproducible from one pulse to another but the form of the neutron pulses is not rectangular. (This is in reality very common. We have limited discussion of this point to the case observed most frequently when the neutron pulses have a trapezoidal form.)

To evaluate the importance of the correction factors corresponding to the cases mentioned above, we calculated[2] the theoretical total number of counts memorised during l successive cycles under the following conditions:

– the neutron pulse amplitude increases from one pulse to another following an arithmetic progression rule, the pulse shape remaining rectangular;

– the neutron pulse shape is trapezoidal and remains reproducible from one pulse to another.

The total number of neutrons received by the sample is considered to be equal to L in both cases.

Two conclusions can be drawn by comparison of the equations thus obtained with the equation corresponding to the use of rectangular pulses of constant amplitude [Eq. (1)]:

– although the theoretical amplitude variation we took into consideration is much greater than the fluctuation actually observed, it has a negligible influence on the final results (we assume the number of cycles l to be great enough);

– the irradiation results depend upon the shape of the neutron pulse. If rectangular neutron pulses are replaced by trapezoidal pulses, the statistical improvement is equal to 2% for a trapeze slope of 15%.[2]

This should be taken into consideration when quantitative analysis is the purpose of the work. The neutron flux-time fluctuation may also be a source of error when the results of a single irradiation-analysis are normalized on the basis of simple neutron monitoring.

One can also see that the rectangular form of the neutron pulse does not correspond to the best target exploitation: if the rectangular form is replaced by the triangular one, the same sample activity can be obtained with a resulting economy of 20% in neutron output.

Apparatus

The electronic system used (Fig. 3) enables the duration of the four parts of the cycle t_1, t_2, t_3, t_4, to be varied and also controls repetition of the cycle and memorizing of counts detected during all successive cycles. The operations are programmed beforehand and executed automatically by the programmer.

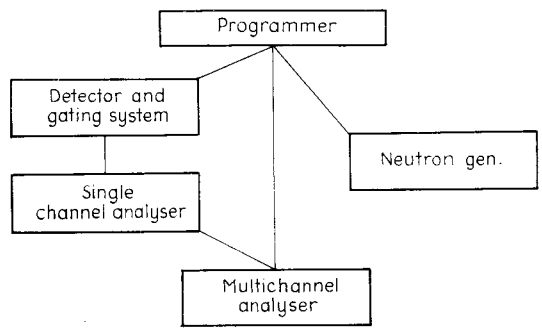

Fig. 3. Diagram of apparatus

Programmer

The programmer is composed of a quartz-timer MHQ and five gating units M3DP – 10 (Constructions Radiotechniques et Électroniques du Centre C.R.C., Saint Etienne, France). The gate width corresponds to the length of the various cycle steps (Fig. 4).

The programmer offers the possibility to preset beforehand:
– cycle step duration (t_1, t_2, t_3, t_4);
– counting time per channel (when the multichannel analyser is working in the recycled multiscaler mode);
– number of cycles required.

Cycles are repeated automatically, until the experiment is stopped either manually or automatically after a preset cycle number has been reached.

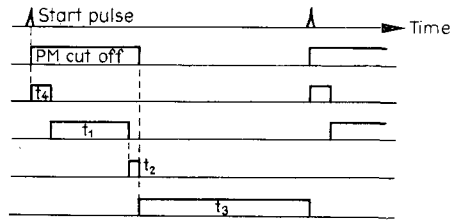

Fig. 4. Programmer sequence

Neutron generator

The small Sames BS–1 14 MeV neutron generator is used. Its total neutron yield (4π) is approximately equal to 10^8 n · sec^{-1}. The maximum neutron pulse length is about 100 msec.

Detector

A scintillation counter is used with a 3/4 1″ × 2″ NaI(Tl) scintillator and a 153 AVP or 153 AVP/O4 (La Radiotechnique, Paris, France) photomultiplier tube. Some beta emitters (^{6}He, ^{8}Li, ^{39}Ca) are studied with plastic scintillators.

In our particular geometry the limitations of the normal operation of a photomultiplier can easily be overcome.

In fact, the particles resulting from neutron bombardment produce in the scintillator a significant number of strong light pulses. The resulting anodic current may then reach an excessive value and produce important gain fluctuations. In order to observe the gain fluctuations an indirect method is adopted and the apparatus described above (Fig. 3) is used. A gamma source (^{137}Cs or ^{54}Mn) is set in the sample position (Fig. 1). The single-channel analyser energy band is fixed to cover half (left or right) of the photopeak. This energy band must not contain any short half-life activity due to the neutron bombardment. The pulses then go to the multi-channel analyser operating in the recycled multiscaler mode (allowing the memorising of counts detected during all successive cycles). The result of such an experiment is a curve with counting rate-time co-ordinates. If the photomultiplier gain is constant, one obtains theoretically (*i.e.* with no sta-

tistical uncertainty) a straight line parallel to the time axis. The fluctuations of gain may then be observed because of the non-linear form of the corresponding experimental curve. The test is quite severe: one percent energy displacement of the photopeak corresponds to 20 percent change in counting rate.[2]

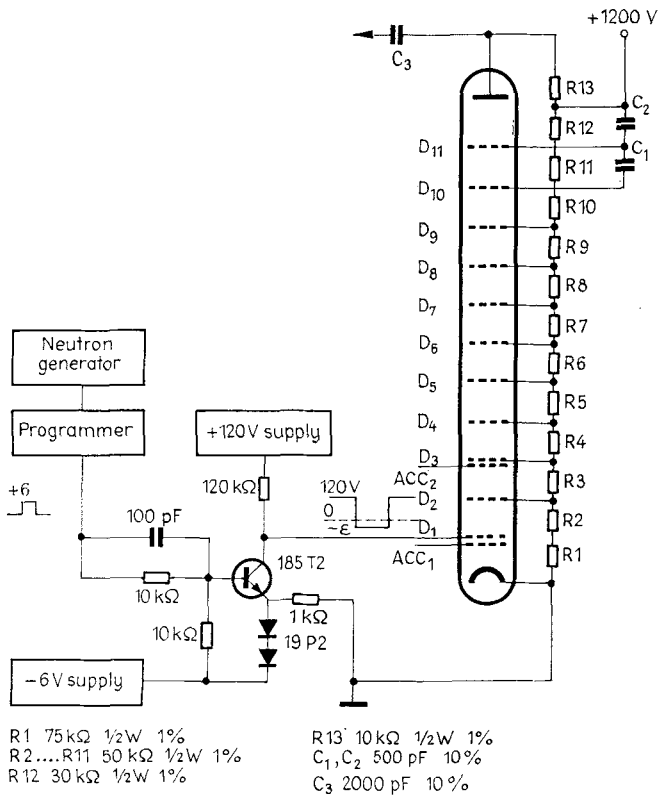

Fig. 5. Photomultiplier gating system

To protect the photomultiplier against excessive anodic current following the neutron bombardment, a gating system is used. The first dynode is supplied independently. During neutron bombardment the supply is cut off and the first dynode is set to the cathode potential (zero) (Fig. 5). At the beginning of the detection period the supply is re-energized and tube operation becomes normal again. This procedure is repeated in every cycle. This gating method is efficient for the neutron flux used (maximum 10^6 n · cm^{-2} · sec^{-1}) at the scintillator location.

However, some supplementary precautions are necessary to guarantee good gain stability. In fact, gating corresponds to a rapid change of counting rate. Now

gain is sensitive to a change of anodic current: even a single scintillation involves a gain variation[3]:

$$\frac{\Delta G}{G} = t_0 \frac{i_{A\max}}{i_p} \frac{\exp(-t/t_0) - \exp(-t/RC)}{t_0 - RC}$$

t_0 – time constant of the scintillation;
$i_{A\max}$ – maximum anodic current;
i_p – dynode-resistance current;
RC – time constant of the last dynode's supply circuit.

Gain instability is temporary. Thus detector operation becomes normal after some re-stabilizing time depending principally upon two elements: the time constant RC and the $i_{A\max}/i_p$ ratio. To decrease gain fluctuations one should diminish the $i_{A\max}/i_p$ ratio.

That is why we increased the dynode-resistance current ten times up to 2 mA (we did not, however, change the capacity C because of its stabilizing role).

Solutions adopted in this work are satisfactory in our experimental conditions. No gain fluctuations are observed and a reproducibility of 4% is obtained. More improvements can be made, particularly in the case of a higher neutron flux.

It should be pointed out that detector study was not our purpose, but rather a way of making the detector performance satisfactory for quantitative analysis. That is why we did not study in detail all the phenomena that neutron bombardment can involve in the photomultiplier tube.

Experimental

Gamma scintillation spectrometry is used to identify the elements to be determined and to study the background and interfering activities. For a few beta emitters some approximate preliminary measurements are taken by means of beta scintillation spectrometry. However, no precise determination of the maximum energy is sought.

Decay curves are then obtained by means of the multi-channel analyser operating in the recycled multiscaler mode. (The dead-time per channel is equal to 12 μsec. The lower limit of half-lives which can be studied is then equal to a few hundred microseconds.) The *IRIS* computer programme[4] is used for a quantitative analysis of decay curves.

Background

Background is composed of two principal components:

– general background of long half-life observed when the neutron generator is not being operated;

– low energy background due to X-rays produced by the neutron generator after the high voltage is set up.

(The *BS*–1 generator is operated with the target at high voltage.)

The second component is often quite important. In fact, discrimination against a low energy background does not change by the fact that the detector is exposed to it. The counting rate is still increased and may contribute to gain instability. To diminish the X-ray intensity, a suitable neutron generator adjustment is made. (The use of a generator having its target at ground potential would be preferable.)

Interferences

The principal interference results from activation of the structural aluminium of the neutron generator tube.

The reaction $^{27}Al(n, \alpha)^{24m}Na$ (T = 19.3 msec, 475 keV) is frequently observed. A typical background spectrum is presented in Fig. 6.

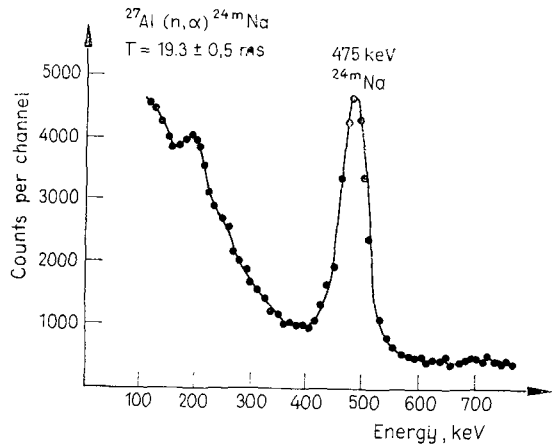

Fig. 6. Spectrum of ^{24m}Na resulting from irradiation of the neutron generator tube

Some contribution from the reaction

$$^{203}Tl(n, 2n)^{202m}Tl\,(T = 0.55 \text{ msec}, 480 \text{ keV})$$

due to the activation of thallium present in the scintillator was also observed.

The interferences are particularly unlikely if the interfering half-life is similar to the half-life studied. A typical example is the ^{24m}Na interference when the reaction $^{75}As(n, n')^{75m}As$ (16.2 msec, 305 keV) is studied. Two irradiations are made in such a case: the first "with" and the second "without" the sample. The resulting decay curves are then normalized to the same neutron flux and the second curve is subtracted from the first.

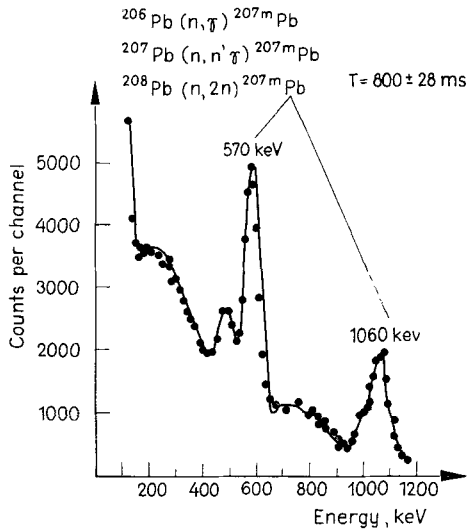

Fig. 7. Spectrum of ^{207m}Pb, $t_1 = 5$ msec; $t_2 = 2$ msec; $t_3 = 40$ msec; $t_4 = 3$ msec

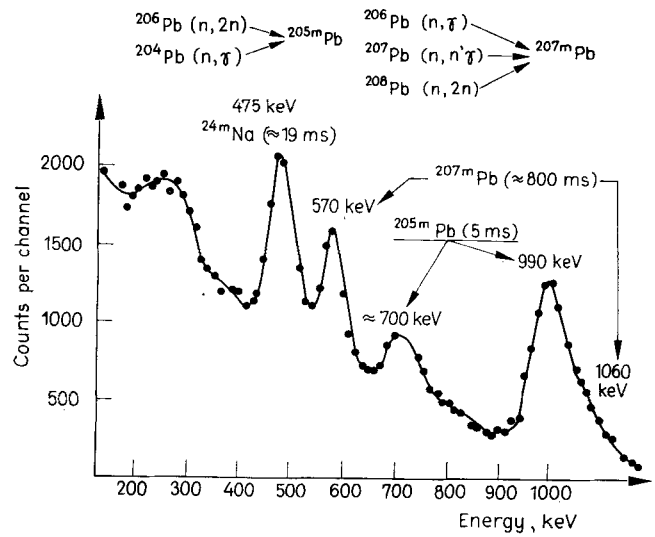

Fig. 8. Spectrum of ^{205m}Pb, $t_1 = 5$ msec; $t_2 = 0.7$ msec; $t_3 = 10$ msec; $t_4 = 160$ msec

In order to reduce interferences, suitable cycle step times and electronic adjustment are chosen in each particular case. Typical results of the step duration variation are presented in Figs 7, 8, 9. A natural lead sample is irradiated and three isomers are observed simultaneously: ^{207m}Pb, ^{205m}Pb, ^{206m}Pb. The corresponding gamma energies are similar[5–8] but the half-lives are actually different (800; 5.3; 0.13 msec respectively). In order to obtain good statistics for one isomer, the contribution of the two other isomers is diminished by the use of suitable t_1, t_2, t_3, t_4 parameters.

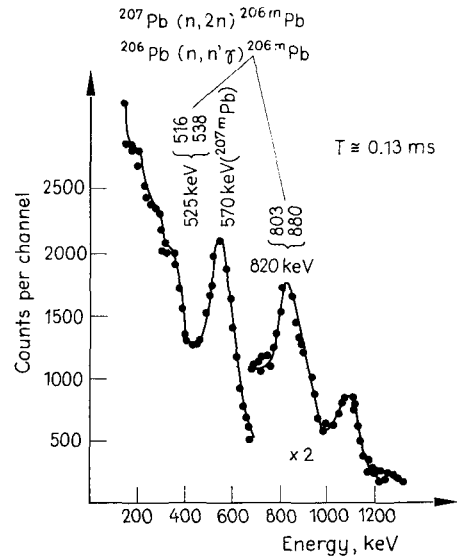

Fig. 9. Spectrum of ^{206m}Pb, $t_1 = 0.2$ msec; $t_2 = 0.03$ msec; $t_3 = 0.4$ msec; $t_4 = 3.5$ msec

Results

Detection limits and average precision of analysis are presented in Table 1 for a range of half-lives. The half-lives were measured several times. The results are selected by means of the DIXON[9] test and presented as

$$T = T_{average} \pm \sigma_T$$

The detection limit is defined as the mass corresponding to the activity exceeding the background by 3 σ, where σ is the background standard deviation. The detection limits are normalized to a neutron flux of 10^5 n · cm^{-2} · sec^{-1}.

Table 1
Experimental results

Reaction	Period (msec) $T \pm \sigma_T$	Detection limit (g) For 10^5n/cm^{-2} sec	Number of cycles	Total exper. time	Average precision (%)
^{40}Ca (n, 2n) ^{39}Ca	873 ±15	0.41	2 000	8 h	4
^{9}Be (n, α) ^{6}He	844 ±29	0.46	1 260	15 min	3.4
^{90}Zr (n, n') ^{90m}Zr					
^{91}Zr (n, 2n) ^{90m}Zr	815 ±28	1.8	6 000	14 h	3
^{11}B (n, α) ^{8}Li	810 ±51	0.18	4 000	9 h	6
^{206}Pb (n, γ) ^{207m}Pb					
^{207}Pb (n, n,γ) ^{207m}Pb	800 ±28	3.3	1 000	1 h	3.5
^{208}Pb (n, 2n) ^{207m}Pb					
^{115}In (n, 2n) ^{114m}In	40.4 ± 2.5	2.5	1 800	15 min	4.5
^{27}Al (n, α) ^{24m}Na	19.3 ± 0.5	5.4	300	2 min	2.5
^{75}As (n, n') ^{75m}As	16.2 ± 1.8	0.75	10 000	34 min	11
^{204}Pb (n, γ) ^{205m}Pb	5.31± 0.09				
^{206}Pb (n, 2n) ^{205m}Pb		12	40 000	1 h 20 min	1.6
^{209}Bi (n, 2n) ^{208m}Bi	2.54± 0.12	25	4 000	6 min	4.7
^{203}Tl (n, 2n) ^{202m}Tl	0.55± 0.22	7.1	80 000	13 min	3.6

Discussion

Detections limits

It should be pointed out that all quantitative results presented above have been obtained under our particular experimental conditions. A considerable improvement of the detection limits seems possible by means of an appropriate neutron generator. In fact, the use of a neutron flux of 10^6-10^7 n·cm^{-2}·sec^{-1} would improve the detection limits by a factor of 10–100. (Such extrapolation, however, must be carried out carefully, because the flux increase may increase photomultiplier gain instability.) The use of a neutron generator tube made for example of iron would also help to improve detection limits because of the diminution of ^{24m}Na interference.

Precision

In order to evaluate the precision of analysis, the experimental result is compared to a known mass of the element to be determined. Several samples of the same element are used, and the average deviation is calculated. It should be pointed out that the experimental results are corrected neither for self-absorption nor for self-shielding, and the neutron pulse shape is not taken into consideration. The precision may therefore be improved by taking into account suitable correction factors.

Time considerations

As mentioned above, the maximum neutron pulse length is equal to about 100 msec. When half-lives longer than 100 msec are studied a greater number of cycles must be used and the total analysis time becomes extremely long. Here again, the use of a suitable neutron generator would solve the problem.

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The author wishes to thank the Commissariat à l'Energie Atomique and in particular Professor L. NEEL, director of the Centre d'Etudes Nucléaires de Grenoble, for giving the opportunity to undertake this work. He gratefully acknowledges Professor A. MOUSSA's invaluable advice and making the neutron generator available. Thanks are also due to J. LAVERLOCHERE for advice, for assistance and for criticism in the preparation of this paper. The author is indebted to R. CORNUET for many helpful suggestions and to E. JUNOD for help in the numerical treatment of the experimental results. The friendly cooperation of M. GIGNOUX from the Service de l'Electronique is greatly appreciated. This study was supported by the Commissariat à l'Energie Atomique. Scholarships were due to the Association pour l'Organisation des Stages en France (ASTEF) and Fondation Joliot-Curie.

References

1. H. P. LUKENS, *J. Radioanal. Chem.*, 1 (1968) 349.
2. A. GOLAŃSKI, Thèse, April 1968, CEA-R-3694, 1969.
3. Les tubes photomultiplicateurs, La Radiotechnique, 1965.
4. E. JUNOD, Personal communication.
5. E. MONNAND, CEA-R-2900, 1965.
6. P. DUPONT-GAUTIER, S. CHANTELOT, N. MOISSON, CEA-R-2830, 1967.
7. J. BERGKVIST, *Arkiv För Fysik*, 24 (1965) 4.
8. D. F. ALBURGER, *Phys. Rev.*, 95 (1954) 1492.
9. Méthodes Statistiques en Chimie Analytique, Cetema, Vol. 3, Fasc. 4.