J. Indian Chem. Soc.,
Vol. 66, August—October 1989, pp. 728-729

Instrumental Neutron Activation Analysis. The Need for Assessing Signal Purity for Acceptance of Quality of Data on the Basis of Counting Statistics

M. SANKAR DAS* and S. YEGNASUBRAMANIAN**

Analytical Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085

Analytical data by instrumental neutron activation analysis are usually accepted on the basis of good counting statistics. These measurements are expected to be made on signals which are higher than the limits of quantitation, properly computed as suggested by Currie. In paired observations, as in INAA, the limits of detection and quantitation, as well as the related standard deviations are related to the period for which the spectral background is counted. There exists, therefore, a risk of acceptance of results on signals of poor signal-to-background (*S/B*) ratios. Hence the need to have an independent criterion on the *S/B* ratio which assures the quality of data.

FREQUENTLY the analytical data by instrumental neutron activation analysis (INAA) are accompanied by the uncertainties of the data computed from counting statistics (CS)[1]. Such estimates of precision of the data do not give any information about the purity of the signals on which the CSs are computed. A high precision could be the outcome of long counting ($\sqrt{N}$) of signals which are weak, but defined well above the background, or from the counting of high intensity gross signals encompassing equally large spectral background (poor signals). These signals could be close to the limit of detection (LOD) or, the limit of quantitation (LOQ)[2] of the methodology. In this paper we discuss the need to assess the quality of INAA data in terms of the signal purity in relation to its background (*S/B*) in addition to the criterion that the signal be above the LOQ of the methodology.

Experimental

The samples (100 mg) were irradiated for 20 h at a neutron flux of 1×10^{13} n cm^{-2} s^{-1} at the CIRUS reactor of the Bhabha Atomic Research Centre. They were counted after a cooling period 15 days using a 45 cc Ge(Li) detector coupled to a 1024 channel analyser having a system resolution of 2.3 keV for the cobalt-60 1332 keV gamma-ray[3].

The samples were AGV-1 and BCR-1 of the U. S. Geological Survey[4]. Two elements, thorium and chromium, present in the andesite. AGV-1 at 6 4 and 12.2 ppm[4] respectively, and chromium in the basalt BCR-1 at 16±4 ppm[5], have been selected for focussing the problems in INAA. The nuclear data of interest in this analysis are given in Table 1. The counting data are given in Table 2 which lists the *S/B* ratios, LOD, LOQ, CS and the observations on the signals.

TABLE 1—NUCLEAR DATA OF INTEREST*

Parent nuclide	Product nuclide	$t_{1/2}$ d	γ-ray energy counted keV
^{232}Th	^{233}Pa^{a}	27.0	312
^{50}Cr	^{51}Cr	27 8	320

*Refs. 3, 6.

^{a} $^{232}\text{Th}\ (n, \gamma)\ ^{233}\text{Th} \xrightarrow[\text{24 min}]{\beta} {}^{233}\text{Pa} \xrightarrow[\text{27 d}]{\beta} {}^{233}\text{U}$

Results and Discussion

Recently, the American Chemical Society has specified that analytical data should be reported only if the analytical signal is higher than the LOQ of the methodology[7], which in turn, depends on the mean process blank, $\bar{X}_{Bl}$ and its standard deviation, S_{Bl} ($n=15-20$). The relationship is $X_L=\bar{X}_{Bl}+10\ S_{Bl}$, where, X_L is the smallest signal which qualifies to be the LOQ. This has also been discussed by one of the present authors[8].

In techniques which involve photon counting, as for example XRF, or INAA, S_{Bl} is estimated from a single count of X_{Bl} from the relationship,

$$S_{Bkd}=S_{Bl}=\sqrt{X_{Bl}}=\sqrt{Bkd}$$

This was first pointed out by Kaiser[9], discussed at length by Currie[2] and accepted by the IUPAC[10]. Currie developed statistically valid working expressions for the computation of LOD and LOQ from X_{Bkd}. They are mutually consistent with the ACS ones. In this study the limits computed by the Currie's formulae have been used.

Let us now consider whether adherence to the above criterion of LOQ is adequate to provide high

---

*20, Udayagiri Cooperative Hsg. Soc., Deonar, Bombay-400 088.
**Present address : Bell Laboratories, Murry Hill, NJ, U.S.A.

TABLE 2—COUNTING DATA ON SIGNALS OF DIFFERENT PURITIES

Sample/ nuclide	Counting period s	Gross counts GPCC	Spectral background $BKD \pm S_{Bkd}$	Net counts NPPC	S/B	LOD[a]	LOQ[b]	RSD[c] %	Remarks
1. AGV-1									
1.1 Pa-233[d]	400	651	290±17	361	1.2	82	296	8	S=1.2 LOQ
1.2 „	800	1 334	650±25	684	1.1	121	414	6	S=1.5 LOQ
1.3 „	2 000	3 583	1 500±39	2 083	1.4	182	600	3	S=3.5 LOQ
2. AGV-1									
2.1 Cr-51	400	356	290±17	66	0.23	81	296	(38)	Undetected[e]
2.2 „	2 000	1 838	1 450±38	388	0.27	180	590	(15)	Detected[e]
2.3 „	10 000	9 500	7 000±84	2 500	0.26	392	1 234	5	S=2 LOQ
3. BCR-1									
3.1 Cr-51	2 000	3 858	3 640±60	218	0.06	283	904	(40)	Undetected
3.2 Cr-51[f]	[14.4 h	1×10^6	9.5×10^4	5 000	0.05	1 435	4 410	6	S=1.34 LOQ]

[a] $LOD = 2.71 + 4.65\sqrt{Bkd}$ (Ref. 2). [b] $LOQ = 50 \times [1 + (1 + Bkd/12.5)^{1/2}]$ (Ref. 2). [c] RSD% = Relative standard deviation = $\sqrt{GPPC + Bkd}/NPCC \times 100$ (Ref. 1) ; RSD values in brackets are not valid for uncertain signals. [d] Irradiation time = 20 h ; coolling for counting = 15 days. [e] Undetected : <LOD ; detected : LOD<signal <LOQ. [f] The data in square-brackets are computed from 3.1.

quality data, particularly for data badly needed for the preparation of reference samples. Examination of the data in Table 2 reveals that the net signal from ^{233}Pa is higher than the LOQ and is counted with a reasonable precision of 8 per cent. The net signal is 1.2 times the spectral background. On counting for a longer period the RSD improves by $1/\sqrt{t}$ where, t is the factor by the counting period is increased. Here is a case in which the improvement in the CS is worth the effort spent in counting.

In case of ^{51}Cr in AGV-1 one starts with a poor signal ($S/B = 0.23$). The causes for this have been pointed out in an earlier publication[11]. This signal, after the first count for 400 s is 'undetected', but on further counting for 2000 s is 'detected' and becomes 'quantifiable' after 10000 s of counting ! It can be shown that if one accumulates 1×10^6 counts, encompassing a background of 9.5×10^4 counts, the net signal of 5000 counts of a S/B ratios of only 0.05 is higher than the corresponding LOQ and hence can be quantitated ! This is not an imaginary situation but quite possible, if the 2000 second counting of BCR-1 for ^{51}Cr were to be extended 'overnight'—not an uncommon practice in INAA ! Hence the need to have another criterion on S/B over and above the LOQ criterion.

Recommendation : (i) In INAA, reporting the LOD and LOQ values, on the lines by Currie[2], provides critical information about the magnitude of the signals on which the analyses have been made. Alternately, authors may be required to state that the signals were in fact higher than LOQs. (ii) In gamma-ray spectrometry, the above limits, as well as the relative standard deviations are dependent on counting period. There exists, therefore, an attendant risk of acceptance of results on signals of poor S/B ratios counted long enough to be higher than the corresponding LOQs and of acceptable CS. (iii) In view of the above it is felt desirable that the data be reported with information on the S/B ratios of the signals which are quantitated. Further, if a protocol is to be defined for quality assurance programme, or, for intercomparison work meant for the preparation of reference samples, it is desirable that only those signals of at least $S/B = 1$ be accepted so that at all the levels of acceptable CS, one is also assured of the purity of the signals. (iv) The above criteria should also be applied for the reference standard used for comarative INAA.

Acknowledgement

The authors are thankful to the authorities of BARC for facilities for the work which was carried out at the Analytical Chemistry Division, Bhabha Atomic Research Centre, where the authors were staff members.

References

1. "The Application of Mathematical Statistics in Analytical Chemistry ; Mass Spectrometry ; Ion-selective Electrodes" in "Comprehensive Analytical Chemistry", ed. G. SVEHLA, Elsevier, 1981, Vol. XI, p. 70.
2. L. A. CURRIE, *Anal. Chem.*, 1968, **40**, 586.
3. S. GANGADHARAN, M. SANKRA DAS and S. YEGNASUBRAMANIAN, Indian National Science Academy, 1974, 47.
4. F. J. FLANAGAN, *Geochim. Cosmochim. Acta*, 1973 **37**, 1189.
5. E. S. GLADNEY, C. E. BURNS and I. ROELANDTS, *Geostandards Newslett.*, 1983, **7**, 226.
6. A. V. MURALI, R. PARTHASARATHY, T. M. MAHADEVAN and M. SANKAR DAS, *Geochim. Cosmochim. Acta*, 1983, **47**, 2047.
7. *Anal. Chem.*, 1983, **55**, 2210 ; 1980, **52**, 2242.
8. M. SANKAR DAS, *J. Indian Chem. Soc.*, 1985, **62**, 1043.
9. H. KAISER, "Two Papers on the Limit of Detection of a Complete Analytical Procedure", Adam Hilger Ltd., London, 1968.
10. *Spectrochim. Acta, Part B*, 1978, **33**, 242.
11. H. B. DESAI, S. R. KAYASTH, C. G. UDAS and M. SANKAR DAS, *Geostandards Newslett.*, 1983, **7**, 325.