ACTIVATION ANALYSIS OF MINOR CONSTITUENTS IN HIGH ALLOY STEELS

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L'auteur montre que l'analyse par activation n'est pas uniquement un moyen précieux pour la détermination d'éléments à l'état de traces, mais qu'elle permet aussi de déterminer la concentration d'éléments entrant pour une faible proportion dans la constitution de substances très complexes.

Les résultats obtenus sur des échantillons d'aciers spéciaux du National Bureau of Standards contenant du vanadium et du tungstène à une concentration allant de 0,01 à quelques pour cent indiquent que l'exactitude et la précision de cette méthode sont équivalentes, sinon supérieures, à celles de l'analyse chimique, même si l'on n'a pas effectué de séparation chimique préalable. L'auteur examine en détail une méthode employant un étalon interne qui permet de corriger avec précision les irrégularités du flux de neutrons entre l'échantillon et l'acier témoin.

Most authors have, until now, rightly stressed the importance of activation analysis as one of the most sensitive analytical tools for the determination of a large number of elements.

In our opinion, however, activation analysis is not only useful for the analysis of traces, but also for the determination of minor constituents in complex materials.

For elements occuring in concentrations of 0·01 per cent up to a few per cent, activation analysis can compete favourably with classical electrochemical or optical methods, as far as speed and accuracy are concerned. In most cases the latter methods will indeed require either a quantitative separation prior to the determination of the constituent to be analysed, or the removal of interfering substances, as the number of really specific reactions is rather limited. Such preliminary treatment of the sample can give rise to considerable errors and is often time-consuming.

It is obvious that this cause of errors can usually be avoided by activation analysis. After irradiation, a suitable amount of inactive carrier can be added to the sample, and a quantitative separation is not required if the yield is computed. Moreover, in many cases a separation is not even necessary as interference from other radioactive species can be avoided or corrected for. In the case of gamma emitters, for instance, the use of a single or multichannel analyser often allows selective measurement in the presence of other gamma radiations of different energy, while analysis of composite decay curves sometimes offers a means of accounting for interfering activities.

ACCURACY OF ACTIVATION ANALYSIS

It is obvious that in most cases involving activation analysis of minor constituents, errors due to poor counting statistics will usually be small,

as the concentration ranges involved are several orders of magnitude larger than in trace analysis. They will not be discussed in this place.

An important source of errors can, however, be due to differences in neutron flux between sample and reference. The content of a sample is indeed usually computed from the ratio of the activities of the sample and of a known amount of standard, rather than by absolute disintegration rates. These differences in neutron flux are mainly to be attributed to two causes: neutron flux irregularities between sample and reference, as they obviously cannot occupy the same place, and different self-shielding effects if absorption cross-sections of sample and reference are substantially different.

To correct for these differences we have developed a method of activation analysis using an internal standard[1].

Instead of irradiating a known amount of the element as a reference, two quantities a and b of the sample are irradiated, an amount c of the element X to be determined being mixed homogeneously with b. The material subjected to analysis should contain at least one element Y, which gives rise to an isotope measurable with good accuracy and having a half-life long in comparison with that of the isotope of the analysed species.

When both samples are measured at a time t after the complete decay of the species due to X, the ratio of the activities due to Y will be given by

$$\frac{A_{t(\mathrm{Y})}}{A'_{t(\mathrm{Y})}} = \left(\frac{a}{b}\right)\alpha$$

α being a correction factor which compensates for any difference in the neutron flux received by the two samples and/or for a different neutron shadowing.

By analysis of the decay curves, the activities $A_{t_0(\mathrm{X})}$ and $A'_{t_0(\mathrm{X})}$, due to the element X, can be computed at the end of the irradiation time t_0.

The specific activity of the sample, due to X, will be given by

$$S_{t_0(\mathrm{X})} = \frac{1}{c}\left[A'_{t_0(\mathrm{X})}\,\alpha - \frac{b}{a}\,A_{t_0(\mathrm{X})}\right]$$

and the percentage of X present by

$$\frac{A_{t_0(\mathrm{X})} \times 100}{aS_{t_0(\mathrm{X})}}$$

A second source of error, which is likely to be important when determining minor constituents, will be due to (n,p) and (n,α) reactions. The cross-sections of these reactions for fast neutrons in the B.E.P.O. reactor have recently been determined by Mellish *et al.*[2] and are usually several orders of magnitude smaller than those of (n,γ) reactions with thermal neutrons. As ultimate sensitivity is not needed when determining minor constituents, these interferences can be avoided by using the irradiation facilities of the reactor reflector or even of the thermal column. At these sites the ratio of thermal to fast neutron fluxes is small and enough activity is still induced to achieve accurate counting.

As will be illustrated later by the determination of vanadium and tungsten in National Bureau of Standards high alloy steels, the standard error on a series of determinations varies between 1 and 15 per cent. These errors appear to be of the same magnitude as those computed from the certificates of the N.B.S.

ACTIVATION ANALYSIS OF VANADIUM[3]

Natural vanadium gives rise to only one product by the (n,γ) reaction, namely ^{52}V, a β–γ emitter (β = 2·7 MeV; γ = 1·46 MeV) having a half-life of 3·75 min. The activation cross-section is 4·5 barns.

Since the half-life of ^{52}V is too short to permit isolation of this element after irradiation, interference by a number of steel constituents is to be expected. The radiochemical properties of the most usual constituents in high alloy steels are summarized in *Table 1.*

Table 1. Radiochemical properties of steel constituents, subject to activation by thermal neutrons

Target nuclide	*Abundance* (%)	*Activation cross-section* (barns)	(n,γ) *reaction product*	$t_{\frac{1}{2}}$	*Radiation and energy* (MeV)
^{30}Si	3·05	0·11	^{31}Si	2·62 h	β–1·47
^{31}P	100	0·23	^{32}P	14·3 d	β–1·70
^{34}S	4·2	0·26	^{35}S	87 d	β–0·16
^{36}S	0·016	0·14	^{37}S	5·0 min	β–1·6; 4·3; γ 2·7
^{50}Ti	5·34	0·14	^{51}Ti	5·8 min	β–1·9; 2·2; γ 0·32
^{51}V	100	4·5	^{52}V	3·75 min	β–2·7; γ 1·46
^{54}Cr	2·38	0·3	^{55}Cr	3·52 min	β–2·8
^{55}Mn	100	13·4	^{56}Mn	2·58 h	β–2·81; 1·04; 0·73; γ 0·82; 1·81; 2·13
^{54}Fe	5·84	0·7	^{55}Fe	3·0 y	E.C. ϵ 0·21
^{58}Fe	0·31	0·7	^{59}Fe	45·1 d	β–0·46; 0·27 γ 1·10; 1·29
^{59}Co	100	100	^{60m}Co	10·5 min	γ 0·058
			^{60}Co	5·2 y	β–0·306; γ 1·17 ; 1·33
^{58}Ni	67·7	4·2	^{59}Ni	10^5 y	E.C. ϵ 1·07
^{62}Ni	3·66	15	^{63}Ni	85 y	β–0·065
^{64}Ni	1·16	2·6	^{65}Ni	2·56 h	β–2·10; 1·10; 0·60 γ 1·49; 1·12; 0·37
^{63}Cu	69·1	4·3	^{64}Cu	12·8 h	E.C., β–0·571; β+0·66; γ 1·34
^{65}Cu	30·9	2·1	^{66}Cu	5·1 min	β–2·63; 1·59; γ 1·04
^{93}Nb	100	1·0	^{94m}Nb	6·6 min	I.T.: 0·042
^{98}Mo	23·75	0·13	^{99}Mo	67 h	β–1·23; 0·45; γ 0·04–0·78
^{100}Mo	9·62	0·20	^{101}Mo	14·6 min	β–1·2; 2·2; γ 0·191; 0·96
^{181}Ta	100	21	^{182}Ta	113 d	β–0·51; γ 0·334–1·18
^{184}W	30·6	2·1	^{185}W	73 d	β–0·43; 0·37; γ 0·058
^{186}W	28·4	34	^{187}W	23·9 h	β–0·62; 1·33; γ 0·072–0·78

It appears that if a short irradiation time is used and measurements are carried out with a single-channel analyser, restricting the counting within a band ranging from 1·3 to 1·5 MeV gamma's, the only radiations giving appreciable interference are the 1·81 and 2·13 MeV gamma's of ^{56}Mn, which produce Compton recoil pulses in this energy band.

Possible interference from ^{52}Cr and ^{55}Mn, which also give rise to ^{52}V by (n,p) or (n,α) reactions, was investigated. At a site near the reflector of the BR-1 reactor, with a Cd ratio and a neutron flux of respectively

280 and 10^{10} neutrons cm^{-2} sec^{-1}, samples of 51·7 mg of manganese, 149 mg of chromium and 13·9 mg of vanadium were irradiated during 10 sec periods and counted in a well-type scintillation detector connected to a single-channel analyser, set to measure an energy band as described above. The results are illustrated in *Figure 1*, from which it is seen that no evidence of

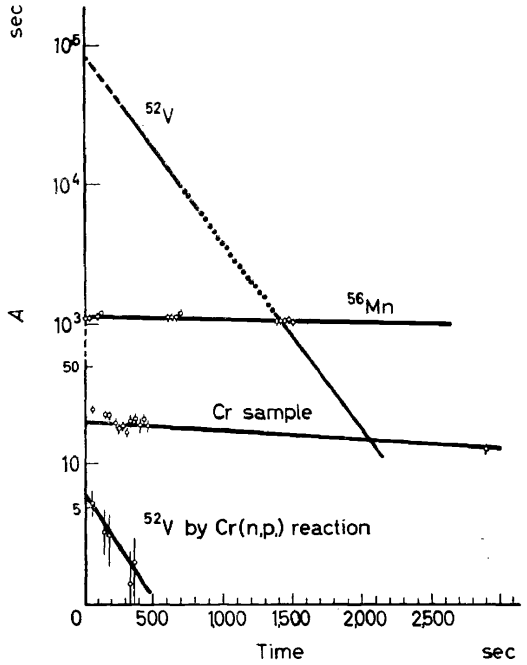

Figure 1. Interference by (n,p) and (n,α) reactions

a ^{55}Mn (n,α) ^{52}V reaction was found, whereas ^{52}V is formed to a small extent by (n,p) on ^{52}Cr. In our experimental conditions this error will be of the order of 1 per cent for a chromium/vanadium ratio of 1000/1 and consequently negligible for most practical purposes. In less favourable conditions, however, this error can become quite important. In activation analysis with the Amsterdam cyclotron, where neutrons are produced with 26 MeV deuterons on a beryllium target and thermalized in a 20 cm paraffin block, a chromium/vanadium ratio of 1000/1 would give rise to a 220 per cent error.

The internal standard procedure, described above, was tested on a number of N.B.S. high alloy steels. In most cases an irradiating facility near the reflector of the BR-1 reactor was used with a neutron flux of 10^{10} neutrons cm^{-2} sec^{-1}. The steel turnings were transferred into the neighbourhood of the counting room by means of a pneumatic tube. The samples *a* and *b* were counted alternately during 20 sec periods with a lapse of 10 sec between successive periods in a well-type detector connected to a single-channel analyser. A typical plot is shown in *Figure 2* from which

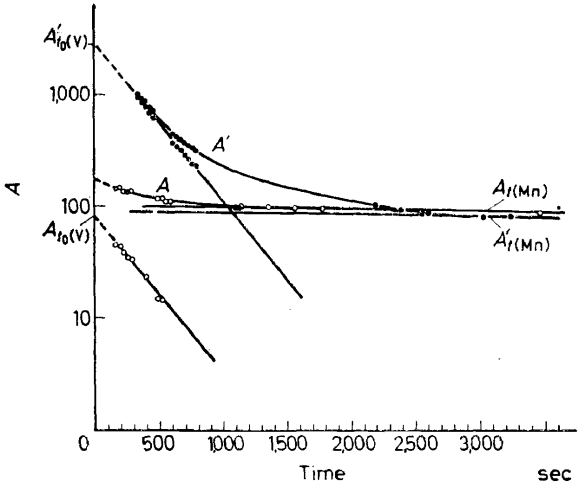

Figure 2. Determination of vanadium with internal standard

α, the neutron correction factor, as well as the vanadium activities at the time t_0 can be computed by analysis of the decay curve and extrapolation.

Results for a number of N.B.S. steels are given in *Table 2.*

The standard error on sample 155, for instance, as computed from the eight analyses given by the N.B.S. is 27 per cent, whereas it is 16 per cent on seven activation analyses. On sample 101d the standard error on ten N.B.S. analyses is 5·6 per cent, whereas the corresponding error on four activation analyses is 7·9 per cent.

It is also apparent that all the results obtained by activation analysis are in excellent agreement with those of the N.B.S.

ACTIVATION ANALYSIS OF TUNGSTEN[4]

The classical analysis of tungsten in high alloy steels presents a number of difficulties as the quantitative separation of small amounts of tungstic acid is difficult to achieve. Furthermore, the precipitate is impure due to co-precipitation or adsorption of molybdenum, vanadium, tantalum, niobium, silicon, *etc.*

These difficulties can be avoided by activation analysis, as the nuclear properties of tungsten are rather favourable. Natural tungsten gives rise to several isotopes, by the (n,γ) reaction on the natural element, of which ^{187}W, a β–γ emitter with a 24 h half-life was used for our purpose.

Two procedures were considered, namely with and without chemical separation of the tungsten as tungstic acid.

In the former case a number of radioactive species, produced by (n,γ) reaction on the other steel constituents, are likely to interfere. Short-lived isotopes, such as ^{52}V, ^{66}Cu, ^{60m}Co and ^{101}Mo will decay completely within a few hours after the end of the bombardment, while the half-life of ^{56}Mn differs sufficiently to allow correction to be made for this activity by analysis of the decay curve. The long-lived species, such as ^{51}Cr, ^{59}Fe, ^{182}Ta and

Table 2. Activation analysis results for some N.B.S. steels

N.B.S. standard sample	V (%)	Mn (%)	Cr (%)	W (%)	Ni (%)	*Sample weight* (mg) *a*	*b*	*c*	*Correction factor*	$A_{t_0(V)}$ (counts/sec)	$A'_{t_0(V)}$ (counts/sec)	V (%) *found by activation analysis*	*Standard error* (%)
155* Cr–W steel	0·014	1·24	0·485	0·517	0·100	296·7	447·2	3·236	1·062	24·5	1,516	0·0170	15·8
						604·5	610·4	5·942	1·046	28·4	2,510	0·011	
						600·3	824·4	9·806	0·979	3·5	384·0	$0·017_4$	
						642·9	654·9	8·605	1·062	29	2,130	$0·017_4$	
						657·5	548·8	15·077	1·079	3·65	578	$0·013_4$	
						527·3	649·3	13·684	1·044	4·7	840	0·014	
						661·4	793·6	8·470	1·028	26·4	1,920	$0·017_4$	
												$\bar{m} = 0·015_3 \pm 0·0024$	
161* Ni–Cr casting alloy	0·029	1·28	16·88	—	64·29	336·8	132·3	2·190	0·9023	55	1,620	0·025	10·2
						397·4	363·9	5·358	1·108	87	3,800	$0·028_5$	
						332·7	504·3	3·620	1·063	19·2	680	0·030	
						472·7	412·3	7·490	0·961	64·8	3,400	0·032	
												$\bar{m} = 0·029 \pm 0·0029$	
101d* Cr–Ni steel	0·049	0·739	18·68	—	9·05	36,198	403·6	6·998	1·236	82	2,868	0·046	7·9
						193·3	205·9	1·521	1·074	76	1,316	0·045	
						223·8	239·7	5·273	1·007	62·5	3,122	0·048	
						221·5	386·9	3·877	1·059	47·5	1,530	0·054	
												$\bar{m} = 0·048_3 \pm 0·038$	
153† Co–Mo–W steel	2·04	0·219	4·14	1·58	0·107	1,137·3	937·2	26·28	0·995	66·2	133·60	1·95	
						640·6	474·3	21·74	0·882	44·0	115·20	2·16	
						640·8	634·2	11·95	0·985	63·2	129·60	1·81	
												$\bar{m} = 1·97 \pm 0·17$	

* 10 sec irradiation in BR-1 reactor, neutron flux: 10^9–10^{10} neutrons cm^{-2} sec^{-1}; Cd ratio: 280.
† 60 sec irradiation with Amsterdam cyclotron, neutron flux: 10^7 neutrons cm^{-2} sec^{-1}; Cd radio: 7.

^{60}Co can also be easily distinguished from ^{187}W. The half-lives of ^{64}Cu, ^{76}As and ^{99}Mo are, however, similar to that of ^{187}W and will cause interference if certain limiting proportions are exceeded. The interference (per cent) for definite ratios as a function of time is given in *Figure 3.*

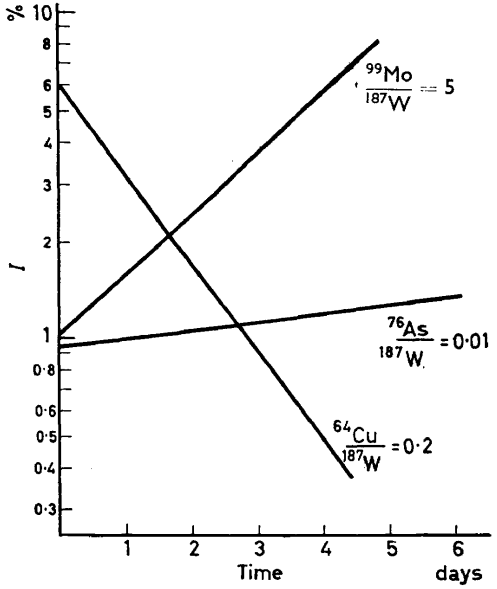

Figure 3. Interfering activities due to ^{64}Cu, ^{76}As and ^{99}Mo

Typical decay curves for two steel samples are given in *Figure 4.*

As the cross-sections of tungsten and of some cobalt steels are quite high, self-shielding effects are far from negligible, as illustrated in *Figure 5*, where the specific activity is measured as a function of sample size.

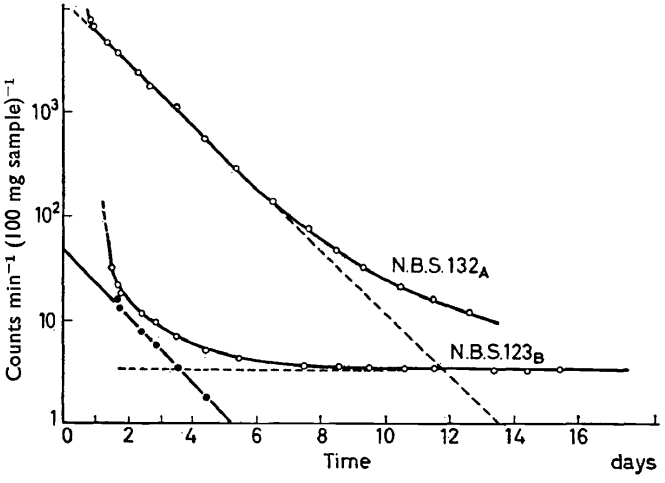

Figure 4. Decay of activated steel samples

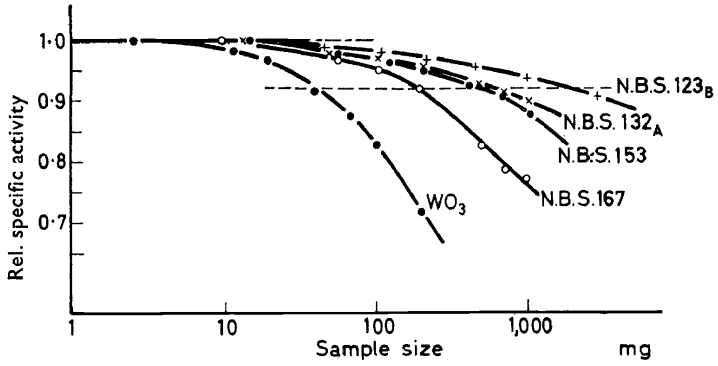

Figure 5. Influence of sample size on the neutron self-shielding

It appears that samples should be kept quite small if errors due to self-shielding are to be avoided. To obviate this, use was made of the internal standard procedure. The total activities of the long-lived species were used to compute α, the neutron correction factor. A typical example is illustrated in *Figure 6*, whereas results on a number of N.B.S. steels are represented in *Table 3*.

It appears from *Table 3* that the results are in good agreement with those of the N.B.S. and that the mean error is of the same order of magnitude.

The method without chemical separation has, however, the disadvantage that accurate results cannot be obtained if larger amounts of copper, arsenic and molybdenum are present than those indicated above. Furthermore, results are only available after about fifteen days, as graphical analysis of the decay curves are necessary.

It is possible to avoid these disadvantages by separating tungsten as tungstic acid after addition of a suitable amount of tungsten carrier. Double homogeneous precipitation of tungstic acid from perchloric acid and hydrogen peroxide in the presence of vanadate, to reduce molybdenum

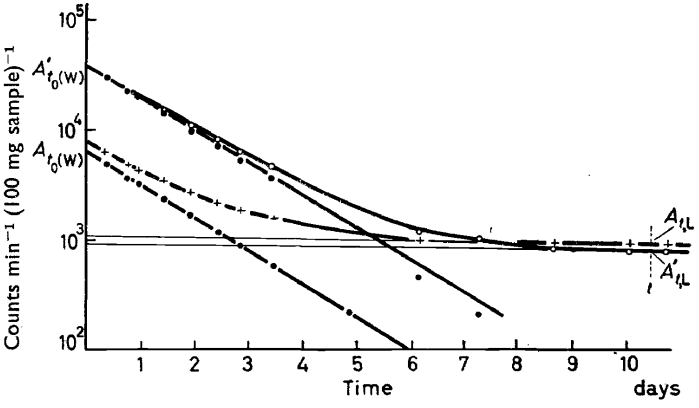

Figure 6. Determination of tungsten in N.B.S. steel 123_B by means of internal standard

adsorption, ensures a tungsten recovery better than 99·8 per cent and gives a sufficient radiochemical purification from most of the steel constituents, except tantalum. Results of the analysis of a number of N.B.S. steels are summarized in *Table 4*.

Table 3. Activation analysis for tungsten without chemical separation

N.B.S. steel	*N.B.S. results*	*Mean error*	*Sample size* (mg)	W (%)	*Mean value*	*Mean error*
132_A	6·20	0·07	510·9	6·07	6·14*	0·08
			506·4	6·13		
			601·9	6·15		
			601·2	6·05		
			603·4	6·21		
			614·6	6·25		
			22·272	6·24		
			22·484	6·25	6·20†	0·045
			18·363	6·20		
			17·748	6·11		
167	4·5	provis. certif.	190·0	4·25	4·30*	0·05
			190·0	4·30		
			11·082	4·39		
			14·174	4·41	4·40†	0·020
			13·230	4·42		
			20·284	4·37		
153	1·58	0·027	506·4	1·58		
			501·2	1·59	1·59*	0·01
			17·672	1·61		
			32·379	1·56	1·60†	0·02
			23·084	1·60		
			28·259	1·62		
155	0·517	0·006	1,055·9	0·516		
			1,092·9	0·512	0·514*	0·01
			66·851	0·527		
			68·547	0·528	0·520†	0·007
			34·519	0·508		
				0·518		
123_B	0·18	provis. certif.	2,122·0	0·191	0·20*	0·02
			2,009·6	0·209		

* Cyclotron activation.
† BR-1 reactor activation.

Table 4. Activation analysis for tungsten, with chemical separation

N.B.S. steel	*N.B.S. results*	*Mean error*	*Sample size* (mg)	W (%)	*Mean value*	*Mean error*
132_A	6·20	0·07	491·4 507·0 596·7 598·5	6·17 6·28 6·25 6·22	6·23*	0·04
155	0·517	0·006	4008·1 1067·6	0·52 0·52	0·52[2]*	0·001
167	4·5	provis. certif.	190·5 190·0	4·17 4·25	4·21*	0·04
			5·075 5·382 9·816	4·30 4·26 4·35	4·30†	0·03
153	1·58	0·027	467·6 518·1	1·60 1·60	1·60*	0·01
123_B	0·18	provis. certif.	1967·8 2085·5	0·170 0·172	0·171*	0·001

* Cyclotron irradiation.
† BR-1 reactor irradiation.

References

[1] G. Leliaert, J. Hoste and Z. Eeckhaut. " Neutron activation analysis using an internal standard ", *Nature*, **182**, 600 (1958)

[2] C. E. Mellish, J. A. Payne and R. L. Otlet. " The production of threshold reactions in a graphite reactor ", *Proc. 1st U.N.E.S.C.O. Int. Conf., Paris 1957*, Vol. I, p. 35

[3] G. Leliaert, J. Hoste and Z. Eeckhaut. " Activation analysis of vanadium in high alloy steels using manganese as internal standard ", *Anal. Chim. Acta*, **19**, 100 (1958)

[4] G. Leliaert, J. Hoste and Z. Eeckhaut. " Activation analysis of tungsten in high alloy steels ", *Talanta*, **2**, 115 (1959)

DISCUSSION

D. Gibbons (*U.K.*): What procedure is used to ensure that the amount of impurity added to the reference sample is homogeneously dispersed so that it receives the same neutron flux as the impurity already present? If the internal standard method corrects for varying neutron fluxes and self-shielding effects, why is the precision of the tungsten results higher for smaller samples, in which the self-shielding effect is smaller?

J. Hoste (*Belgium*): The vanadium was added to the finely divided steel turnings in the form of ammonium vanadate, which adhered satisfactorily; similarly, the tungsten was added as tungsten oxide.

With regard to Dr Gibbons's second question, some of the analyses were carried out, before the BR-1 reactor was in operation, on the cyclotron at Louvain at a neutron flux of only 10^7 neutrons cm^{-2} sec^{-1}.

P. Leveque (*France*): How do you construct your decay curves from the experimental plots? Some people prefer to trace a straight line at a mean distance from the plots, while others prefer the least square method.

J. HOSTE (*Belgium*): I have used the former method, but in the case of tungsten the direction of slope was made to fit the half-life of tungsten (24 h).

W. W. MEINKE (*U.S.A.*): I should like your comments on the accuracies of the results quoted in your paper, which are in many cases more precise than those of the chemical analyses given in the N.B.S. standards.

J. HOSTE (*Belgium*): It is difficult to distinguish between accuracy and precision in chemical analysis. I assumed that the N.B.S. standards were accurate and computed the standard error from about ten analyses given for one steel. Subsequently I performed radioactivation analysis and computed the standard error, which was in many cases smaller than the error from the N.B.S. standards. The results are therefore more precise without necessarily being more accurate.

G. W. REED (*U.S.A*): May I propose that we discuss further this matter of accuracy? In particular I should like to hear what types of systematic errors are considered by workers applying these techniques.

J. HOSTE (*Belgium*): I agree. I have found it very difficult to obtain accurate standards for emission spectroscopy work on alloys.

D. MAPPER (*U.K.*): Dr Reed has stated an important problem in activation analysis. In our work on the determination of copper, nickel, and cobalt in geochemical materials, we extended the work to a study of standard (B.C.S.) steels. Although the content of these three elements is higher in these steels than one desires in trace element analysis, it is very difficult to obtain materials with accurately known trace content. We found that though the nickel and copper results were in excellent agreement, some of the cobalt results were quite different from those reported. Further investigation by B.C.S. showed that the previously published cobalt determinations were in error.

In our germanium work, too, we have obtained excellent agreement with the results by other methods, and those reported by different workers.

It would be of great help to chemists in the field of activation analysis, to be able to obtain standard samples, which have an accurately known trace element content.

G. W. LEDDICOTTE (*U.S.A.*): I agree with Dr Hoste's suggestion that internal standards should be used. Since the absolute disintegration rate of cobalt-60 may be determined, a cobalt monitor would serve as a good internal standard.

With regard to the size of samples, I think that small samples must be used in all cases except where the flux is very low. Our experience in the determination of sulphur (about 10 parts/million) in chromium by the (n,p) reaction has shown that the results vary by a factor of five when the sample size varies from 100 mg to several grams. While the neutron flux is fairly homogeneous in a graphite reactor, there may be quite pronounced variations of flux in other types of reactor. Again, a cobalt monitor or some other comparative sample technique would solve the problem.

G. LELIAERT (*Belgium*): The use of ^{60}Co as a monitor is not always feasible as there is also a time dependence, quite apart from variations in the neutron flux. I think that a monitor should be used in which the radioisotope produced has a half-life comparable with that of the radioisotope under examination.

G. W. REED (*U.S.A.*): I should like to say a word of warning about using internal standards. Using a nuclide, different from that being measured, to monitor an irradiation is probably quite satisfactory in a uniform thermal flux as found in the thermal columns of some reactors. However, many reactors today are water boilers, swimming pools, *etc.*, and a high percentage of the neutrons used are in the epi-thermal region. Most nuclides have resonance cross-sections, and these, coupled with high resonance fluxes, spell trouble. We feel it is necessary to construct calibration curves of activity against weight for the sought-after activity, and to make the monitor as nearly similar to the sample as possible; otherwise one cannot be sure of what is being measured.

F. GIRARDI (*Italy*): With regard to the cobalt monitoring suggested by Dr Leddicotte, I should like to add that while the nuclear constants of cobalt are generally well known, the resonance integral of cobalt, which may be important where fast fluxes are involved, is not so well known.

At Chalk River cobalt wires 1/5,000 in. thick were used and it was assumed that no self-absorption occurred; but after some experiments using highly dilute cobalt in aluminium the resonance absorption peak of cobalt was found to be mainly due to scattering. The resonance integral of cobalt changed from 48·6 to 75 barns so that a big correction had to be made on all measurements.

G. LELIAERT (*Belgium*): The complete decay curve is not always necesary in order to obtain a correction for the internal standard. One can also use a gamma spectrometer and the correction factor obtained from the ratio of the areas of the photo-peaks of the control isotope and the element under investigation.