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The Homogeneity Control of Reference Materials by Photon Activation

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Instrumental photon activation analyses can present two aspects: the bulk determination of trace elements with good sensitivity in the sub-ppm levels for some elements and the homogeneity control of reference materials with high precision.

For the non-destructive and multi-element control of homogeneity by photon activation, the reference materials are activated in the 44 MeV bremsstrahlung produced by the GELINA electron linear accelerator using two irradiation arrangements. (a) In the case of Ce, Co reference samples and NBS SRM-1645 river sediment samples; the samples (400 mg each) and standards (In and Sn) are placed around the rotation axis of the sample holder so that each sample or standard is alternatively rotated through the centre of the photon beam and activated. (b) In the case of Bessines mineral samples and natural Moroccan phosphate rock samples BCR CRM 32, the central position irradiation arrangement is used and a stack of samples (250 mg each) and standards are activated together continuously. The inhomogeneity found in the five reference samples is less than 1% at the 99.73% confidence level.

INTRODUCTION

The reference materials are characterised by the elemental composition and also by the uniform distribution of the elements to be certified. For homogeneity tests, it is not necessary to determine accurately the concentration of elements present in the samples and standards are not needed for the direct comparison of activities in

the samples. When the values obtained of an element in a reference material by different methods differ considerably, the bremsstrahlung activation of samples in identical conditions provides valuable informations on the distribution of this element in the reference samples.

EXPERIMENTAL

Homogeneity tests by photon activation were initiated in 1973 by late Prof. A. H. W. Aten Jr., director of CBNM. A rotating wheel of 180 mm diameter was used as a sample holder for 11 discs of 1% Au-Al alloys and one disc of pure aluminium. The discs were rotated, one after another, through the centre of the photon beam and activated in the bremsstrahlung produced by the impact of the Linac electron beam (27 MeV) on a platinum target, placed in the same position of the uranium target which was removed for this purpose. The activities were measured with a 3" × 3" NaI crystal.

For the work to be described in the following, the samples are activated during 6–20 hours, in the 44-MeV bremsstrahlung produced by the magnetic deflected electron beam (35–50 μ A) of the Gelina accelerator.¹ The irradiation arrangement with a rotating sample holder and the activity measurements have been described elsewhere.²

Sampling of reference materials

The reference material is placed in identical pure aluminium cans of 10 mm \emptyset . Each Al can is weighed before and after the introduction of the sample (250–400 mg), and then covered by a thin layer of pure lithium sulphate to avoid any loss of the sample during the encapsulation. The Al cans, after the encapsulation, are placed in the rotating sample holder which is locked in a cylindrical rabbit of 52 mm diameter and sent from the counting laboratory to the irradiation station by pneumatic transfer.

For homogeneity tests of three reference materials, the following samples have been prepared: 2 synthetic reference samples containing 1000 μ g Ce/g in Li_2SO_4 and 2 reference samples containing 1000 μ g Co/g in Li_2SO_4 , these reference materials are used for the

quantitative evaluation of interferences in 44-MeV bremsstrahlung activations;³ in the case of the SRM-1645 river sediment of the National Bureau of Standards, 5 samples have been prepared and irradiated in identical conditions with the rotating target, 2 sediment samples, 1 reference sample containing 1000 $\mu\text{g In/g}$ in Li_2SO_4 , 1 reference sample containing 1000 $\mu\text{g Sn/g}$ in Li_2SO_4 and 1 sample of pure lithium sulphate. The indium and tin reference samples are used for the determination of In and Sn concentrations in the river sediment. The blank sample (Li_2SO_4) is used for the eventual correction of impurities present in aluminium and lithium sulphate; it is also used for the correction of the aluminium contribution, by the reaction $^{27}\text{Al}(n, \alpha)^{24}\text{Na}$, to the activity of magnesium in the river sediment samples. The Angela computer program is used for the subtraction of the blank sample spectrum or the Ge(Li) detector spectrum, including the natural radiations of the environment, e.g. ^{40}K , daughter radionuclides of radon,⁴ from the spectrum of each sample, before the photopeak integrations.

Homogeneity control of Ce, Co reference samples and river sediment samples

The maximal photon energy and the maximal flux density lie along the electron beam axis, the diameter of electron exit slit being 20 mm in front of the Pt-converter; the main photon activation takes place when the sample is rotated through the centre of the high-energy photon beam. Since the spatial distribution of gamma flux is not uniform,⁵ only the average activity of the sample can be determined; a sample of 400 mg is estimated to be sufficiently representative of the material to be assayed. The counting sequences of activated samples have been already described,² the geometric mean activity is generally used to minimise the uncertainty on the half-life ($T_{1/2}$) and the drift of the electronic system.

In the comparison of specific activities of samples irradiated in the same conditions with the rotating specimen rack, the saturation factor $(1 - \exp - \lambda t_{ir})$ is identical for a radionuclide, where the decay constant is $\lambda = \ln 2 / T_{1/2}$ and t_{ir} is the length of irradiation, and the integrated gamma-flux is the same for all the samples. The longitudinal gradient of the incident gamma-flux and also the self-absorption effect for a specified γ -ray of a radionuclide are identical

for the two samples having the same weight, the same geometry and similar chemical composition. The conditions of activity counting is the same for the samples, with practically the same dead time which is kept at minimum by increasing the distance between the activated samples and the Ge(Li) detector.

For a specified radionuclide, a set of n measurements of specific activity ratio between two samples gives the mean ratio $\bar{r} = \text{Sum } r_i/n$ and the variance $s^2 = \text{Sum } (r_i - \bar{r})^2/n - 1$. The uncertainty of the mean ratio, at the 99.73% confidence level, is $e_R = ts/n^{1/2}$ where the factor t corresponds to a probability of 0.99730 for $(n-1)$ degrees of freedom.⁶

Table I gives the data evaluations of three reference materials, the γ -line and the half-life of the radionuclide used for the calculation of \bar{r} and e_R , are also indicated.

It must be taken into account for the total error e_T on the ratio measurements between two samples, the uncertainty e_R and the uncertainty e_w on the weight of the samples: $e_T^2 = e_R^2 + e_w^2$ where

TABLE I
Homogeneity control of reference materials

RM	n	\bar{r}	e_R	Reaction	γ -line (keV)	Half-life ($T_{1/2}$)
Ce	10	1.00095	0.00246	$^{140}\text{Ce}(\gamma, n)^{139}\text{Ce}$	165.85	137.6 d
Co	11	1.00056	0.00276	$^{59}\text{Co}(\gamma, n)^{58}\text{Co}$	810.76	70.78 d
NBS-1645						
As	9	0.99738	0.00546	$^{75}\text{As}(\gamma, n)^{74}\text{As}$	595.90	17.79 d
Ca	10	1.00012	0.00504	$^{44}\text{Ca}(\gamma, p)^{43}\text{K}$	372.90	22.2 h
Cr	10	0.99855	0.00363	$^{52}\text{Cr}(\gamma, n)^{51}\text{Cr}$	320.08	27.701 d
Fe	7	0.99707	0.00611	$^{57}\text{Fe}(\gamma, p)^{56}\text{Mn}$	846.75	2.5785 h
Mg	12	0.99687	0.00631	$^{25}\text{Mg}(\gamma, p)^{24}\text{Na}$	1368.6	15.03 h
Na	10	0.99886	0.00415	$^{23}\text{Na}(\gamma, n)^{22}\text{Na}$	1274.55	2.602 y
Pb	12	1.00565	0.00657	$^{204}\text{Pb}(\gamma, n)$ $^{206}\text{Pb}(\gamma, 3n)$	^{203}Pb 279.18	52.02 h
Sn	11	0.99887	0.00910	$^{112}\text{Sn}(\gamma, p)^{111}\text{In}$	245.35	2.83 d
Sr	7	1.00173	0.00462	$^{88}\text{Sr}(\gamma, n)$ $^{87}\text{Sr}(\gamma, \gamma')$	$^{87\text{m}}\text{Sr}$ 388.40	2.805 h
Ti	11	0.99755	0.00479	$^{48}\text{Ti}(\gamma, p)^{47}\text{Sc}$	159.39	3.422 d
Zn	10	1.00099	0.00511	$^{68}\text{Zn}(\gamma, p)^{67}\text{Cu}$	184.53	62.01 h
Zr	11	0.99939	0.00652	$^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$	909.20	78.43 h

$e_w^2 = e_A^2 + e_B^2$. The relative values e_A and e_B on the weight of the samples A and B are about two orders of magnitude smaller than the random uncertainty e_R , and can be neglected.

The precision of a series of measurements depends on the half-life and the γ -ray intensity of the radionuclide, its concentration and effective specific activity in the sample, the length of irradiation, the weight of the sample and the counting time. The effective specific activity is a function of the intrinsic specific activity, the yield of the detector and the background spectrum corresponding to the energy of the photopeak. The concentration of arsenic in the NBS river sediment is low, but the effective specific activity is relatively high for the long-lived ^{74}As nuclide at 596 keV. On the other hand, the effective specific activity of the ^{51}Cr -320.1 keV photopeak is low, but the chromium concentration is very high.⁷ The activity measurements of ^{74}As can start when the γ -ray intensities of ^{43}K -593.60 keV and ^{62}Zn -596.56 keV induced by the reaction $^{64}\text{Zn}(\gamma, 2n)^{62}\text{Zn}$, become negligible.

A limited number of measurements has been carried out on the relative short-lived nuclides, ^{56}Mn and $^{87\text{m}}\text{Sr}$, with a counting time of 2000 s. For the $^{87\text{m}}\text{Sr}$ -388.4 keV photopeak, seven ratio measurements between the two sediment samples (Table II), give a mean ratio $\bar{r}=1.00173$ and a standard deviation $s=2.495 \times 10^{-3}$. The uncertainty of the mean ratio at 99.73% confidence limits is $e_R=4.904 \text{ s}/7^{1/2}=4.62 \times 10^{-3}$.

The high efficiency of the single open-ended coaxial Ge(Li) detector for γ -rays of low energy, provides high net counts (above the background) of the ^{139}Ce -165.85 keV photopeak. For ten ratio data obtained with a counting period of 5000 s (Table II), the calculated mean ratio is $\bar{r}=1.00095$ and the corresponding standard deviation is $s=1.900 \times 10^{-3}$. At the 99.73% confidence level, the uncertainty of the mean ratio is $e_R=4.094 \text{ s}/10^{1/2}=2.46 \times 10^{-3}$. Examples of data evaluations for some elements are indicated in the Table II.

Determination of Sn and In concentrations in the river sediment

Homogeneity and concentration measurements of tin in the NBS sediment SRM-1645 are performed at the same time, based on the

TABLE II
Evaluations of ratio data

RM	Ratio data	\bar{F}	$e_R(99.73\% \text{ c.l.})$
Ce	1.00162-0.99828-1.00149-1.00165-0.99768 1.00034-1.00094-1.00057-1.00306-1.00386	1.00095	$1.900 \times 10^{-3} \times 4.094/10^{1/2} = 2.46 \times 10^{-3}$
Co	1.00523-0.99713-1.00203-1.00045-1.00304 1.00027-0.99922-1.00046-1.00137-0.99899 0.99802	1.00056	$2.310 \times 10^{-3} \times 3.957/11^{1/2} = 2.76 \times 10^{-3}$
NBS-1645			
As	0.99641-0.99716-0.99935-1.00078-0.99176 0.99428-0.99377-0.99893-1.00402	0.99738	$3.827 \times 10^{-3} \times 4.277/9^{1/2} = 5.46 \times 10^{-3}$
Fe	0.99204-0.99425-1.00164-0.99866-0.99985 0.99626-0.99681	0.99707	$3.294 \times 10^{-3} \times 4.904/7^{1/2} = 6.11 \times 10^{-3}$
Mg	0.99582-0.99741-1.00167-1.00043-0.99046 0.99035-1.00627-1.00605-0.99552-0.99114 0.99195-0.99532	0.99687	$5.678 \times 10^{-3} \times 3.850/12^{1/2} = 6.31 \times 10^{-3}$
Sr	0.99823-1.00496-1.00141-1.00429-1.00315 1.00036-0.99970	1.00173	$2.495 \times 10^{-3} \times 4.904/7^{1/2} = 4.62 \times 10^{-3}$

induced activity of ^{111}In in the river sediment samples, in the Sn RM and In RM, which are irradiated under identical circumstances. Taking into account the uncertainty of the Sn and In reference samples which are measured only from time to time—most of the measurements are devoted to the comparison of activities between the two sediment samples—the concentration found for tin, is (416 ± 15) μg per gram. The concentration of indium is determined by the reaction $^{115}\text{In}(\gamma, n)^{114\text{m}}\text{In}$ and the value obtained is ≤ 0.79 $\mu\text{g}/\text{g}$. From the results of interference evaluations,³ the contribution of indium via the reaction $^{113}\text{In}(\gamma, 2n)^{111}\text{In}$ is equivalent to a tin concentration of ≤ 0.50 $\mu\text{g}/\text{g}$ and the correction is negligible. The analyses of tin and indium contents are summarised in the Table III.

TABLE III
Sn and In contents in the NBS SRM-1645 sediment

Element	Conc. ($\mu\text{g}/\text{g}$)	Radionuclide	γ -ray (keV)
Sn	416	^{111}In	171.29; 245.35
In	≤ 0.79	$^{114\text{m}}\text{In}$	190.24

For the Ce and Co reference samples used for interference evaluations in photon activation analyses, the inhomogeneity is less than 0.28%. For the elements assayed in the NBS river sediment samples: As, Ca, Cr, Fe, Mg, Na, Pb, Sn, Sr, Ti, Zn, Zr, the inhomogeneity is less than 1% from 0.36% (Cr) to 0.91% (Sn).

Comparison of variances and grand average ratio of the 12 groups. In the NBS river sediment, the concentration range of the 12 elements selected for homogeneity tests is very large, from 11.3% (Fe) to 70 ppm (Zr). However, it is worthwhile to test the homogeneity of variances and mean values for $N=120$ observations of the 12 groups ($p=12$). The estimation of the within series variance $S_{\text{in}}^2 = \text{Sum}(n_i - 1)s_i^2 / (N - p)$, of the between series variance $S_{\text{ex}}^2 = \text{Sum} n_i (\bar{r}_i - \bar{r})^2 / (p - 1)$ and of the grand mean ratio $\bar{r} = \text{Sum} n_i \bar{r}_i / N$, where n_i , s_i^2 , \bar{r}_i are respectively the number of measurements, the variance and the mean ratio of the i th group, gives the following values: $S_{\text{in}}^2 = 2.4405 \times 10^{-3} / 108 = 2.2597 \times 10^{-5}$, $S_{\text{ex}}^2 = 7.3890 \times 10^{-4} / 11 = 6.7173 \times 10^{-5}$ and $\bar{r} = 119.93737 / 120 = 0.99948$. The

variances and the mean values are compatible according to the Bartlett's and F tests for $\chi^2 = 20.68 < \chi_{0.975}^2$ (11) and $F = 2.97 < F_{0.999}$ (11, 108). The high ratio of $F = S_{\text{ex}}^2/S_{\text{in}}^2$ is due to the high mean ratio of lead. The estimation of the uncertainty on the grand average ratio, at the 99.73% confidence level with the factor t corresponding to $(12-1)$ degrees of freedom, is $e_R = 3.850 (S_{\text{ex}}^2/N)^{1/2} = 2.880 \times 10^{-3}$, which gives $\bar{r} = 0.9995 \pm 0.0029$ for the 12 series of measurements.

Homogeneity control of U in the Bessines mineral

Seven Bessines granitic mineral samples containing about 1500 μg U/g have been encapsulated in identical Al cans; the weight of each sample is of the order of 250 mg. A stack of 11 samples (7 U mineral samples and 4 U standards) are placed in the central part of the rotating sample holder and activated continuously during 6 hours, using the sandwich irradiation arrangement.⁵ The standards are placed at the front (1) and back (11) of the mineral samples and two of them are inserted between the samples (4 and 7 positions). The longitudinal gradient of γ -flux is calculated from the specific activities of the four reference samples. After correction for the γ -flux attenuation, the ^{237}U specific activities of the seven Bessines mineral samples at the end of irradiation, are for a counting period of 2000 s: 371, 371, 368, 371, 367, 369 and 367 micrograms. The mean value is 369.1 with a corresponding standard deviation $s = 1.865$ and the uncertainty of the mean at the 99.73% confidence level, is $e_R = 3.46$. The results are summarized in the Table IV.

TABLE IV
Homogeneity control of U in the Bessines mineral

Bessines mineral	Number of samples	Mean value	e_R	Photonuclear reaction	γ -line (keV)	Half-life ($T_{1/2}$)
U	7	369.1	3.5	$^{238}\text{U}(\gamma, n)^{237}\text{U}$	208.0	6.752 d

The inhomogeneity of uranium in the seven granitic mineral samples is less than 0.937%.

Homogeneity control of U in the Moroccan phosphate rock, BCR CRM 32

As the Bessines mineral, the Moroccan phosphate rock, containing about $100 \mu\text{g U/g}$, is analysed in the same way. A stack of 15 phosphate rock samples weighing each 250 mg and $16\,500 \mu\text{g U/g}$ standards are activated together in the 44 MeV bremsstrahlung during 5.5 hours. The intensity comparison of the ^{237}U -208 keV photopeak between samples and U standards, gives the following concentrations: 116-116-117-118-117-116-115-116-117-117-118-118-118-119 and $115 \mu\text{g U/g}$. The mean value is 116.9 with a standard deviation $s=1.188$ and the uncertainty of the mean at the 99.73% confidence level, is $e_R=3.636 s/15^{1/2}=1.115$. The results are summarised in the Table V.

TABLE V
Homogeneity control of U in the Moroccan phosphate rock, BCR CRM 32

Phosphate rock	Number of samples	Mean value	$e_R(99.73\% \text{ c.l.})$
uranium	15	116.9	1.12

The inhomogeneity of uranium in the 15 natural phosphate rock samples is less than 0.954%. The inhomogeneity of U in the Bessines mineral and Moroccan phosphate rock samples is less than 1%, at 99.73% confidence limits.

CONCLUSION

The non-destructive and multi-element control of the homogeneity of reference materials by photon activation can be performed with high precision and requires minimum manipulation and treatment of these materials. The size of the sample to be assayed can be increased or reduced without any difficulty. While a vast array of destructive techniques is currently used, only a limited number of non-destructive methods can be applied for bulk analyses and

236 CH. BERTHELOT, H. L. ESCHBACH, V. VERDINGH AND F. VERHEYEN
uniformity tests of reference materials. The instrumental photon activation analysis is attractive as difficulties and errors associated with sample dissolution are eliminated and the possible contribution of any inhomogeneity to the total analytical error is less than 1% at the 99.73% confidence level for the five reference samples.

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