STANDARD REFERENCE MATERIAL CERTIFICATION: CONTRIBUTION OF NAA WITH A TRIGA REACTOR

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Thousands of independent analytical results, over about one hundred different Standard or Certified Reference Materials (SRM or CRM), have been contributed by the Pavia researchers using the LENA TRIGA reactor.

Being a little group of analysts mainly devoted to a single technique, i. e. Neutron Activation Analysis (NAA), we are not able, alone, to reach the final certification of the elemental contents, which must be achieved confronting the results obtained with different techniques based on different principles.

For these reasons Pavia has cooperative links with the major international agencies devoted to the certification of SRMs or CRMs as the Bureau Communautaire de Reference (BCR), the European Institute for Reference Materials and Measurement (IRMM), the USA National Institute of Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA).

During these cooperative works, a large amount of analytical data obtained with NAA has been compared, and meaningful methodological information achieved therefrom with respect to accuracy and precision in the analysis of several elements at different concentrations in various matrices.

Analytical data on As, Cd, Cr, Co, Cu, Cs, Fe, Zn, K, Sc, U, Th, Al, Sb, Mn, V, Hg, Sr, Rb, Se,Pt, all the Rare Earths and halogens Br, Cl, I, have been obtained and contributed for the final certification [1,2,3].

The choice of the elements analyzed was the final results of many considerations affecting the actual performances of our laboratory.

a) Irradiation positions and fluxes,
b) Instrumentation availability and performances,
c) NAA sensitivities and capability,
d) Community's interest and request,
e) Operator's skill and experience,
f) Operator's motivation.

a) Irradiation positions and fluxes

For the range of concentrations requested for the actual cases encountered in the certification programs, the fluxes available in the 250 kW LENA TRIGA are adequate for most applications.

TRIGA reactors have many irradiation positions and different facilities, which allow the choice of the best solution depending on the matrix, the type of reaction, sensitivity and half-lives of the radionuclides involved.

The **Pneumatic irradiation system**, used for short-lived isotopes evaluations, is positioned in the F ring of the core and has a flux of $4.5\times10^{12}n\times cm^{-2}\times sec^{-1}$ with a fast neutron contribute which must be taken into account; in some cases, trace element determination cannot be performed with irradiation in this position, due to severe interferences deriving from (n, p) reactions.

The highest flux is available in the **central thimble** ($9\times10^{12}n\times cm^{-2}\times sec^{-1}$) but unfortunately this facility allows the irradiation of only a few samples together.

The most useful facility of irradiation is the **rotating specimens rack** with its 80 equivalent irradiation positions with a flux of $1.4\times10^{12}n\times cm^{-2}\times sec^{-1}$.

For special determinations, as in the case of Al by $^{27}Al(n, \gamma)^{28}Al$ reaction, a special **pneumatic facility** was installed in the **thermal column**, to avoid interference by the formation of ^{28}Al also from $^{28}Si(n, p)^{28}Al$.

The absolute fluxes, their energy distribution and reproducibility are routinely checked and found very constant and stable over the 37 years of reactor operation, thus increasing the reliability of the analytical results.

b) Instrumentation availability and performances

Sometimes the instrumentation available in a laboratory does not cover all the different analytical techniques or, in many cases, is not of outstanding quality. Our laboratory has poor alfa and beta equipments but has a network of gamma-ray spectrometers of outstanding quality and reliability connected on-line for real-time and long-distance control, supplied by EG&G Ortec.

c) NAA sensitivities and capability

Due to the principle of the method, mainly affected by the **activation cross-sections**, **half-lives** and **decay schemes**, the method has a wide variability of sensitivity over all the elements. Usually the method is applied to the determination of elements with highest sensitivity, but information on most of the elements present in the samples analyzed can be achieved.

In these way we exploit the **multi elemental capability** of the method and the perfect linearity of the response **from nanogram to gram levels** (*TABLE 1*).

d) Community's interest and request

For some elements as Cd, Fe, Ni, S, Mg or Mo, the NAA technique does not have the highest sensitivity. Nevertheless in some cases the method is applied and gives very useful data for the certification of these elements, when few independent and reliable methods are suitable for their analysis.

e) Operator's Skill and Experience

Our laboratory is especially devoted to radiochemistry and activation analysis. The experience acquired over more than 30 years of activity, obviously suggests us that NAA is the easiest analytical technique while in a normal laboratory other methods could be better utilized.

f) Operator's Motivation

This is the most critical point regarding all the analytical works and may heavily affect the results. The analysis of traces down to the ppm or ppb levels cannot be done as a routine job and cannot be performed in a reliable way without a deep operator's motivation. This is such an important point that some determinations at very low level were performed with good results despite of their analytical difficulties. This is the case, for instance, of Hg, Cu, I, Pt. Here is a review of some radiochemical separations originally studied and applied for these elements in our laboratory.

MERCURY

The most sensitive reaction suitable for mercury determination using NAA is $^{196}Hg(n,\gamma)^{197}Hg$ (half-live: 64.1 hrs) with the best analytical peak at 77.6 keV.

These parameters oblige to make radiochemical separation of the element, giving attention to some specific points:

1. Possibility of losses
2. Selectivity of separation
3. Radiochemical yield
4. Counting geometry

The experience gained in many years of mercury analysis allow us to consider as the best technique for mercury determination the combustion-distillation procedure coupled to a sulphide

precipitation and filtration on a glass paper disk, originally developed in our laboratory [4,5,6]. In this way the mercury losses are minimized, the selectivity of the separation is very good, the radiochemical yield is quantitative and the counting geometry is very reproducible and with negligible self-shielding.

To give an idea of the sensitivity and reproducibility of the method, *TABLE 2* reports a set of results obtained analyzing for the certification four samples of BCR SRM 63-Milk. The contributed value was 1.23 ppb while the certificate value was 1.25.

COPPER

Copper is an element which offers very high sensitivity by NAA and can be determined with two different reactions, $^{63}Cu(n,\gamma)^{64}Cu$ (half-life: 12.7 hrs) and $^{65}Cu(n,\gamma)^{66}Cu$ (half life: 5.1 min).

Unfortunately, both reactions have drawbacks: ^{64}Cu has the most intense line at 511 keV, which is common to many other decays, and ^{66}Cu, due to its short half-life, often have severe limitations from the matrix background.

When only copper must be analyzed, the best and simplest method is that using the inorganic exchanger CuS deposited on a glass-filter, which ensures 100% yields, good counting geometry and satisfactory decontamination.

The method can be applied also to the short-lived ^{66}Cu evaluation if the mineralization and dissolution of the sample is done before the irradiation. The method was applied to the certification of many SRMs and the supplied results by our laboratory are reported in *TABLE 3*.

IODINE

Iodine is an element for which the analytical problems are not completely solved, at least at very low concentration levels. These difficulties are reflected on the fact that only few Standard Reference Materials are certified for iodine content. Nevertheless, iodine is an element with relevant health interest and its determination, also at trace levels, has increasing relevance. The most suitable reaction for NAA is $^{127}I(n,\gamma)^{128}I$ (half-life: 25 min) with the best analytical peak at 443 keV.

When required by matrix interferences or by the low level content of the element, we adopt the gas-phase separation originally proposed by H.L. Rook and optimized in our laboratory[7,8].

In *TABLE 4* the contributed values of our group for the certification of Iodine in SRM-BCR 63, milk powder are reported.

PLATINUM

Platinum determination at ppb level has recently become of great interest due to the increasing knowledge of its effect on human health and due to the spread of contamination related to its utilization in catalyst converters in car industry.

Until now, no Standard Reference Material is certified for Pt content at the actual low levels relevant for human health. In the year 2000, BCR proposed a CRM material, called CW-8, in which the platinum content is being certified.

Due to severe interference by the 169 keV line of ^{47}Sc and the very low Pt content, a preconcentration – separation process was studied in our laboratory and applied[9].

In *TABLE 5* the contributed results from our group are presented, along with the proposed certification value, agreed upon by the participating laboratories.

Final considerations

The contribution of our laboratory for the certification of many trace elements refers mainly to determination done by INAA. Elements such as Zn, Cr, Co, Sb, U, Th, Mo, Ni, Se, Hg, V, Mn, Cl and Br are easily evaluated by INAA in the ppm range unless in very special cases or when the matrices have unusual characteristics as reported before[10,11,12].

Trace analysis done for certification purposes cannot be run as a routine job and the motivation of the analyst is much more important, for the accuracy and reliability of results, than sophisticated and costly equipment.

The selected review of the contributions of Pavia to certification programs of different agencies by RNAA is only a proof of the actual analytical capability of NAA for the certification of some elements down to the ppb range using a 250 kW TRIGA (*TABLES 6* to *12*).

The participation to these programs is still in progress (*TABLE 13)* for many certification campaigns and will continue also in the future.

TABLE 1 Estimated elemental detection limits by INAA, assuming irradiation in a reactor neutron flux of 10^{12} neutrons per square centimeter per second.

DETECTION LIMITS (pg)	**ELEMENTS**
1	Dy, Eu, In
1 - 10	Au, Lu, Mn
10 - 10^2	As, Ho, Ir, Re, Sm, W, V
10^2 - 10^3	Al, Ag, Ar, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Ti, Tb, Th, Tm, U, Yb, Zn
10^3 - 10^4	Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Pt, Rb, Rh, Ru, Sr, Te, Zr
10^4 - 10^5	Bi, Ca, K, Mg, P, Si, Sn, Tl, Xe, Y
10^5 - 10^6	F, Fe, Nb, Ne
10^7	Pb, S

TABLE 2 Mercury - Contributed values for the Certification of BCR 63-Milk

Sample	**Sample Intake (mg)**	**Content (ppb)**	**Final certification (ppb)**
1	432	1.42	1.25±0.09
2	456	1.18	
3	385	0.95	
4	472	1.36	
	Mean	1.23	
	SD	0.21	

TABLE 3 Copper - Contributed values for the Certification of BCR 63-Milk

Sample	**Sample Intake (mg)**	**Content (ppb)**	**Final certification (ppb)**
1	253	760	753±21
2	328	745	
3	274	773	
4	450	762	
	Mean	760	
	SD	40	

TABLE 4 Iodine - Contributed values for the Certification of BCR 63-Milk

Sample	Sample Intake (mg)	Content (ppb)	Final certification (ppb)
1	343	265	273±20
2	421	330	
3	322	315	
4	382	282	
	Mean	298	
	SD	30	

TABLE 5 Platinum - Contributed values for the Certification of BCR CW8

Sample	Sample Intake (mg)	Content (ppb)	Final certification (ppb)
1	485.5	75.4	75.6±6 (Proposed)
2	503.2	73.6	
3	499.7	78.1	
4	476.2	79.0	
5	485.9	80.2	
6	503.3	75.1	
	Mean	76.7	
	SD	2.7	

TABLE 6 Standard Reference Materials Certified with the Contribution of Pavia Group

NBS/NIST SRMs

Reference	Material
NBS SRM 1632	Coal
NBS SRM 1633	Coal Fly Ash
NBS SRM 1634	Fuel Oil
NBS SRM 1572	Citrus Leaves
NBS SRM 1577a	Bovine Liver

TABLE 7 Standard Reference Materials Certified with the Contribution of Pavia Group

IAEA SRMs

Reference	Material
IAEA - 359	Cabbage
IAEA - 331	Spinach
H-9	Mixed Human Diet
V-10	Hay Powder
MA-B-3/TM	Fish Flesh
H-4	Animal Muscle

TABLE 8 Standard Reference Materials Certified with the Contribution of Pavia Group

BCR Environmental Matrices

Reference	Material	Final Report	Year
BCR 38	Coal Fly Ash	EUR8080EN	1982
BCR 176	City Waste Incinerator Ash	EUR9664EN	1984
BCR 40	Coal	EUR9473EN	1984
CRM 181	Coking Coal	EUR10366EN	1986
CRM 182	Steam Coal	EUR10366EN	1986
BCR 176R	City Waste Incinerator Ash	In Progress	
BCR CW7	Road Dust	In Progress	
BCR CW8	Road Dust	In Progress	

TABLE 9 Standard Reference Materials Certified with the Contribution of Pavia Group

BCR Soils, Sediments and Sludges

Reference	Material	Final Report	Year
BCR 140	Sandy Soil	EUR8834EN	1983
BCR 141	Calcareous Soil	EUR8833EN	1983
BCR 142	Light Sandy Soil	EUR8834EN	1983
BCR 143	Amended Soil	EUR8835EN	1983
BCR 144	Domestic Sewage Sludge	EUR8836EN	1983
BCR 145	Sewage Sludge	EUR8837EN	1983
CRM 277	Estuarine Sediment	EUR11850EN	1988
CRM 280	Lake Sediment	EUR11850EN	1988
CRM 320	River Sediment	EUR11850EN	1988
CRM 141R	Calcareous Soil	EUR16890EN	1996
BCR 144R	Domestic Sewage Sludge	EUR16891EN	1996
BCR 146R	Industrial Sewage Sludge	EUR16892EN	1996
CRM 600	Calcareous Soil	In progress	

TABLE 10 Standard Reference Materials Certified with the Contribution of Pavia Group

BCR Health Related Materials

Reference	Material	Final Report	Year
BCR 063	Skim Milk Powder	EUR9138EN	1983
BCR 063	Skim Milk Powder	EUR9251EN	1984
CRM 150	Skim Milk Powder - Spiked	EUR9251EN	1984
CRM 151	Skim Milk Powder - Spiked	EUR9251EN	1984
CRM 150	Skim Milk Powder - Spiked	EUR10364EN	1986
CRM 151	Skim Milk Powder - Spiked	EUR10364EN	1986
CRM 397	Human Hair	EUR13433EN	1991
CRM 422	Cod Muscle	EUR14557EN	1993
CRM 063R	Skim Milk Powder	EUR15021EN	1993
CRM 185R	Bovine Liver	EUR18841EN	1998
CRM 278R	Mussel Tissue	EUR18840EN	1998

TABLE 11 Standard Reference Materials Certified with the Contribution of Pavia Group

BCR Environmental / Botanic Materials

Reference	Material	Final Report	Year
BCR 60	Lagarosiphon Major	EUR8119EN	1982
BCR 61	Platihypnidium Riparioides	EUR8119EN	1982
BCR 62	Olea Europaea	EUR8119EN	1982
CRM 189	Wholemeal Flour	EUR10997EN	1987
CRM 191	Brown Bread	EUR10997EN	1987
CRM 281	Rye Grass	EUR11839EN	1988
CRM 129	Hay Powder	EUR12473EN	1989
CRM 100	Beech Leaves	EUR12680EN	1990
CRM 101	Spruce Needles	EUR12680EN	1990
CRM 402	White Clover	EUR13234EN	1992
CRM 482	Lichen	EUR16841EN	1996
CRM 679	White Cabbage	EUR19777EN	2001

TABLE 12 Standard Reference Materials Certified with the Contribution of Pavia Group

BCR Industrial Matrices

Reference	Material	Final Report	Year
CRM 180	Graphite	EUR10366EN	1986
CRM 274	Single Cell Protein	EUR11001EN	1987
CRM 414	Plankton	EUR14558EN	1993
CRM 664	Glass	EUR18852EN	1999
CRM 680	Polyethylene	EUR19450EN	2001
CRM 681	Polyethylene	EUR19450EN	2001

TABLE 13 Standard Reference Materials Certification in progress

Reference	Material	Final Report	Year
IRMM 802	Acacia Honey	BCR / IRMM	2002
IRMM 803	Eucalyptus Honey	BCR / IRMM	2002
BCR 277R	Estuarine Sediment	BCR / IRMM	2002
BCR 280R	Lake Sediment	BCR / IRMM	2002
BCR 320R	Channel Sediment	BCR / IRMM	2002
CRM IAEA 385	Irish Sea Sediment	IAEA	2002

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