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NEUTRON ACTIVATION OF CHLORINE IN ZIRCONIUM AND ZIRCONIUM ALLOYS USE OF THE MATRIX AS COMPARATOR

I. M. COHEN, C. D. GOMEZ, M. I. MILA

Comisión Nacional de Energía Atómica, Dirección de Radioisótopos y Radiaciones,
Avda. del Libertador 8250, (1429) Buenos Aires (República Argentina)

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A procedure is described for neutron activation analysis of chlorine in zirconium and zirconium alloys. Calculation of chlorine concentration is performed relative to zirconium concentration in the matrix in order to minimize effects of differences in irradiation and counting geometry. Principles of the method, and the results obtained are discussed.

Introduction

Zirconium and zirconium alloys designed for nuclear application are subject to several precise specifications regarding the concentration of some impurities. Thus, the upper level accepted for chlorine concentration is 20 ppm.

Neutron activation analysis is a suitable technique for the determination of chlorine, as it has an activatable isotope which can be successfully used. However, some difficulties may arise with respect to the preparation of a suitable standard when samples have to be analyzed as slabs or shavings, which are the usual shapes when they are taken from ingots; differences in irradiation and counting geometry can affect the accuracy of determination.

An alternative method to minimize these drawbacks is the utilization of a matrix major element, namely zirconium, as a comparator. Such a technique has already been applied for cadmium determination in cadmium doped sodium chloride crystals, using an approximate formula for calculations.[1] In what follows, the principles of the method will be rigorously discussed and its application described for determination of chlorine traces in zirconium.

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Theory

If self-shielding factors are not specifically included, the amount of an element is calculated in the absolute method from the activity induced over one of its stable isotopes, by the formula:

$$m = \frac{C\ AW\ \lambda t_m}{i\ \epsilon\ \Theta\ N_{Av}\ \Phi_{th}\ [\sqrt{\pi}/2\ \sqrt{T_0/T}\ g\,\sigma + L(I + \Delta I)]\,(1 - e^{-\lambda t_i})\ e^{-\lambda t_d}\,(1 - e^{-\lambda t_m})}$$

where m – mass of the element,
C – count rate,
i, ϵ – absolute intensity and detector efficiency for the measured radiation,
AW – atomic weight,
Θ – isotopic abundance,
N_{Av} – Avogadro's number,
Φ_{th} – thermal flux, $\Phi_{th} = nv$, n: neutron density; v: mean velocity of Maxwell's distribution,
t_i – time of irradiation,
t_d – time elapsed between the end of irradiation and the beginning of measurement,
t_m – time of measurement,
λ – decay constant of the nuclide,
T_0 – normal temperature of the distribution: $T_0 = 293.6$ K,
T – neutron temperature,
g – factor which corrects departures of the cross-section from 1/v behaviour in the thermal component of the neutron spectrum,
σ – cross-section at 2,200 m/s,
$L = \dfrac{\Phi_{epi}}{\Phi_{th}}$; Φ_{epi} : parameter which defines the epithermal flux;

I – resonance integral from E_{cd}, cadmium cut-off energy;
$I = \int_{E_{cd}}^{\infty} \dfrac{\sigma(E)\,dE}{E}$; $I = \int_{\mu kT}^{E_{cd}} \dfrac{\sigma(E)\,dE}{E}$; μkT: equivalent cut-off 1/E spectrum. μ: empirical constant ($\mu = 4$ for ligth water reactors), k: Boltzman's constant.

The expression of the concentration of an element with respect to another can be easily derived; concerning chlorine concentration in zirconium alloys as a function of zirconium concentration, the formula is as follows:

$$[\mathrm{Cl}] = [\mathrm{Zr}]\,\frac{C_{cl}\, i_{zr}\, \epsilon_{zr}\, AW_{cl}\, \Theta_{zr}\, [\sqrt{\pi}/2\, \sqrt{T_0/T}\, g_{zr}\, \sigma_{zr} + L(I_{zr} + \Delta I_{zr})]\,(1 - e^{-\lambda_{zr} t_i})}{C_{zr}\, i_{cl}\, \epsilon_{cl}\, AW_{zr}\, \Theta_{cl}\, [\sqrt{\pi}/2\, \sqrt{T_0/T}\, g_{cl}\, \sigma_{cl} + L(I_{cl} + \Delta I_{cl})]\,(1 - e^{-\lambda_{cl} t_i})}\; \frac{e^{-(\lambda_{zr}-\lambda_{cl})t_d}\, \lambda_{cl}(1 - e^{-\lambda_{zr} t_m})}{\lambda_{zr}(1 - e^{-\lambda_{cl} t_m})}$$

[Cl], [Zr]: chlorine and zirconium concentrations, respectively; subscripts denote elements or their corresponding nuclides.

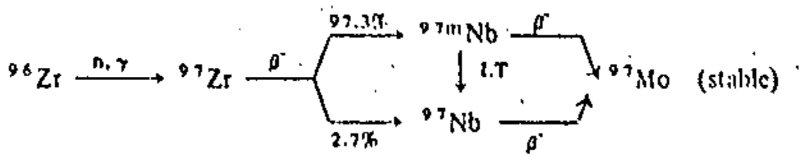
Use of this new formula results in a significant diminution of errors caused by self-shielding effects, as the matrix for both the element to be determined and the comparator is the same. Thermal flux is removed and relative efficiencies may be substituted for the corresponding absolute values, thus lessening the error. All other factors of the expression are either tabulated or can be measured during the experiment, except T and L, which are characteristic parameters of the reactor and the irradiation position and must be known beforehand.

Selection of conditions for chlorine determination

As concerns a purely instrumental method of analysis, all factors which can contribute to improve the sensitivity should be revised. Neglecting the small-yield threshold reactions, chlorine produces by neutron activation only one isotope suitable for analysis, whereas zirconium has two activatable isotopes. The reactions occurring are:

$$^{37}\mathrm{Cl} \xrightarrow{n,\gamma} {}^{38}\mathrm{Cl} \xrightarrow{\beta^-} {}^{38}\mathrm{Ar} \qquad \text{(stable)}$$

$$\begin{tikzcd}
 & & {}^{95m}\mathrm{Nb} \arrow[d, "\mathrm{I.T}"] \arrow[dr, "\beta^-", "2.5\%"'] & \\
{}^{94}\mathrm{Zr} \arrow[r, "n,\gamma"] & {}^{95}\mathrm{Zr} \arrow[ur, "0.9\%"] \arrow[dr, "99.1\%"'] \arrow[phantom, r, "\beta^-"] & & {}^{95}\mathrm{Mo}\ \text{(stable)} \\
 & & {}^{95}\mathrm{Nb} \arrow[ur, "\beta^-"'] &
\end{tikzcd}$$



Since ^{38}Cl is shorter-lived than ^{95}Zr and ^{97}Zr, there is no possibility of selecting optimum conditions for irradiation or decay times, as the chlorine to zirconium activity ratio always decreases as both times are increased. Epicadmium irradiation, sometimes used as a method for improving the activation of an element with respect to an interference, would render the situation worse in this case, because the cadmium ratio is by far higher for chlorine than it is for both zirconium isotopes. A factor which can help chlorine determination is that ^{38}Cl emits more energetic gamma-rays than do ^{95}Zr and ^{97}Zr, so that its measurement can be accomplished without serious interference, although with low efficiency. However, as the bulk of total activity results from zirconium, the irradiated sample has to be measured in a geometry far from the detector in order to avoid disturbances that would be caused by a high dead time, thus lessening the sensitivity. This situation could be changed by measuring the sample nearer to the detector, lead-covered in such a way that zirconium activity facing the detector be reduced to an acceptable level, providing chlorine counting was not so diminished. This possibility of enhancing conditions for chlorine determination appeared as the only practicable alternative, and therefore, was studied. Experimental details will be seen next.

Experimental

Equipment

All measurements were performed with a 70 cm^3 Ge(Li) detector (Princeton Gamma Tech.), having a 2.4 keV resolution for the ^{60}Co 1332 keV peak. The signal passed through a preamplifier (PGT RG-11A) and an amplifier (Ortec 450) to a 4096 multichannel analyzer (Hewlett-Packard, model 5401 A/B) with digital output by teletype.

A desk computer (Hewlett-Packard 9810 A) was used in order to carry out the mathematical treatment of data.

Determination of relative efficiency curves

Sources of ^{110m}Ag, ^{24}Na and ^{56}Co were produced by the reactions: ^{109}Ag(n, γ)^{110m}Ag; ^{23}Na(n, γ')^{24}Na and ^{55}Mn(α, 3n)^{56}Co, from AgNO$_3$, Na$_2$CO$_3$ and metallic manganese targets, all chemicals of high purity. Irradiations were performed for ^{110m}Ag and ^{24}Na production in the core of the RA-3 reactor

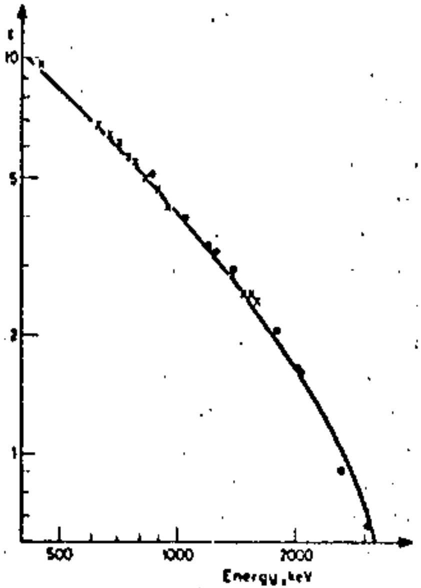


Fig. 1. Efficiency curve for unshielded sources (arbitrary units). ● – ^{56}Co, X – ^{110m}Ag

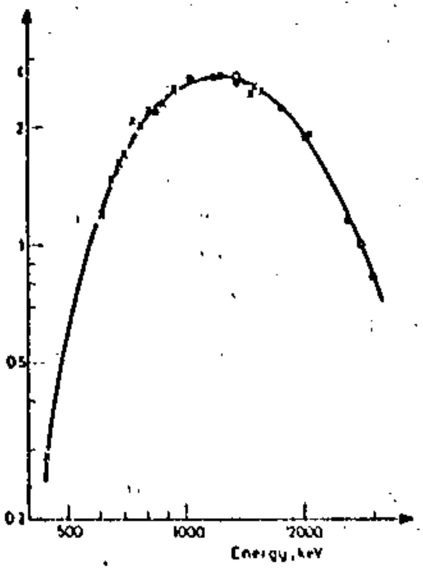


Fig. 2. Efficiency curve for lead shielded sources (arbitrary units). ● – ^{56}Co, X – ^{110m}Ag, o – ^{24}Na

Table 1
Nuclear data for efficiency curves[1]

Energy, keV	Relative intensity	Nuclide
446.812±0.004	38.9±0.4	^{110m}Ag
620.358±0.003	29.4±0.5	^{110m}Ag
657.761±0.002	1000	^{110m}Ag
677.627±0.004	112±1	^{110m}Ag
687.010±0.004	68.3±0.5	^{110m}Ag
706.680±0.005	172.8±1.5	^{110m}Ag
744.279±0.005	49.3±0.8	^{110m}Ag
763.949±0.005	236±2	^{110m}Ag
818.032±0.005	77.1±0.5	^{110m}Ag
846.772±0.013	100 000	^{56}Co
884.684±0.005	771±6	^{110m}Ag
937.491±0.005	363±3	^{110m}Ag
1037.840±0.015	14 000±100	^{56}Co
1175.102±0.016	2 280±20	^{56}Co
1238.282±0.017	67 600±700	^{56}Co
1360.250±0.070	4 330±40	^{56}Co
1368.643±0.020	100	^{24}Na*
1384.300±0.004	261±5	^{110m}Ag
1475.786±0.005	42.4±0.8	^{110m}Ag
1505.036±0.005	140.1±1.2	^{110m}Ag
1562.301±0.006	12.6±0.2	^{110m}Ag
1771.351±0.026	15 700±150	^{56}Co
2015.181±0.028	3 080±30	^{56}Co
2034.755±0.029	7 890±70	^{56}Co
2598.458±0.033	16 900±150	^{56}Co
2754.034±0.036	100	^{24}Na*
3009.591±0.042	1000±10	^{56}Co

*Not used for unshielded source measurements.

whilst ^{56}Co was obtained upon irradiation with 54 MeV α-particles in the internal beam of the Philips synchrocyclotron.

After the end of each irradiation, the targets were placed in such a way as to get extended sources resembling zircaloy samples in shape and size. Gamma-ray spectra were recorded for each source; the occurring nuclides were characterized

Table 2
Efficiency ratios for chlorine and zirconium energies

Energy ratio	Efficiency ratio (bare sources)	Efficiency ratio (shielded sources)
1642/724	0.380	1.352
2167/724	0.237	0.937
1642/743	0.388	1.297
2167/743	0.240	0.899
1642/756	0.393	1.262
2167/756	0.243	0.875

through their energies and their purity was checked. Radiations from ^{54}Mn, ^{58}Co and ^{57}Co were identified in the irradiated manganese, but they did not interfere with the measurement of the outstanding peaks from ^{56}Co.

Two sets of measurements were made, one with bare sources located 11 cm from the detector, the other after placing them into a 2.5 cm thick lead container, which rested on the detector. Both conditions reproduced the actual geometry in which zirconium samples should be measured, as has been proved by previous experience.

After smoothing of the data, peak areas were found by COVELL's method, then calculation of relative efficiencies were performed for each nuclide. Finally, data of efficiency vs. energy were fitted for both experimental set-ups by the least-squares method to a function of the type: $\log \epsilon = a \log^2 E + b \log E + C$ (ϵ: efficiency; E: energy). Fitting correlation factors were 0.996 and 0.989 for measurements with unshielded and lead shielded sources, respectively.

Ratios of relative efficiencies for ^{38}Cl peaks with respect to some of the most prominent zirconium related peaks are summarized in Table 2, showing an improvement for chlorine determination by a factor of nearly 3–4, concerning individual peaks. Though both curves are presented in arbitrary units, they can be normalized against one another; this normalization was made and revealed that, far from the losses in ^{38}Cl counting when measuring with shielding, it is increased by factors ranging from 4.7 for 1642 keV peak to 5.2 for 2167 keV.

Chlorine determination in zirconium and zircaloy samples

Zirconium and zircaloy 4 samples, weighing about 100 mg, were treated with a mixture of dilute HNO_3 and HF, in order to remove surface impurities, washed with bidistilled water, dried, placed in polyethylene vials and mounted into irradiation capsules in such a way that the geometry could be reproduced in all of the experiments. Five-minute irradiations were carried out in one of the positions of the RA-3 reactor core. As ^{97}Zr is highly dependent on epithermal activation the Φ_{epi}/Φ_{th} ratio was previously determined[3] with three monitors (In, Au, Mn) so as to check possible deviations from the 1/E law. Results obtained with these three monitors were coincident within the limits of experimental error, thus proving that the epithermal component could be considered as a very nearly 1/E spectrum.

After the end of the irradiations, the capsules were opened and the samples transferred to measurement vials, this operation lasting approximately 25 min. Measurements of 75 min were performed; data corresponding to ^{38}Cl, ^{95}Zr and ^{97}Zr were smoothed and peak areas calculated as before. C/i c ratios were found, a weighted average was calculated for each nuclide when more than one peak was used.

Chlorine concentration was found relative to zirconium, utilizing the corresponding formula.

Calculations and nuclear data

Accurate knowledge of the nuclear parameters involved is a prerequisite to obtain suitable results by this method, which in this sense resembles the classical absolute method. Table 3 shows the selected values used for calculations which were available from current literature; most of them are in reasonable agreement so that the "best" data could be those with the least error, as quoted by their authors. However discrepancies were found with respect to cross-section and resonance integrals for zirconium nuclides, especially ^{97}Zr (Table 4). In order to test their self-consistency, each group of data was used for calculating ratios of the zirconium mass, as derived from ^{97}Zr activity, to that obtained from ^{95}Zr activity, in series of irradiations carried out at different positions of the reactor. Obviously, the theoretical result should be 1. Table 5 sums up the results; calculated ratios were near one for irradiations performed at the core, but significant departures for two of the cases were observed when irradiating in the thermal column. The most consistent results were obtained using the values published by FULMER et al. and therefore they were taken as the preferred ones. Similar conclusions were reached in a comparative study on data of cross-sections and resonance integrals for several isotopes.[7]

Results and discussion

Two values for chlorine concentration were obtained in each experiment, one for each zirconium nuclide which acts as comparator. According to selected values, they differ by approximately 10% for irradiations in the reactor core. Probably,

Table 3
Selected values for nuclear parameters of chlorine and zirconium isotopes

Nuclide	Cross-section, b	Resonance integral, b	Half-life	Gamma energies, keV	Intensity, %
^{38}Cl	0.433±0.006	0.213±0.009	(37.29±0.04) m	1642.42±0.15 2167.4 ±0.1	32 ±2 42 ±2
^{95}Zr	0.052±0.003*	0.30 ±0.03*	(63.98±0.06) d	724.23±0.04 756.74±0.04	44.2±0.7 54.6±0.5
^{97}Zr	0.020±0.003*	5.0 ±0.4*	(16.90±0.05) h	743.36±0.10**	92.8±0.3**

*See: Calculations and nuclear data.
**From ^{97m}Nb.

Table 4
Cross-sections and resonance integrals for zirconium isotopes

Nuclide	RICABARRA et al.*[4]	FULMER et al.[5]	IAEA Handbook[6]
^{94}Zr σ	0.063 ±0.008	0.052±0.003	0.075±0.008
I	0.396 ±0.037	0.30 ±0.03	0.38
^{96}Zr σ	0.0057±0.0010	0.020±0.003	0.05 ±0.01
I	4.97 ±0.50	5.0 ±0.4	5.0

*Normalized with addition of 1/v contribution, not included in the original reference.

Table 5
Results of mZr (^{97}Zr)/m(^{95}Zr) ratios for different published data

Position	Φ_{epi}/Φ_{th}[3]	Ref.[4]	Ref.[5]	Ref.[6]
Core	0.0164	1.24	0.89	1.00
Core	0.0164	1.25	0.89	1.01
Thermal column	$2.97 \cdot 10^{-4}$	3.70	1.04	0.63
Thermal column	$1.7 \cdot 10^{-4}$	4.01	1.05	0.62

use of the result obtained from ^{95}Zr would be preferable, because the ^{95}Zr activity is so highly influenced by epithermal activation that even small shifts in the Φ_{epi}/Φ_{th} ratio may severely affect the accuracy of the analysis. Although both ^{38}Cl peaks can be used for calculations, the Compton background generated by some peaks from ^{97}Zr or other impurities (^{56}Mn, ^{116m}In) with energies higher than 1642 keV makes the counting error of this peak large in relation to that of 2167 keV; e.g. statistical errors associated with an analyzed sample of 29.5 ppm chlorine concentration reached 11% and 5% for the 1642 keV and 2617 keV peaks, respectively. The former is not detectable when the chlorine concentration is smaller than 1 ppm.

Systematic errors from parameters used in calculations must be included in the final expression so that the total error is larger than that of the external standard method. Nevertheless, statistical counting dispersion has more weight than systematic error when analyzing low concentration samples.

The method is reproducible even at concentrations near the detection limit. Two succesive determinations in samples of low chlorine concentration gave: (1.3 ± 0.3) ppm and (1.6 ± 0.3) ppm. Applying criteria suggested by ROGERS,[8] the detection limit is 0.6 ppm for a 95% confidence interval.

The preceding considerations are valid when a single sample is irradiated and measured each time. Some losses of precision and sensitivity will occur if more samples are analyzed simultaneously, but as the present detection limit is far smaller than the upper level required, such a scheme can be adopted in routine for groups of up to four without affecting the ultimate purpose of the work.

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