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**ISOTOPIC ANALYSIS OF DEPLETED ZINC IN Zn-64 BY THERMAL IONIZATION MASS SPECTROMETRY**

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**Abstract**

Depleted zinc oxide (DZO) in Zn-64 is used as additive in the cooling water of nuclear reactors to reduce the amount of radionuclides produced by radiation, which can be accumulated in the oxide layer. For isotopic characterization of zinc oxide, measurements were performed by thermal ionization mass spectrometry with simple filament configuration and addition of silica-gel/phosphoric acid to enhance the ionization efficiency. Due to the absence in the laboratory of certified reference material, several natural zinc samples were measured to select one of them and assuming that it has the representative isotopic composition published by IUPAC. Mass discrimination factor is then calculated for application to the isotopic determination of the DZO sample.

**Keywords**

Depleted zinc, isotopic analysis, thermal ionization mass spectrometry, mass discrimination.

**Introduction**

In routine operation of nuclear pressurized water reactor plants (PWR), crucial parameters of the filling water in primary circuit are controlled. The water chemistry on piping plays a critical role in the maintenance and safety of the system and the operators. It seeks to minimize the entry of impurities, corrosion products and the deposition of radionuclides to reduce the operating dose rates (personnel exposure). Therefore, optimum water chemistry control must maintain a balance among fuel integrity, materials integrity and reducing radiation fields [1]. The most significant radionuclides that contribute to worker doses at nuclear power plants are Co-60 and Co-58, which are responsible for over 80% of out-of-core radiation fields. Radionuclide precursors are released by corrosion or wear from components in contact with the primary coolant. Co-60 is produced by the bombardment of Co-59 (the only natural isotope of cobalt), with thermal neutrons:  $^{59}\text{Co}(\text{n},\gamma)^{60}\text{Co}$ . Co-60 has a 5.271 years half-life and produces penetrating gamma rays (1.173 and 1.332 MeV, both 100%) through its radioactive decay. Nickel is the major constituent of the structural alloys used in the primary coolant system. Co-58 is produced from Ni-58 by the reaction  $^{58}\text{Ni}(\text{n},\text{p})^{58}\text{Co}$ . Co-58 has a short half-life (70.88 days) and its decay produces a 0.811 MeV gamma ray. It contributes substantially to PWR doses in early plant life.

The addition of zinc to the water of PWRs is to minimize the accumulation of Co-60 on the reactor inner surfaces. Surfaces are prefilmed with a protective zinc oxide layer before exposure and inhibits the subsequent deposit of cobalt.

It involves injection of zinc at 30 - 40 ng.g<sup>-1</sup>. Some authors say that low concentration of 5 ng.g<sup>-1</sup> also reduces shutdown radiation fields [2]. Divalent zinc cations are exchanged in the crystal structure of the passivated film, generating a strong and resistant layer.

However, natural zinc contains 48.27 % of Zn-64 isotope and due to the neutron bombardment in the cooling water of the reactor is transformed in radioactive Zn-65 by the reaction  $^{64}\text{Zn} (n,\gamma) ^{65}\text{Zn}$ .

Zn-65 decays to Cu-65 stable isotope by electron capture and  $\beta^+$  emission (0.330 MeV) and also to an excited state of Cu-65, which emits gamma radiation of 1.115 MeV with a half-decay period of 244.3 days. For this reason, it is necessary to add zinc depleted in the isotope 64 (less 1 %) to the cooling water.

PWR operators have started to evaluate the technology of Depleted Zinc Oxide (DZO) because of the necessities above exposed. Isotopic analyses are performed generally by thermal ionization mass spectrometry (TIMS) or by multi-collector inductive coupled plasma mass spectrometry (MC-ICPMS). In this work the isotopic abundance of DZO was analyzed, as quality control, by TIMS.

In TIMS, samples are loaded on a metal filament. Ions are produced by interactions of the species at the hot surface of the filament.

Natural Zn has five stable isotopes with abundances of Zn-64: 48.27%, Zn-66: 27.98%, Zn-67: 4.10%, Zn-68: 19.02%, Zn-70: 0.63% [3]. Only Zn-64 and Zn-70 have isobaric interferences: Ni-64 (0.91%) and Ge-70 (20.5%) respectively.

Blix et al [4] in one of the earlier publication of isotopic analysis of Zn analyzed different mineral samples from different locations but no variations could be detected. They loaded zinc bromide instead of metallic zinc in order to avoid formation of a conducting layer on the insulators of the ion source.

Rosman [5, 6] used a boat-shaped filament with tantalum sinter into which the sample was loaded in the chloride form and converted to the oxide by treatment with HNO<sub>3</sub> and the application of heat. A tracer highly enriched in  $^{67}\text{Zn}$  and  $^{70}\text{Zn}$  isotopes was employed to calculate the mass fractionation. Völkening et al. [7] measured Zn isotope heterogeneities in meteorites. Sample was loaded with silica-gel and phosphoric acid in a V-shaped Re filament. At 1500-1600 °C a stable beam is obtained with typical ionization efficiency for Zn<sup>+</sup> ions of 0.05%. The Zn isotope ratios were normalized for mass fractionation using  $^{68}\text{Zn} / ^{64}\text{Zn}$  ratio. Chang et al. [8] measured absolute isotopic composition employing synthetics mixtures from enriched isotopes 64, 66 and 68, to calibrate the TIMS, calculating correction factors for each ratio. Ghidan et al. [9] also analysed Zn isotope fractionation ( $\delta\text{Zn}$ ) by TIMS and the double spiking technique in natural materials, enhancing the ionization mixing the sample with H<sub>3</sub>PO<sub>4</sub> and silica gel solution. They also employed a double spike solution enriched in the isotopes  $^{67}\text{Zn}$  and  $^{70}\text{Zn}$ . Maréchal et al. [10] perform analysis of copper and zinc by MC-ICPMS. The instrumental mass fractionation for Zn was corrected with a standard reference material of Cu. Tanimizu et al [11] and Ponzevera et al [12] also employed synthetic isotope mixtures to determine the mass discrimination of their MC-ICPMS.

## Theory

Thermal Ionization Mass Spectrometry is the reference technique to validate isotopic composition. It has a low resolution magnetic field which provides flat-topped peak and a multicollector system to detect simultaneously the different isotopes to preven

fluctuations in signal stability affect the accuracy of the analysis. Both characteristics contribute to be the most precise and accurate of the mass spectrometric techniques [13-17]. In spite of the long time measurement and the rigorous cleanup of the sample, it has relative precision of 0.05 to 0.5% for zinc isotopic ratio measurements [18]. The possibility of observing a significant natural isotopic fractionation for Zn isotopes critically depends on the precision of the measurement.

One of the most important tasks in TIMS is to correct the mass fractionation that occurs due to the preferential sublimation of the lighter isotopes from the filament of the ions source [19, 20].

To determine the mass discrimination factor, it is necessary to measure a certified reference material and its isotopic ratio is compared with the certified value. Unfortunately, it was not available in our laboratory a zinc isotopic reference material, then, it was necessary to measure a pure zinc sample and assume it has the composition listed by IUPAC. An internal normalization cannot be applied because a specific isotopic ratio has not been well studied.

## Experimental

A Finnigan MAT 262 thermal ionization mass spectrometer (Thermo Fischer Scientific, Bremen, Germany) was used. It is equipped with a sample turret for 13 samples, a magnetic sector analyzer and a multi-collector with seven Faraday cups, six of which are adjustable and an ion counter for small signals. The sample was loaded on a zone-refined rhenium filament (Rhenium Alloys, North Ridgeville, OH, USA) in a simple-filament configuration (previously degassed at 4.5 A for 20 minutes). Filaments and holders were used only once.

Analytical reagent grade nitric acid (Biopack, Buenos Aires, Argentina) was purified in-house prior to use by sub-boiling distillation (Berghof Products, Einingen, Germany).

High purity (18 MΩ.cm) deionised water was obtained from an ion exchange deionization resins system Water Pro PS Station (Labconco Co, Kansas City, MO, USA).

In an agate mortar, an amount of silica gel (Yamani, Shiga, Japan) was milled. When a fine powder was obtained, deionised water was added, stirred for a few minutes and let decant most of the silica. The slightly opaque supernatant was transferred and reserve for analysis.

A 0.05 M H<sub>3</sub>PO<sub>4</sub> solution was prepared by dilution from concentrated phosphoric acid 85.0 % (J.T. Baker, Xalostoc, Mexico).

Different natural zinc sources were analyzed: a) Zinc oxide (UCB, Brussels, Belgium), b) zinc metal powder (May&Backer, Dagenham, UK), c) zinc metal powder 100 mesh, 99.999% (Aldrich Chem. Milwaukee, WI, USA), d) zinc metal granular 20 mesh, (Mallinckrodt Chem., St. Louis, MO, USA), e) zinc granular 20 mesh (J.T. Baker Chem. Phillisburg, NJ, USA), f) zinc technical 20 mesh (Matheson, Coleman & Bell, NJ, USA). Samples were dissolved in concentrated nitric acid, dried and redissolved in 0.2 M HNO<sub>3</sub>, obtaining solutions of 5 mg.mL<sup>-1</sup>.

A commercial DZO powder was purchased as one of the typical reagent PWRs used to enhance the passivation of the pipe of the primary circuit. Sample solution was prepared in the same conditions.

## Analysis

Samples were loaded on the filament as  $\text{Zn}(\text{NO}_3)_2$  solutions. In order to avoid that too much heat evaporates the sample from the filament, a double filaments assembly was chosen as first option but no promising results were found with very low and unstable signals. Simple filament configuration was employed later. The signal was too unstable at the beginning due to the high temperature needed to ionize the zinc producing a fast volatilization of sample from the filament. Many loading procedures with different reagents to delay the volatilization and increase ionization of zinc (silica-gel, nitrocellulose, EDTA) were tested. Finally the silica gel/phosphoric acid method [8, 9, 21] with some changes as is described below, was used. A stable and high enough signal was achieved. The addition of these compounds to the sample on a single filament enhances the ionization efficiency [22]. The mechanism is not well known, however it seems that the sample is trapped in a porous ceramic layer at the surface of the rhenium filament, reducing the evaporation rate, maintaining or increasing the ionization efficiency.

Many works studied Zn for naturally produced isotopic variations. Zn is volatile in thermal processes and it has high mobility in liquid environments. Its high ionization potential (9.3942 eV) [23] and relatively low melting point (419.53 °C) [24] hinders an efficient ionization makes it unsuitable for use in conventional mass spectrometer analyses, but the addition of silica gel slurred in phosphoric acid produces a glass as emitter. It produces more stable and reproducible signals.

5  $\mu\text{L}$  of supernatant moist silica gel was placed on the filament and passed a current of 0.7 A to dryness. Then, 10  $\mu\text{L}$  of  $\text{Zn}(\text{NO}_3)_2$  solutions was loaded and let get dry. Finally, 5  $\mu\text{L}$  of  $\text{H}_3\text{PO}_4$  was added and when the first effervescence was detected the current was increased to 1.5 A and maintained at this value until a white fine layer was formed.

During the initial heating of the filament at about 1.3 A, a signal of  $^{39}\text{K}^+$  was first adopted as the monitor mass to centre and focus the ion beam. Then the peak of  $^{66}\text{Zn}^+$  was used as the pilot signal for further heating and centred of the ion beam. The current increased to 2.5 A at which signal of  $^{66}\text{Zn}^+$  appeared and keep heating until a signal of about 0.4 V is reached to ensure a signal higher than 1 mV for the minor isotopes.

When the analysis started, between block of data, the current of the filament was increased to maintain the pilot signal nearly constant during all the analysis.

Loading technique and measuring program were kept identical during the measurements of the sample and the natural sample used as reference, so that the fractionation effect due to the mass discrimination was the same between analyses.

Each measurement consisted in 5 blocks and each one included 10 cycles of the isotope ratios  $^{64}\text{Zn}/^{66}\text{Zn}$ ,  $^{67}\text{Zn}/^{66}\text{Zn}$ ,  $^{68}\text{Zn}/^{66}\text{Zn}$  and  $^{70}\text{Zn}/^{66}\text{Zn}$  simultaneously in static mode using the Faraday multi-collector system (each Faraday cup contains a  $10^{11}\Omega$  resistor) and integration time was 16 seconds. Mass numbers 58 and 74 were analyzed looking for the majority isotopes of Ni and Ge respectively in order to detect the presence of isobaric interferences with their isotopes at 64 and 79 amu. No traces of Ni and Ge were observed so no correction was necessary to apply.

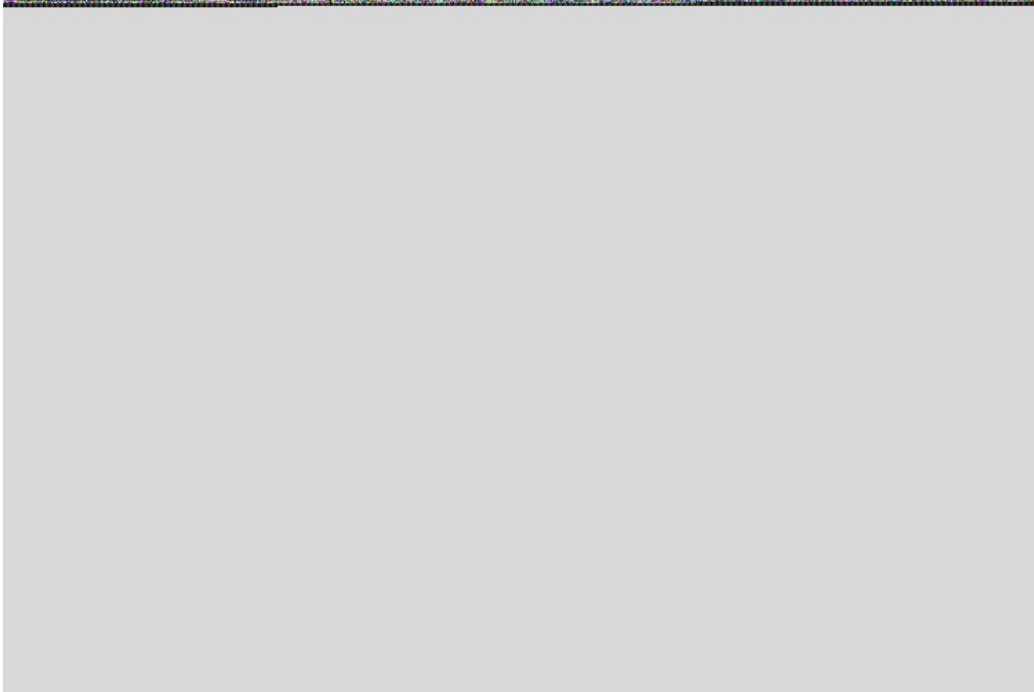
## Results and Discussion

In TIMS analysis, a mass fractionation occurs due primarily to the preferential evaporation of the lighter isotopes from the filament and by selective extraction of the ions by the focusing lens of the ion source.

In Fig. 1 can be seen the time dependency of the  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio of the natural zinc oxide sample.



Fig. 1 Measurement of the isotopic ratio  $^{64}\text{Zn}/^{66}\text{Zn}$  for the natural zinc sample. The full line indicates the average of the ratio.



Six commercial high purity natural zinc samples were analyzed to determine if there were significant differences between each of them with the known value of the isotopic composition of natural zinc published by IUPAC [3]. The observed ratios were not corrected by mass discrimination of the mass spectrometer. The results are shown in Table 1.

Table 1 Isotopic ratio of different commercial natural Zn samples

Sample	$^{64}\text{Zn}/^{66}\text{Zn}$	$^{67}\text{Zn}/^{66}\text{Zn}$	$^{68}\text{Zn}/^{66}\text{Zn}$	$^{70}\text{Zn}/^{66}\text{Zn}$	Rm/Rs <sup>*</sup>
Zinc Metal Aldrich	1.7378 (35)**	0.14602 (12)	0.67459 (90)	0.022425 (66)	1.0072
Zinc Metal Mallinckrodt	1.7570 (05)	0.14534 (09)	0.66802 (29)	0.022017 (49)	1.0183
Zinc Metal J.T.Baker	1.7513 (31)	0.14565 (10)	0.66833 (66)	0.021982 (27)	1.0150
Zinc Metal May & Baker	1.7420 (40)	0.14566 (20)	0.67186 (90)	0.022117 (50)	1.0096
Zinc Metal Math.Col.Bell	1.7533 (13)	0.14558 (14)	0.66963 (90)	0.022172 (93)	1.0162
Zinc oxide UCB	1.7390 (12)	0.14607 (08)	0.67233 (90)	0.022181 (50)	1.0079
IUPAC	1.725 (12)***	0.14663 (85)	0.6800 (48)	0.02256 (33)	

<sup>\*</sup>Rm/Rs: Measured  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio and known  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio (1.725) according with abundances published by IUPAC.

<sup>\*\*</sup>One standard deviation of ratios is given in parentheses.

<sup>\*\*\*</sup>Expanded uncertainty of IUPAC value is given in parentheses.

The first and the last sample of the Table 1 have the closest values to the IUPAC data, but the last one, zinc oxide powder was chosen as reference material for the mass discrimination bias, because it has the same chemical form that the sample to be measured. Besides the natural variations in the isotopic compositions of the element itself, difference between samples may be produced by fractionation during the industrial purification process [11, 12]. The expanded uncertainties of abundance, published by IUPAC [3] include the range of variations among different materials and experimental errors. They were converted to uncertainties of the ratios using conventional procedures.

For correction of mass discrimination, several laws are applied. Determination of the  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio on natural Zn was employed to calculate the mass discrimination bias ( $B$ ); the following formula was used [25, 26]:

$$B = \left( \frac{1}{C} \right) \left[ \left( \frac{R_m}{R_s} \right) - 1 \right]$$

Where  $R_m$  is the average measured  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio,  $R_s$  is the known value of the  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio according with IUPAC and  $C = \Delta M/M$  for various ratios, for example ( $^{64}\text{Zn}/^{66}\text{Zn}$ ) for  $^{64}\text{Zn}$ . The mass fractionation factor was then applied to the measurement of the depleted sample. The  $B$  value in this analysis was 0.2601 ( $1\sigma = 0.0036$ ). The loading technique, the sequence of heating current and measuring program were identical for all the samples.

Table 2 shows the results of five separate repeat measurements of the DZO sample.

Table 2 Isotopic ratios of the depleted zinc sample (DZO)

Analysis	$^{64}\text{Zn}/^{66}\text{Zn}$	$^{67}\text{Zn}/^{66}\text{Zn}$	$^{68}\text{Zn}/^{66}\text{Zn}$	$^{70}\text{Zn}/^{66}\text{Zn}$
1	0.03256	0.3272	1.9866	0.07817
2	0.03273	0.3267	1.9825	0.07738
3	0.03392	0.3251	1.9854	0.07699
4	0.03248	0.3251	1.9762	0.07785
5	0.03323	0.3253	1.9726	0.07740
Average	0.03298	0.3259	1.9807	0.07756
Corrected	0.03272	0.3272	1.9964	0.07880
1 $\sigma$	0.00060	0.0010	0.0060	0.00046

The isotopic abundance of the DZO is shown in Table 3. The relative standard deviation (RSD) is about 1.8 % for the  $^{64}\text{Zn}/^{66}\text{Zn}$  ratio. The combined standard uncertainty was calculated by propagation of three sources of uncertainties: the combined uncertainty of the natural zinc sample used as reference according with the uncertainty in abundance published by IUPAC (considering a  $k$  of 2 for a normal distribution and a 95% of confidence), the standard deviation of the measurements of the reference and the standard deviation of the measurements of the DZO sample. The expanded uncertainty of the sample was obtained multiplying the combined standard uncertainty by a covered factor of 2.

The main source of uncertainty was due the material used as reference, since, as mentioned above, takes into account not only the uncertainty of measurements but also the variation in the natural isotopic abundance of zinc in different samples.

Table 3 Isotopic Abundance of DZO

Isotope	Atom %
64	0.95 ± 0.04
66	29.11 ± 0.16
67	9.53 ± 0.08
68	58.12 ± 0.63
70	2.29 ± 0.04

As can be seen in Table 3, the abundance of <sup>64</sup>Zn is less than 1 %, suitable for use in nuclear power station. As expected, the uncertainty of the most abundant isotopes is greater.

Conclusion

A simple and precise method was developed for zinc isotopic measurements using TIMS. External mass fractionation correction was performed using natural zinc oxide sample as reference in absence of a certified reference material at the laboratory. The method was successfully applied to control the Zn isotopic abundance in a ZnO sample, depleted in Zn-64 isotope, which is employed as corrosion inhibitor in nuclear power plants.

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