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Determination of zinc in geological samples using Compton suppression with thermal and epithermal instrumental neutron activation analysis

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Abstract The determination of Zn in geological samples using instrumental neutron activation analysis is usually done using the $^{64}Zn(n,\gamma)^{65}Zn$ reaction and its 244 day half-life. However this analysis has proven to be potentially difficult. This is due to its relatively low neutron absorption cross section and gamma ray intensity, and the relatively high neutron absorption cross section and gamma intensity of ^{46}Sc, which has an energy peak that is only 5 keV greater than ^{65}Zn. The use of a high resolution detector makes it possible to differentiate between the ^{65}Zn and ^{46}Sc photopeaks peaks. However, the dominating ^{46}Sc gamma ray can even make peak fitting routines unsuccessful in the proper determination of ^{65}Zn. The use of a Compton suppression system suppresses the ^{46}Sc peak, which has two coincident gamma-rays, and this greatly improves the ratio of the height of the ^{46}Sc 1120.5 keV photopeak to the ^{65}Zn 1115.4 keV photopeak. Irradiating the sample with epithermal neutrons also improves the measurement since ^{65}Zn has a higher cross section for epithermal neutrons rather than thermal neutrons, whereas ^{46}Sc has a higher thermal cross section. Another technique to determine zinc is the use of $^{68}Zn(n,\gamma)^{69m}Zn$ reaction with its 13 h half-life using epithermal neutrons and Compton suppression INAA. However, the 438 keV gamma ray of ^{69m}Zn has no interference with any adjoining photopeak. A critical comparison of these two methods is given.

Keywords Zinc · Compton suppression · Geological samples

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Introduction

Instrumental Neutron Activation Analysis (INAA) is one of five primary methods recognized by the Comité Consultatif pour la Quantité de Matière (CCQM), and is often used by the National Institue for Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA) for multielemental analysis of select trace and major elements [1]. INAA is also a non-destructive method, unlike ICP-MS, which is another major method for finding Zn in small samples less than 500 mg [2]. Zinc is potentially a difficult element to measure using INAA, depending especially on the ratio of zinc to scandium which is present in the sample. In the 1980s it was reported that zinc was difficult to determine in geological samples if the scandium to zinc ratio was approximatley the same [3]. In 1990 an exhaustive comparison of 160 geological samples with ICP-MS and NAA, found lack of sensitivity of activation analysis for zinc and other elements [4].

Zinc has a low absorption cross section, especially compared to scandium and europium, both of which can interfere with the major ^{65}Zn photopeak at 1115.5 keV. Natural Zn is made up of ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and a trace of ^{70}Zn. Radiative capture by ^{66}Zn and ^{67}Zn will lead to stable isotopes, and there are no other predominant reactions with neutrons of thermal or epithermal energy that produce radioactive isotopes. The isotope ^{70}Zn is less than 1 % of natural Zn and does not have a high radiative capture cross section. The predominant neutron absorption reactions of ^{64}Zn and ^{68}Zn are radiative capture. We identified both of these isotopes in order to determine which is the best to use to measure zinc concentrations in geological samples by NAA. [5].

The isotope ^{64}Zn, which makes up 49 % of natural zinc, captures a neutron to become ^{65}Zn, which has a half- life of

244 days. It has three decay energies, but only the decay energy of 1115.5 keV has a high enough intensity to be detected at 50.6 % [5]. The difficulty in measuring this peak in geological samples comes from the presense of ^{45}Sc in most geological samples, which is the only naturally occuring scandium isotope. When irradiated, ^{45}Sc becomes ^{46}Sc, which has an 84 day half -life. Scandium has a major peak at 1120.5 keV, which has a much higher intensity than the 1115.5 keV ^{65}Zn decay peak at just under 100 % [5]. Scandium also has a much higher radiative capture cross section than ^{64}Zn, which can be seen in Fig. 1. On the other side of ^{65}Zn peak on the energy spectrum, a ^{152}Eu peak at 1112.1 keV also causes some interference with the ^{65}Zn decay peak. However, the ^{151}Eu from which it is derived is 49 % of the natural abundance of europium, the intensity of the peak is only 37 %, and europium is usually present at lower levels than zinc or scandium. Also, the ^{152}Eu has a 13.5 year half-life, so it decays at a much slower rate than ^{65}Zn, so the interference is less significant than the ^{46}Sc interference. However, ^{151}Eu has a very high radiative capture cross section, as can be seen in Fig. 1. This triplet of 1112.1, 1115.5 and 1120.5 keV gammas can be very challenging to correctly fit in any peak fitting routines, and so the ability to accurately measure zinc from this peak is not only determined by the resolution of the detector, but the peak fitting algorithm as well.

Based on the properties of the ^{65}Zn peak, we expect the detection of zinc to be optimized by using epithermal neutrons and by using a Compton suppression system. It can somewhat be seen from Fig. 1 that the radiative cross section for ^{64}Zn is actually higher for higher energy neutrons than for thermal neutrons, while ^{45}Sc and ^{151}Eu have a much higher radiative cross sections for thermal rather than epithermal neutrons. In fact the ratio of the thermal cross section to the resonance integral for ^{64}Zn is 1.73 ± 0.09, while for ^{45}Sc it is 0.44 ± 0.02 and for ^{151}Eu it is 0.26 ± 0.06 [6]. This means that the peak will be enhanced for ^{65}Zn and suppressed for ^{46}Sc and ^{152}Eu when the samples are irradiated with epithermal neutrons.

The ^{46}Sc gamma ray of 1120.5 keV and the ^{151}Eu gamma ray at 1112.1 keV are both in coincidence with other gamma rays, while the ^{65}Zn gamma ray at 1115.5 keV is not in any conicidence. A Compton suppression system, which is primarily used to reduce background counts in spectra due to Compton scattering, will suppress any coincident gamma rays [7, 8]. Therefore the use of a Compton suppression system and epithermal neutrons should give the best measurement of the ^{65}Zn peak, because of the better ratios of the ^{65}Zn peak to both the ^{46}Sc peak and the ^{152}Eu peak. However, ultimately the accuracy of the detemination of the 1115.5 keV gamma is a function of the resolution of the detector in conjunction with the peak-fitting algorithms.

The isotope ^{68}Zn makes up 19 % of natural zinc, and captures a neutron to become ^{69}Zn, which will decay with a half-life of 56 min, or will decay from a metastable state of ^{69m}Zn with a half-life of 13.8 h. The stable decay emits a gamma ray with almost no intensity, but the metastable isotope decays 99.97 % of the time by isomeric transition to stable ^{69}Zn by a gamma ray of 438.6 keV with an intensity of 94.8 % [5]. Since this decay energy is within the Compton region of the spectra, the background counts will be high, especially for geological samples which have many different photpeaks with a range of energies all

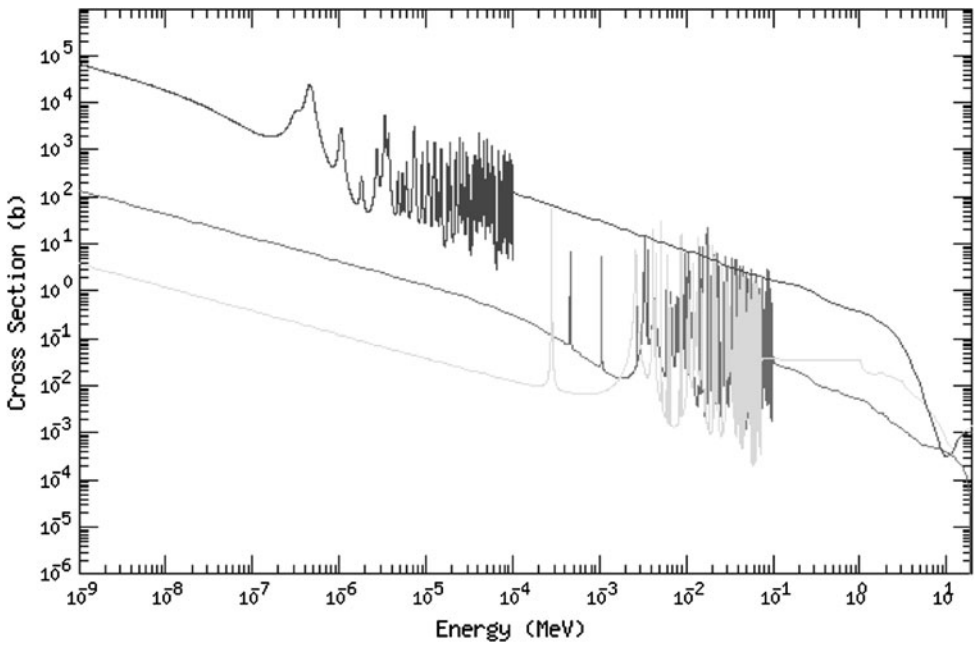

Fig. 1 Radiative capture cross section versus neutron energy of ^{64}Zn (*light grey*, *bottom line*), ^{45}Sc (*dark grey*, *middle line*), and ^{151}Eu (*dark grey*, *top line*). [5]

contributing to the continuum. Since this gamma ray is not in coincidence with other gamma rays, the Compton suppression system can be used to increase the peak to background ratio.

Experimental

In order to determine the best technique for measuring zinc using INAA, the concentration of zinc in NIST coal 1632c, soil NIST 2709, and fly ash NIST 1633a was measured by using three different techniques on each type of sample. Each sample was made in duplicate. Samples were weighed and put into polyethylene containers along with aluminum or molybdenum wires to compare the neutron flux of each sampel. Calibration was done using a liquid standard with a concentrations of 100 ± 0.48 μg/g of zinc. A gram or less of each type of NIST sample was also dried in a 105 °C oven over night and weighed before and after so that the masses could be corrected for moisture content. Irradiations were done at the University of Texas at Austin in a 1 MW TRIGA reactor. The irradiated samples were counted with an ORTEC Gamma-X germanium detector with an efficiency of 32.7 % and FWHM of 2.0 keV at 1.33 MeV ^{60}Co source, and a Na(I) detector used for the Compton suppression system [8]. The different methods used are summarized in Table 1. The neutron fluxes given are estimated based on a flux of 4.5×10^{12} neutrons cm^{-2} s^{-1} at the reactor's maximum power of 1 MW. To get an epithermal neutron flux, the samples are put in a tube lined with cadmium, which reduces the overall flux by about 90 %.

Results and discussion

The results can be seen in Table 2. The results show very good agreement with the certified values, with all measurements falling within the certified range and all deviations lower than 15 %. It is clear from the results that the concentration measurements based on the ^{65}Zn peak had lower uncertainty and detection limits than the measurements based on the ^{69m}Zn peak. However, despite the higher detection limits, at these zinc concentratations this method using the ^{69m}Zn peak is still viable for the measurement of zinc.

In Fig. 2, a spectrum from a short irradiation of NIST 1633a shows the ^{69m}Zn peak at 438.6 keV. When comparing this to Fig. 3, which is of both long irradiations of NIST 1633a showing the ^{65}Zn peak at 1115 keV, it is clear that the peak of ^{69m}Zn has a much lower peak to background ratio than the ^{65}Zn peak. In Fig. 3, the ^{65}Zn peak is not quite as well separated from the ^{46}Sc or ^{152}Eu photopeaks for the thermal spectrum as it is for the epithermal spectrum. The insuffitient separation of the overpowering ^{46}Sc peak may explain why the measurement of the ^{65}Zn peak in 1633a ends up with extra counts and an overestimation of the concentration of zinc, as can be seen in Table 2.

If it is known that the sample has fairly low levels of zinc, scandium, and europium, then it is clear from Table 2 that either thermal or epithermal neutrons can be used to get very good measurements of the zinc concentration providing Compton suppression is employed. When comparing our results to the certified values, all results from the epithermal neutron irradiation gave results that had low

Table 1 Irradiation and decay information for all samples

Sample description	Technique	Flux (n.cm^{-2} s^{-1})	Irradiation time	Decay time
Three of each type NIST sample weighing ~0.3 g	Epithermal	2.25×10^{11}	2 h	3 weeks
Three of each type NIST sample weighing ~0.3 g	Thermal	2.25×10^{12}	2 h	3 weeks
Two of each type NIST sample weighing ~1 g	Epithermal	4.5×10^{10}	5 min	12 h

Table 2 Results and comparison to certified values

*All values in units of (μg/g)		NIST 1632c	NIST 2709	NIST 1633a
Certified values	Concentration	12.1 ± 1.3	106 ± 3	220 ± 10
Measurement by epithermal irradiation and analysis of ^{65}Zn peak	Concentration	11.1 ± 2.7	101 ± 5	218 ± 8
	Detection limit	1.9	3.4	5.6
Measurement by thermal irradiation and analysis of ^{65}Zn peak	Concentration	11.8 ± 1.9	108 ± 4	235 ± 7
	Detection limit	1.4	2.7	5.0
Measurement by epithermal irradiation and analysis of ^{69m}Zn peak	Concentration	12.4 ± 5.9	105 ± 12	222 ± 16
	Detection limit	4.0	6.5	11.4

All uncertainty calculations are a sum of the counting statistics with a slight contribution from drying measurements added in quadrature

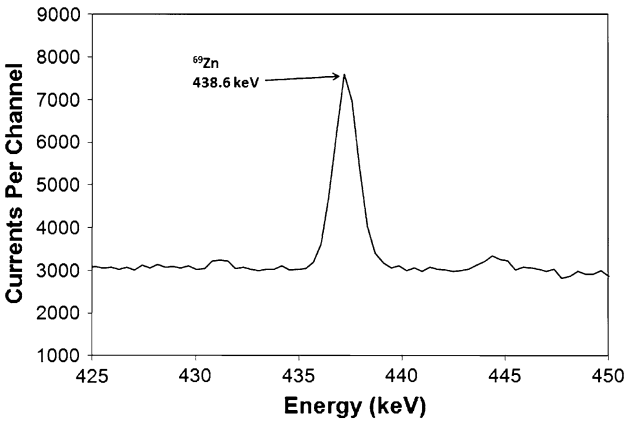

Fig. 2 ^{69m}Zn peak at 438.6 keV from a NIST 1633a sample

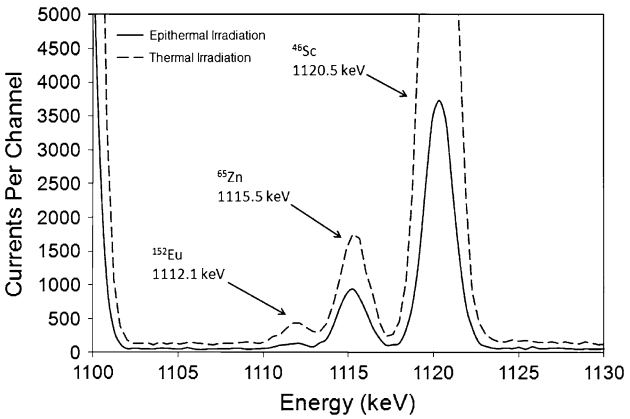

Fig. 3 ^{65}Zn peak at 1115.5 keV with interfering ^{46}Sc and ^{152}Eu from a NIST 1633a sample. The thermal ^{46}Sc photopeak goes was cut off to better see the ^{65}Zn and ^{152}Eu photopeaks

uncertainties and deviations. The thermal neutron irradiation also gave very good results with even lower deviations for NIST 1632c and NIST 2709, except that the deviation for NIST 1633a is fairly high, with measurements of around 133 and 136 μg/g. This overestimation may be due to due to the ^{46}Sc photopeak. NIST 1633a has 40 μg/g of scandium, which is far more than NIST 1632c or NIST 2709, with around 3 and 12 μg/g of scandium respectively. While the separation of the peaks for thermal are still fairly good for the 1633a, the counts between the three peaks do not go quite down to background, as can be seen in Fig. 3. Even though there is more than five times more zinc in the sample than scandium, the ^{46}Sc peak still overpowers the ^{65}Zn peak. The epithermal irradiation reduces this effect quite a bit. For the NIST 1633a peaks, the ratio of scandium to zinc is around 13 for thermal neutrons, and only 5.5 for epithermal. This reduction in peak area ratio should give better results for samples with significant scandium content. This may explain our results, but it is hard to say for certain without more sample repetition.

Conclusion

INAA is often used for multi-element analysis, and is capable of measuring a large number of different elements. Having a reliable INAA method for measuring zinc concentrations increases the usefulness of INAA as a technique. All three methods are in very good agreement with the certified NIST values. However,. if there are low levels of zinc and high levels of scandium or europium are present, using a long irradiation with epithermal neutrons and a Compton suppression system will likely give the most reliable measurement of zinc concentrations.Using the ^{69m}Zn isotope with epithermal neutorns yields good results but the detection limits are higher than using either thermal or epithermal neutrons and ^{65}Zn. While detector resolution and good peak fitting programs are essential for determining zinc the ratio of the ^{46}Sc 1120.5 photopeak to the ^{65}Zn 1115.4 keV photopeak is also an important consideration.

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