# Budget Uncertainty and Minimum Detectable Concentrations for the INAA Laboratory of the ETRR-2

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**Abstract.** The objective of this work is to determine the uncertainty budget and sensitivity of the measurements of the INAA laboratory of the ETRR-2. Concentrations of 9 elements, Ca, Co, Cr, Cs, Fe, K, Mn, Na, and Rb, were measured against a certified test sample. Relative, absolute, and K0-IAEA standardization were employed. Measurements of samples were carried out at 7 cm from the top of HPGe detector. Detector resolution FWHM is 2.1keV for the Co-60 line at 1332.4 keV. The detector is coupled to a computer controlled gamma ray spectrometric system through a chain of associated linear electronics which contain a multi-channel analyzer, and adapted nuclear data software (Gamma Vision) for neutron activation analysis employed for online spectral evaluation.The uncertainty budget in the relative, the K0-IAEA, and the absolute standardization methods ranged from 2-11%, 3-15%, and 6-27%, respectively. Despite that the relative method is the most accurate among the three methods tested, the K0 method is more handy and easier to employ when large amount of data must be processed. The minimum detectable concentration was the lowest for Cs ranging between 0.36 and 0.59 ppb and the highest being for the K in the range of 0.32 to 8.64 ppb.

## 1. Introduction

The Instrumental Neutron Activation Analysis (INAA) is one of the most important applications of research reactors [1]. The INNA laboratory of Egypt Second Training and Research Reactor (ETRR-2) is increasingly requested to perform multi-element analysis to large number of samples from different origins. The INAA laboratory has to demonstrate competence by conforming to appropriate internationally and nationally accepted standards [2]. This includes quantifying the uncertainty in measurements according to some standard methods [3][4][5]. The relative, absolute and k0 methods are used competitively for that purpose [1][2][3][4][5][6]. The objective of this work is to determine the uncertainty budget and sensitivity of the INAA laboratory measurements. Concentrations of 9 elements, Ca, Co, Cr, Cs, Fe, K, Mn, Na, and Rb, were measured against a certified test sample. Relative, absolute, and K0-IAEA standardization were employed. The flux was monitored using two methods (cadmium cover method, and multi-foil method).

## 2. Material

### 2.1. Reference materials

Two reference materials were used. One is certified rock-type test sample (P1), and the other is Certified Reference Material (CRM). The sample and reference were provided from a proficiency test study under the AFRAIV-7 project. Table 1 shows the elements and concentration values in the certification of the CRM.

Table 1. Certificate of the Certified Reference Material (CRM)

| Element | Units | Certified values | Element | Units | Certified values |
|---------|-------|------------------|---------|-------|------------------|
| Ca | g/kg | 57.53 | K | g/kg | 13.78 |
| Co | mg/kg | 2.8 | Mn | mg/kg | 836 |
| Cr | mg/kg | 12 | Na | g/kg | 52.67 |
| CS | mg/kg | 1.5 | Rb | mg/kg | 55 |
| Fe | g/kg | 43.43 | | | |

### 2.2.  Flux monitors

The flux monitors were gold, cadmium cover (foil, tube), gold diluted with aluminum of (gold 0.1% and aluminum 99.9%), nickel, and zirconium, all with purity (99.9%).

### 2.3.  Blanks

Empty polyethylene vials were irradiated with the samples or flux monitors to eliminate the blank and background effects. They can be also used to eliminate the spectrum baseline, which is the sum of the instrumental background and any signal due to interfering species, observed in the region of interest.

## 3.   Procedure

### 3.1.  Sample preparation

Two different reference rock samples with certified analysis were used. One was considered a test (unknown) sample and the other as a comparator. All samples had identical geometrical shape (powder) and were homogenous. Some elements under consideration produce long half-life radionuclides after irradiation and the others produce short ones. Hence, samples were divided into two groups. One group, for counting of short lived isotopes, was irradiate in thermal column position by means of the rabbit system. The other group, for counting of long lived isotopes, was irradiated in the irradiation grid.

Sample number, mass, and irradiation position are summarized in table 2. All samples, short and long irradiation, were placed in polyethylene vials. Pure gold flux monitors were fixed in the cover of the sample or reference vials of the short irradiation samples (Rabbit).  Long irradiated samples were placed into three aluminum cans. Each can contained one vial of test sample, reference sample, gold diluted with aluminum, nickel, zirconium, and empty polyethylene vial as blank. One can contained gold diluted with aluminum covered with cadmium tube of about (2.7 mg). Aluminum cans were placed into sample holder, which were lowered into the irradiation grid position.

### 3.2.  Sample irradiation

Samples and flux monitors were irradiated simultaneously in the rabbit system to control the effect of the flux variation with time. Irradiation in the rabbit system lasted for 60 sec. for the samples and the standards alike. Samples were irradiated in the reactor grid for 4 hours and 35 minuets, and kept in the hot cell until reached safe handling dose.

### 3.3.  Sample counting

Measurements of samples were carried out at 7 cm from the top of HPGe detector with relative efficiency 100%. Detector resolution FWHM is 2.1keV for the Co-60 line at 1332.4 keV.

Table 2**.** Samples identification

| Sample # | Samples type | Irradiation position | Sample mass, mg | Flux monitor, mg |
|---|---|---|---|---|
| 1S | Test sample & pure gold | Rabbit | 122.0 | 9.4 |
| 2S | Test sample& pure gold | Rabbit | 111.1 | 21.4 |
| 3S | Test sample& pure gold | Rabbit | 123.6 | 8.9 |
| 4S | Test sample | Grid | 133.9 | - |
| 5S | Test sample | Grid | 119.8 | - |
| 6S | Test sample | Grid | 140.7 | - |
| 7R | Reference sample &pure gold | Rabbit | 114.8 | 9.0 |
| 8R | Reference sample & pure gold | Rabbit | 117.3 | 7.2 |
| 9R | Reference sample & pure gold | Rabbit | 118.6 | 18.4 |
| 10R | Reference sample | Grid | 134.9 | - |
| 11R | Reference sample | Grid | 117.4 | - |
| 12R | Reference sample | Grid | 135.7 | - |
| Monitors | | | | |
| 13 | Pure gold covered with cadmium | Rabbit | - | 8.4 |
| 14 | Ni sheet | Grid | - | 20.4 |
| 15 | Ni sheet | Grid | - | 12.2 |
| 16 | Ni sheet | Grid | - | 9.2 |
| 17 | Zr sheet | Grid | - | 3.2 |
| 18 | Zr sheet | Grid | - | 3.8 |
| 19 | Zr sheet | Grid | - | 3.2 |
| 20 | Au (1%) +Al (99%) | Grid | - | 3.5 |
| 21 | Au (1%) +Al (99%) | Grid | - | 5.6 |
| 22 | Au (1%) +Al (99%) | Grid | - | 7.1 |
| 23 | Au + Al covered with Cd | Grid | - | 2.7 |

The detector is coupled to a computer controlled gamma ray spectrometric system through a chain of associated linear electronics which contain a multi-channel analyzer, and adapted nuclear data software (Gamma Vision) for neutron activation analysis employed for online spectral evaluation.

In all measurements the samples, references, and the flux monitors were fixed toward the detector in the same position in which the efficiency calibration was performed. For the samples irradiated in the rabbit system the measurements were carried out at two decay times, one after 15 minutes of the irradiation and the second after 3 hours. The counting time was 1800 seconds each.

For the samples irradiated in the reactor irradiation grid the measurements were carried out after different decay times (6, 9, 10, 13, 21, 33 days).

## 4. Results and calculations

Test and reference samples were irradiated sequentially and later measured under the same counting conditions. The net area correction was applied and the concentration of the elements under consideration was calculated and given in table 3.

Table 3. The average calculated concentrations and certified values

| Element | Concentration | Concentration in certificate |
|---------|---------------|------------------------------|
| Ca (Sc-47) | 42.47 g/kg | 37.16 g/kg |
| Co-60 | 15.69 mg/kg | 13.2 mg/kg |
| Cr-51 | 32.44 m g/kg | 32 mg/kg |
| Cs-137 | 1.85 mg/kg | 2.3 mg/kg |
| Fe-59 | 35.01 g/kg | 34.27g/kg |
| K-42 | 13.49 g/kg | 15.69 g/kg |
| Mn-56 | 612.57 mg/kg | 604 mg/kg |
| Na-24 | 27.47 g/kg | 28.64 g/kg |
| Rb-86 | 39.02 mg/kg | 38 mg/kg |

### 4.1.1. Identifying and analyzing uncertainty

The sources of standard uncertainty are grouped according to the individual steps of analysis into three categories uncertainty in sample preparation, uncertainty in sample irradiation, and uncertainty in sample counting. The uncertainties (U) arising from each individual source were evaluated and given in table 4 together with the calculated statistically combined uncertainty.

The final stage is to multiply the combined standard uncertainty by chosen coverage factor in order to obtain the expanded uncertainty. In choosing the value of the coverage factor k set to be 2 with 95% confidence, and the expanded uncertainties shown in table 5.

Table 4. Individual uncertainty components

| Element | $U_{mass} S^a$ | $U_{mass} Std^b$ | $U_{net\ area} S^a$ | $U_{net\ area} Std^b$ | $U_{flux}$ | $U_{Geometry\ difference}$ | $U_{Pulse\ pile\ up}$ | Combined uncertainty |
|---------|------|------|------|------|------|------|------|------|
| Ca | 0.15 | 0.15 | 1.8 | 1.61 | - | 7.3 | 3.2 | 8.33% |
| Co | 0.15 | 0.15 | 0.2 | 0.82 | - | 0.75 | 3.5 | 3.68% |
| Cr | 0.15 | 0.15 | 0.8 | 2.13 | - | 6.2 | 9 | 11.16% |
| Cs | 0.15 | 0.15 | 1.4 | 1.62 | - | 0.5 | 2.5 | 3.34% |
| Fe | 0.15 | 0.15 | 0.1 | 0.12 | - | 0.77 | 2.76 | 2.8% |
| K | 0.15 | 0.15 | 3.1 | 6.79 | 0.8 | 2.1 | - | 7.8% |
| Mn | 0.15 | 0.15 | 0.2 | 0.23 | 0.8 | 3.95 | - | 4.05% |
| Na | 0.15 | 0.15 | 0.1 | 0.14 | 0.8 | 2.33 | - | 2.48% |
| Rb | 0.15 | 0.15 | 2.0 | 1.87 | - | 0.4 | 4.2 | 5.05% |

[a] Sample

[b] Standard

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Table 5. Expanded (budget) uncertainties

| Element | Expanded uncertainties % | Concentration |
|---------|--------------------------|---------------|
| Ca (Sc) | 16.66 | 42.47±7.10 g/kg |
| Co | 7.36 | 15.69 ±1.15 mg/kg |
| Cr | 22.32 | 32.44 ±7.24 m g/kg |
| Cs | 6.68 | 1.85 ±0.123 mg/kg |
| Fe | 5.6 | 35.01 ±1.96 g/kg |
| K | 15.6 | 13.49±2.1 g/kg |
| Mn | 8.1 | 612.57 ±49.61 mg/kg |
| Na | 4.96 | 27.47 ±1.36 g/kg |
| Rb | 10.1 | 39.02 ±3.94 mg/kg |

## 4.2. *Concentration using absolute standardization*

Similar to the relative method, the individual uncertainties were estimated and given in table 6. The combined standard uncertainties were calculated using the absolute standardization equations [4]. Finally the expanded uncertainties were calculated and given in table 7.

Table 6. Individual uncertainty components

| Element | U flux monitor Mass | U Sample Mass | U flux monitor Concentration | U Flux monitor Net area | U Sample Net area | U Geometry difference | U Pulse pile up | U efficiency |
|---------|------|------|------|--------|------|-------|-------|------|
| Ca | 0.15 | 0.15 | 0.01 | 0.037 | 2.49 | - | - | 2.4 |
| Co | 0.15 | 0.15 | 0.01 | 0.037 | 0.31 | 0.32 | 5.7 | 2.4 |
| Cr | 0.15 | 0.15 | 0.01 | 0.037 | 1.13 | 7.83 | 10.75 | 2.4 |
| Cs | 0.15 | 0.15 | 0.01 | 0.037 | 2.08 | 3.17 | 0.89 | 2.4 |
| Fe | 0.15 | 0.15 | 0.01 | 0.037 | 0.13 | 0.32 | 11.05 | 2.4 |
| K | 0.15 | 0.15 | 0.01 | 0.0251 | 3.10 | 10.1 | - | 2.4 |
| Mn | 0.15 | 0.01 | 0.01 | 0.0251 | 0.24 | 2.1 | - | 2.4 |
| Na | 0.15 | 0.15 | 0.01 | 0.0251 | 0.19 | 2.475 | - | 2.4 |
| Rb | 0.15 | 0.15 | 0.01 | 0.037 | 2.89 | 5.03 | 1.12 | 2.4 |

Table 7. Combined and expanded uncertainties

| Element | Combined uncertainty % | Expanded uncertainty % | Concentration |
|---------|------------------------|------------------------|---------------|
| Ca (Sc) | - | - | None |
| Co | 6.2 | 12.4 | 13.15 ± 1.63 mg/kg |
| Cr | 13.56 | 27.12 | 37.43 ± 10.15 mg/kg |
| Cs | 4.5 | 22.64 | 38.20 ± 8.65 g/kg |
| Fe | 11.32 | 9.0 | 2.46 ± 0.22 mg/kg |
| K | 10.83 | 21.66 | 18.78 ± 4.06 g/kg |
| Mn | 3.2 | 6.4 | 541.25 ± 34.6 mg/kg |
| Na | 3.46 | 6.92 | 26.52 ± 1.83 g/kg |
| Rb | 6.38 | 12.76 | 39.95 ± 5.10 mg/kg |

## 4.3. *Concentration using the K0-IAEA method*

The concentration in the K0-IAEA method is determined in three steps. One is to calibrate the detector using a calibration source. Second is to characterize the irradiation positions using gold and zirconium samples for the rabbit system, and gold, zirconium, and nickel samples for the grid positions. The k0-IAEA software need all comparators to be counted simultaneously to construct a single spectrum. All sets of parameters, thermal, epithermal, fast, cadmium ratio factor, non 1/v factor (Alpha factor) of the epithermal neutron flux were determined and stored. Finally, the spectrum and the GammaVision report associated to every sample and comparator were fed to the k0-IAEA software. The program interpreted every series of samples plus comparators and produced the elements concentration given in table 8.

Table 8. The results obtained from the k0-IAEA software

| Element | Concentration | Unit | Detection | Dl units |
|---------|---------------|------|-----------|----------|
| Ca | 32.27±3.22 | g/kg | 0.48 | ppm |
| Co | 11.65±1.4 | mg/kg | 0.0008 | ppm |
| Cr | 31.81±4.14 | mg/kg | 0.0196 | ppm |
| Cs | 1.755±0.31 | mg/kg | 0.0007 | ppm |
| Fe | 34.91±1.43 | g/kg | 0. 782 | ppm |
| K | 13.28±5.4 | g/kg | 0.32 | ppm |
| Mn | 600.1±20.40 | mg/kg | 0.004 | ppm |
| Na | 30.24±1.54 | g/kg | 0.01 | ppm |
| Rb | 40.81±1.38 | mg/kg | 0.61 | ppm |

## 4.4. *Measuring the minimum detectable concentration*

The values of uncertainties obtained in the relative and absolute standardization methods were substituted in the equation;

$$MDC = \frac{(k \cdot s_b)}{m}.$$

Where m is defined as analytical sensitivity and expressed as peak area per concentration in the standard reference material, $S_b$ is the standard deviation of the blank, and k is a factor that is chosen to be 3 for 99.86% confidence level. The minimum detectable concentration evaluated for the three standardization methods is given in table 9.

Table 9. MDC of elements under consideration

| Element | Relative method | Absolute | K0-IAEA |
|---------|-----------------|----------|---------|
| | | ppm | |
| Ca | 0.20 | - | 0.48 |
| Co | 0.0008 | 0.0001 | 0.0008 |
| Cr | 0.0011 | 0.0015 | 0.0196 |
| Cs | 0.0004 | 0.0007 | 0.0007 |
| Fe | 0.26 | 0.12 | 0. 782 |
| K | 0.47 | 8.64 | 0.32 |
| Mn | 0.002 | 0.002 | 0.004 |
| Na | 0.26 | 0.59 | 0.01 |
| Rb | 0.23 | 2.24 | 0.61 |

## 5.  Conclusion

The uncertainty budget in the relative, the K0-IAEA, and the absolute standardization methods ranged from 2-11%, 3-15%, and 6-27%, respectively. Despite that the relative method is the most accurate among the three methods tested, the K0 method is more handy and easier to employ when large amount of data must be processed. The minimum detectable concentration was the lowest for Cs ranging between 0.36 and 0.59 ppb and the highest being for the K in the range of 0.32 to 8.64 ppb.

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