

## ASSESSMENT OF INDUSTRIAL DIAMONDS FOR Co, Cr, Fe, Mn, Ni, AND Si USING THERMAL AND EPITHERMAL NEUTRON ACTIVATION ANALYSIS WITH COMPTON SUPPRESSION

C. Brenan, S. Landsberger\*

University of Texas at Austin, Nuclear Engineering Teaching Lab, Austin, Texas, USA

**Abstract.** An assessment of the trace elemental content in industrial diamonds was performed using thermal and epithermal neutron activation analysis (NAA). For NAA, the elements determined were Mn and Si (short-lived radionuclides) Co, Cr, Fe, Ni (long-lived radionuclides) using normal and Compton suppression counting modes. Quality control was achieved using a NIST standard reference material.

**Keywords:** Diamonds, trace elements, neutron activation analysis

### 1. INTRODUCTION

As with all types of geological materials diamonds have been studied for their trace element concentrations for decades. However, diamonds are unique in that more than 99.95% is made up of only one element, that being carbon. Elemental composition of diamonds can provide evidence to the origin of natural diamonds, including their host rocks and the ever-long processes of evolution [1]. The geochemical signature of diamond-forming fluids can be used to unravel diamond-forming processes [2]. Zonal distribution of inclusions in diamond [3] and impurities [4] has been previously described. Neutron analysis (NAA) has been used for trace analysis in diamonds in several studies [5], including the investigation of the provenance from different areas [6] and comparison of elemental concentration of colorless, pink and brown diamonds [7]. Recently, there has been several studies strongly suggesting that boron is responsible for the blue color in diamonds [8]-[10]. Diamonds made from almost pure carbon is an ideal matrix to use NAA. There are not the usual high backgrounds from the typical activation products of  $^{28}\text{Al}$ ,  $^{24}\text{Na}$ ,  $^{46}\text{Sc}$ , etc. seen in much more abundance in typical activated geological material.

At the request of a private company the Nuclear Engineering Teaching Lab (NETL) was tasked to determine Co, Cr, Fe, Mn, Ni, and Si in industrial diamonds which are used in cutting, grinding, drilling, and polishing procedures. These industrial diamonds typically are not as pure as gem diamonds.

The goal of this research was to maximize the analytical capabilities using thermal and epithermal NAA, and Compton suppression [11]-[13].

### 2. NEUTRON ACTIVATION ANALYSIS

Six elemental concentrations were determined in the diamond samples using instrumental NAA – Co, Cr, Fe, Mn Ni, and Si. Of these elements silicon and nickel are elements not routinely analyzed using NAA.

Silicon is an often-difficult element to analyze in samples with high background count rates for several reasons. There are two candidate reactions for acquiring a silicon signal:  $^{29}\text{Si}(n,p)^{29}\text{Al}$ , which decays via a 1273.4 keV gamma emission with a half-life of 6.56 minutes, and  $^{30}\text{Si}(n,\gamma)^{31}\text{Si}$ , which decays via a 1266.2 keV gamma emission with a half-life of 2.62 hours with a poor branching intensity of 0.05%. Neither of these reactions are ideal – they are not the primary silicon stable isotope ( $^{28}\text{Si}$ , with greater than 90% abundance) and there is a problematic interference in samples with large aluminum concentrations [14]-[16]. The radiative capture of  $^{27}\text{Al}$  produces  $^{28}\text{Al}$ , an isotope which decays with a 2.24-minute half-life and creates peaks at 1778.9 keV (primary emission) and 1267.9 keV (single escape peak from pair production). This single escape peak cannot be resolved from the  $^{31}\text{Si}$  peak within the resolution of most HPGe detectors and can interfere with the  $^{29}\text{Al}$  peak when the aluminum concentration is sufficiently large. For this reason, silicon analysis can be quite complicated, and the choice of reaction is dependent on the concentration of aluminum in the sample, as well as that of other problematic background contributors like  $^{24}\text{Na}$ . The combination of these phenomena suggests another pathway. It has been previously shown [17], [18] the preferred method is to use the 1273.4 keV emission from  $^{29}\text{Al}$  with Compton suppression.

Nickel has similar disadvantages as silicon for traditional NAA. The only feasible the (n, $\gamma$ ) reaction is

\* [s.landsberger@mail.utexas.edu](mailto:s.landsberger@mail.utexas.edu)

$^{64}\text{Ni}(n,\gamma)^{65}\text{Ni}$  reaction with its 2.52 h half-life. However,  $^{64}\text{Ni}$  is only 0.92% abundant and the signal of its strongest gamma-ray at 1481.8 keV belonging to  $^{65}\text{Ni}$  is weak. The  $^{58}\text{Ni}(n,p)^{58}\text{Co}$  charged particle reaction is much better suited.  $^{58}\text{Ni}$  has an abundance of 68.1% and  $^{58}\text{Co}$  has a 70.9-day half-life. Since  $^{58}\text{Co}$  has mainly one gamma ray in its decay at 810.8 keV with 98.8 % intensity, it is ideal to be determined with Compton suppression [19].

### 3. EXPERIMENTAL

#### 3.1. NAA Sample Preparation

Samples were prepared by loading ~2 grams of the diamond powder, ~1 ml of the liquid standard, and ~1 gram of the standard reference material (SRM) into individual 1 cm diameter and 1.5 cm height polyethylene vials and then further encapsulation in 1.5 cm diameter and 5.5 cm height polyethylene vials, which is the diameter required by the pneumatic transfer system. For the liquid standards, both polyethylene vials were heat sealed in order to prevent evaporative losses and radiological contamination of the experimenter and irradiation facility from leakage. Liquids were weighed post-irradiation to account for changes in any mass losses.

#### 3.2. NAA Irradiation and Counting

Irradiations were performed in UT Austin's TRIGA Mark II research reactor using two different facilities. For Fe, Co, Ni, and Cr, which are routinely done and have long-lived activation products, the diamond samples were irradiated with thermal spectrum neutrons in the rotary specimen rack (RSR) facility for 1 hour at a reactor power of 950 kW. Samples were stored and allowed to decay for 2 weeks before being counted for 12 hours each. Si and Mn were determined simultaneously by irradiation in the epithermal pneumatic facility for 10 minutes each at a reactor power of 500 kW (neutron flux  $2.09 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ ). Samples were allowed to decay for 5 minutes before counting for 20 minutes each. The pneumatic and RSR facilities are shown in Figure 1 and Figure 2, respectively.



Figure 1. Pneumatic facility

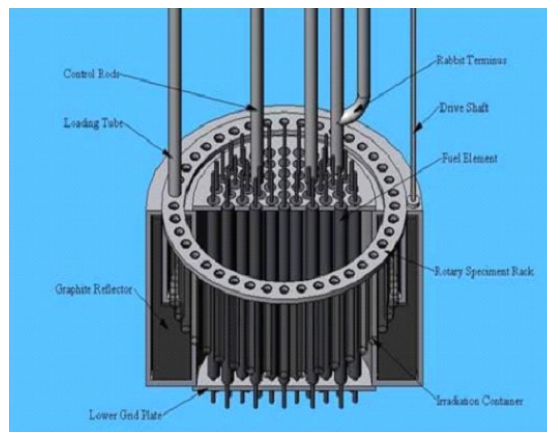


Figure 2. RSR facility

Gamma ray spectroscopy was performed using an ORTEC HPGe detector system with a full width at half maximum of 2 keV for the 1332.4 keV emission of  $^{60}\text{Co}$ . The system is equipped with a Compton suppression system, which consists of a NaI detector annulus in a lead shield into which the HPGe assembly may be raised. With this assembly, counts can be taken in anti-coincidence between these two detectors – this has the effect of eliminating a high fraction of Compton scattering events from the spectra, as Compton scattered photons will be coincident on both detectors within the timing resolution of the gating. In this work, gated and un-gated spectra were collected simultaneously. Compton suppression is advantageous for analysis of peaks which may otherwise be poorly separated from the Compton continuum, but disadvantageous for higher energy peaks or those with coincident emissions. A cutaway view of the Compton system is shown in Figure 3.



Figure 3. Cutaway view of Compton system

The Compton-suppressed data was used for analysis of only Cr, Ni and Si. A summary of the irradiation and counting procedures can be found in Table 1. The reference materials and standards had different irradiation, decay and counting times which were considered by the NADA program [20]. A summary of the isotopic data can be found in Table 2.

Table 1. Irradiation procedure for diamond analysis

Reactor Power	t <sub>i</sub>	t <sub>d</sub>	t <sub>c</sub>
500 KW Epithermal 2.09 x 10 <sup>11</sup> n cm <sup>2</sup> s <sup>-1</sup> (Si, Mn)	10 m	2 m	20 m Si (Compton)  Mn (normal)
950 KW Thermal 2.55 x 10 <sup>12</sup> n cm <sup>2</sup> s <sup>-1</sup> (Co, Cr, Ni, Fe)	1 h	2 weeks	12 h Cr, Ni (Compton)  Co, Fe (normal)

t<sub>i</sub> = irradiation time; t<sub>d</sub> = decay time; t<sub>c</sub> = counting time; Si and Mn had the same counting time of 20 m; Cr, Ni, Co and Fe had the same counting time of 12 h.

Table 2. Relevant isotopic data

Reaction	Half-Life	Gamma-Ray (keV)
<sup>59</sup> Co(n,γ) <sup>60</sup> Co	5.27 y	1332.5
<sup>50</sup> Cr (n,γ) <sup>51</sup> Cr	27y.7 d	320.1
<sup>58</sup> Fe(n,γ) <sup>59</sup> Fe	44.5 d	1099.3
<sup>55</sup> Mn(n,γ) <sup>56</sup> Mn	2.58 hr	1810.7
<sup>58</sup> Ni(n,p) <sup>58</sup> Co	70.9 d	810.8
<sup>29</sup> Si(n,p) <sup>29</sup> Al	6.5 m	1273.4

A comparison of the normal and Compton modes for the determination of silicon is seen in Figure 4. As can be seen the 1273.4 keV peak is almost impossible to discern in the normal mode showing the unique advantage of Compton suppression.

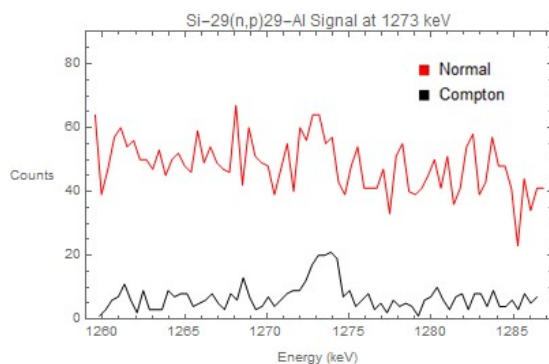


Figure 4. Comparison of normal and Compton modes for silicon determination

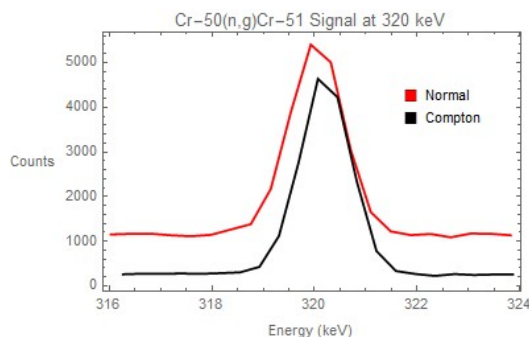


Figure 5. Comparison of normal and Compton modes for

silicon determination

The efficacy of Compton suppression is also depicted in Figure 5 which shows the decrease in background for 320.2 keV photopeak from <sup>50</sup>Cr(n,γ)<sup>51</sup>Cr reaction. Like <sup>29</sup>Al, <sup>51</sup>Cr decays with one gamma ray (Figure 6) making it an ideal radionuclide for Compton suppression. Further, its energy is still in the high end of the efficiency of HPGe detectors.

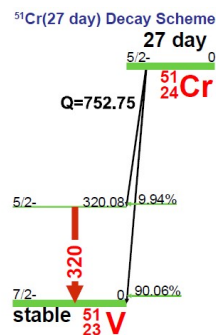


Figure 6. Decay scheme of <sup>51</sup>Cr [21]

#### 4. RESULTS

The results for two industrial diamonds are shown in Table 3 while the quality control results for the National Institute of Standards and Technology (NIST) Montana Soil 2709a are shown in Table 4.

Table 3. Trace element concentration typical detection limits for two industrial diamonds.

Element	Concentration μg/g	Detection Limit [22] μg/g
Cr	3.04 ± 0.17 2.94 ± 0.17	0.06
Ni	42.4 ± 0.9 798 ± 15	0.8
Fe	106 ± 3 1995 ± 40	7
Co	46.3 ± 3.1 (ng/g) 74.2 ± 4.0 (ng/g)	9 (ng/g)
Mn	0.70 ± 0.02 1.74 ± 0.05	0.02
Si	8.31 ± 2.09 9.22 ± 2.15	6.21

Table 4 Trace elemental concentrations of NAA vs NIST 2709a soil

Element	NAA Value μg/g	NIST Value μg/g
Cr	133 ± 7	130 ± 7
Ni	76.1 ± 3.4	85 ± 2
Fe	3.32 ± 0.06 (%)	3.36 ± 0.07 (%)
Co	12.5 ± 0.1	12.8 ± 0.2
Mn	501 ± 15	529 ± 18
Si	29.4 ± 0.9 (%)	30.3 ± 0.4 (%)

As can be seen from Table 3 the results for two industrial diamonds are comparable for Cr, Co, Mn and Si, while those for iron and nickel vary by a factor of

almost twenty. The uncertainty measurements for all the elements vary from 2-6%, except for Si which is 22%. A longer irradiation and counting time could reduce this uncertainty. Quality control results for NAA vs NIST values for 2709a soil are in excellent agreement except for Ni where the result is outside the uncertainty of the NIST value.

## 5. CONCLUSIONS

We have demonstrated that the NAA with epithermal neutrons and with Compton suppression are ideal to determine Cr, Ni and Si. This technique can enhance the range of elements typically seen in conventional NAA. Quality control measurements using NIST standard reference materials were in excellent agreement for all elements except Ni which was just outside the uncertainty range.

**Acknowledgements.** *The authors would like to thank the staff of the Nuclear Engineering Teaching Lab for the support of this research.*

## REFERENCES

1. Y. Weiss, W.L. Griffin, S. Elhoul, O. Navon, "Comparison between LA-ICP-MS and EPMA analysis of trace elements in diamonds," *Chem. Geol.*, vol. 252, no. 3 – 4, pp. 158 – 168, Jul. 2008.  
DOI: 10.1016/j.chemgeo.2008.02.008
2. J. McNeill et al., "Quantitative analysis of trace element concentrations in some gem-quality diamonds," *J. Phys. Condens. Matter*, vol. 21, no. 36, Sep. 2009.  
DOI: 10.1088/0953-8984/21/36/364207  
PMid: 21832313
3. D. M. Bibby, "Zonal distribution of impurities in diamond," *Geochim. Cosmochim. Acta*, vol. 43, no. 3, pp. 415 – 423, Mar. 1979.  
DOI: 10.1016/0016-7037(79)90206-0
4. D. M. Bibby, "Impurities in natural diamond," *Chem. Phys. Carbon*, vol. 18, pp. 1 – 91, 1982.  
Retrieved from:  
<https://ci.nii.ac.jp/naid/80001518268/>  
Retrieved on: Sep. 3, 2019
5. H. W. Fesq, D. M. Bibby, J. P. F. Sellschop, J. I. W. Watterson, "The determination of trace-element impurities in natural diamonds by instrumental neutron activation analysis," *J. Radioanal. Chem.*, vol. 17, no. 1 – 2, pp. 195 – 216, Mar. 1973.  
DOI: 10.1007/BF02520785
6. A. Damarupurshad, R. J. Hart, J. P. F. Sellschop, H. O. Meyer, "The application of INAA to the geochemical analysis of single diamonds," *J. Radioanal. Nucl. Chem.*, vol. 219, no. 1, pp. 33 – 39, May 1997.  
DOI: 10.1007/BF02040261
7. J. J. Fardy, Y. J. Farrar, "Trace-element analysis of argyle diamonds using instrumental neutron activation analysis," *J. Radioanal. Nucl. Chem.*, vol. 164, no. 5, pp. 337 – 345, Mar. 1992.  
DOI: 10.1007/BF02164957
8. E. M. Smith et al., "Blue boron-bearing diamonds from Earth's lower mantle," *Nature*, vol. 560, pp. 84 – 87, Aug. 2018.  
DOI: 10.1038/s41586-018-0334-5
9. E. Gaillou, J. E. Post, D. Rost, J. E. Butler, "Boron in natural type IIb blue diamonds: Chemical and spectroscopic measurements," *Am. Mineral.*, vol. 97, no. 1, pp. 1 – 18, Jan. 2012.  
DOI: 10.2138/am.2012.3925
10. J. M. King, et al., "Characterizing natural-color type IIb blue diamonds," *Gems Gemol.*, vol. 34, no. 4, pp. 246 – 268, Dec. 1998.  
DOI: 10.5741/GEMS.34.4.246
11. S. Landsberger, J. Yellin, "Minimizing sample sizes while achieving accurate elemental concentrations in neutron activation analysis of precious pottery," *J. Archaeol. Sci.*, vol. 20, pp. 622 – 625, Aug. 2018.  
DOI: 10.1016/j.jasrep.2018.05.029
12. M. B. Stokley, S. Landsberger, "A non-destructive analytical technique for low level detection of praseodymium using epithermal neutron activation analysis and Compton suppression gamma-ray spectroscopy," *J. Radioanal. Nucl. Chem.*, vol. 318, no. 1, pp. 369 – 373, Oct. 2018.  
DOI: 10.1007/s10967-018-6071-2
13. S. Landsberger, J. Yellin, "Minimizing sample sizes while achieving accurate elemental concentrations in neutron activation analysis of precious pottery," *J. Archaeol. Sci.*, vol. 20, pp. 622 – 625, Aug. 2018.  
DOI: 10.1016/j.jasrep.2018.05.029
14. I. K. Baidoo et al., "Determination of aluminium, silicon and magnesium in geological matrices by delayed neutron activation analysis based on ko instrumental neutron activation analysis," *Appl. Rad. Isot.*, vol. 82, pp. 152 – 157, Dec. 2013.  
DOI: 10.1016/j.apradiso.2013.07.032  
PMid: 23999324
15. J. Kučera, R. Zeisler, "Low-level determination of silicon in biological materials using radiochemical neutron activation analysis," *J. Radioanal. Nucl. Chem.*, vol. 263, no. 3, pp. 811 – 816, Feb. 2005.  
DOI: 10.1007/s10967-005-0663-3
16. S. Yusuf, "Improving the detection limit of silicon, magnesium and aluminum in neutron activation analysis of polymers using a TRIGA® reactor," *J. Radioanal. Nucl. Chem.*, vol. 282, pp. 99 – 104, Oct. 2009.  
DOI: 10.1007/s10967-009-0212-6
17. S. Landsberger, S. Peshev, D. A. Becker, "Determination of silicon in biological and botanical reference materials by epithermal INAA and Compton suppression," *Nucl. Instrum. Methods Phys. Res.*, vol. 353, no. 1 – 3, pp. 601 – 605, Dec. 1994.  
DOI: 10.1016/0168-9002(94)91732-9
18. S. Landsberger, D. Wu, "Improvement of analytical sensitivities for the determination of antimony, arsenic, cadmium, indium, iodine, molybdenum, silicon and uranium in airborne particulate matter by epithermal neutron activation analysis," *J. Radioanal. Nucl. Chem.*, vol. 167, no. 2, pp. 219 – 225, Jan. 1993.  
DOI: 10.1007/BF02037181
19. B. Canion, S. Landsberger, "Determining trace amounts of nickel in plant samples by neutron activation analysis," *J. Radioanal. Nucl. Chem.*, vol. 296, no. 1, pp. 315 – 317, Apr. 2013.  
DOI: 10.1007/s10967-012-2070-x
20. S. Landsberger, W. D. Cizek, R. H. Campbell, "NADA92: An automated, user-friendly program for neutron activation data analysis," *J. Radioanal. Nucl. Chem.*, vol. 180, no. 1, pp. 55 – 63, May 1994.  
DOI: 10.1007/BF02039903
21. *Gamma-ray Spectrometry Catalog*, Idaho National Laboratory, Idaho (ID), USA.  
Retrieved from:  
<https://gammaray.inl.gov/SitePages/Home.aspx>  
Retrieved on: Sep. 29, 2019
22. L. A. Currie, "Limits for qualitative detection and quantitative determination. Application to radiochemistry," *Anal. Chem.*, vol. 40, no. 3, pp. 586 – 593, Mar. 1968.  
DOI: 10.1021/ac60259a007