

Improving Accuracy, Precision, Detection Limits, and Sample Throughput in PGAA Using Cold and Thermal Neutrons and Element Ratios

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Abstract. A combination of thermal neutron (TN) and cold neutron (CN) PGAA has been used to improve accuracy, precision, detection limits, and sample throughput time in PGAA. CNPGAA was used to measure element ratios relative to a comparator element, while TNPGAA was used for measurement of the comparator element. Low-Z elements with normally poor sensitivity (C, N, and S) were measured with expanded uncertainties of < 2 % in coal and fuel oil using H as comparator element. Using the combined method, measurements can be made with good counting statistics in less than a third of the time needed for TNPGAA alone, with a 20-30 improvement in detection limits.

Key words: prompt gamma-ray activation analysis, thermal neutrons; cold neutrons; radiochemistry; analytical chemistry; hydrogen; carbon; nitrogen; sulfur; low-Z elements; elemental analysis

INTRODUCTION

Prompt gamma-ray activation analysis has long been used for nondestructive elemental analysis of materials. The method is of particular interest for measurement of the light elements (e.g. H, C, N, S, P, Cl), which are difficult to measure by other methods. However, the accuracy and precision of PGAA for elemental determination of hydrogenous materials is limited by the uncertainty in the calibration of elemental sensitivities (cps/mg element), which vary with both neutron scattering power (i.e. hydrogen content) and target geometry.

Up until a few years ago, the thermal neutron (TN)PGAA instrument at VT5 at the NIST Center for Neutron Research (NCNR)¹ was used exclusively at NIST for certification of elements in hydrogenous reference materials. However, this instrument yields poor sensitivities for many low Z elements (C, N, S, P) without irradiations spanning several days, often resulting in poor counting statistics, and hence poor detection limits. Although the NCNR also maintains an instrument for cold neutron (CN)PGAA instrument at neutron guide NGD², which has 15-20 times the sensitivity of the TNPGAA instrument due to the greater neutron capture cross sections, this instrument was not until recently used for certification of elements in hydrogenous materials. This was due largely to the effects of neutron scattering. Neutron scattering by hydrogen in TNPGAA can introduce up to a 10 % bias in element sensitivities over non-hydrogenous materials by altering the paths and hence capture probabilities of neutrons in the sample.³ This effect, which varies with both geometry and hydrogen content can be mitigated by careful matching of geometries and matrices of samples and standards, or by calibrating sensitivities as a function of the two variables. Neutron scattering in CNPGAA introduces a much larger effect (over 50 % bias vs a non-hydrogenous target for a 10 mm thick pellet, arising

from both energy change of neutrons in a room temperature target and the greater neutron scattering cross section, which is more difficult to calibrate.⁴ However, a combination of TNPAA and CNPAA utilizing measurement of element ratios by CNPAA and careful measurement of a comparator element by TNPAA has shown promise. The method takes advantage of the fact that ratios of element sensitivities remain constant with both neutron scattering power and target geometry.⁵ Hence, a comparator element yielding good counting statistics in a short period of time (typically a major component matrix element like hydrogen) may be measured by TNPAA, while element ratios relative to the comparator element are measured by CNPAA. Combination of the data allows determination of all elements measured. A combination of CNPAA and TNPAA was used to measure sulfur in fuel oils at levels down to 0.2 mg/kg with good precision and accuracy in a fraction of the time necessary to make the measurements by TNPAA alone.⁶

In this paper we show how the combination of CNPAA and TNPAA and use of element ratios continues to improve accuracy, precision, and sample throughput time in PAA, with an emphasis on low Z elements that have been difficult to measure with low uncertainty in the past.

EXPERIMENTAL

Measurements were carried out using a combination of the CNPAA and TNPAA instruments, which have been described previously. The TNPAA instrument at VT5 utilizes a vertical beam of thermal neutrons extracted from the NBSR reactor core and passing through an evacuated aluminum beam tube. The CNPAA instrument at NGD makes use of cold neutrons, chilled by passage through liquid helium at 20K, and guided by total reflection through a ⁵⁶Ni lined evacuated guide. Targets for both instruments are suspended by Teflon threads in an aluminum sample holder and irradiated in an evacuable aluminum sample chamber. Prompt gamma-rays emitted from the target upon neutron capture are measured by a high resolution high purity germanium detector inserted into a bismuth germanate Compton suppressor which improves signal to noise ratio. Gamma-ray signal is processed using a digital analyzer, and spectra up to 10 MeV are collected on a PC using commercial software. Table 1 summarizes materials analyzed, standards used and gamma ray peaks analyzed for CNPAA/TNPAA

measurements. A minimum of four replicate samples were measured for each material analyzed with a minimum of four replicate standards used for determination of H, C, N, and S sensitivities and ratios.

Hydrogen, carbon, nitrogen, and sulfur were measured in fossil fuels. The first such measurements using CNPGAA and TNPAA in tandem were carried out for determination of sulfur in fuel oils using hydrogen as the comparator element.⁶ Samples, up to 1.5 g, for CNPGAA were irradiated in Teflon bags analyzed for determination of S/H ratio. Pelletized mixtures of SRM 912a Urea, graphite (Spectrographic Services, 200 mesh), and SRM 143d L-cystine, and urea, graphite, and sodium sulfate (Alfa Puratronic, 99.9955 % metals basis) were used for determination of S/H sensitivity ratios. Approximately 0.5 g samples for H determination by TNPAA were packaged in 1 cm diameter Teflon vials with water, Na₂SO₄ solutions, and ethanol used for calibration of H sensitivity. Hydrogen, carbon, nitrogen, and sulfur were measured in SRM 1632d Trace Elements in Coal (Bituminous) Coal, and SRM 2775 Foundry Coke also using hydrogen as the comparator element. C/H, N/H, and S/H ratios were measured by CNPGAA on 1 g portions of SRM 1632 d powder, which were pressed into pellets using a 13 mm stainless steel die and hydraulic press, and wrapped in aluminum foil to avoid C background from the Teflon packaging normally used. Pelletized urea was used for determination of C/H and N/H sensitivity ratios, while S/H sensitivity was determined using the previously described set of standards. TNPAA measurements were made on 750 mg pelletized samples, with hydrogen sensitivity (cps) calibrated as a function of pellet thickness using pellets prepared from a urea/graphite with similar hydrogen density to the samples (see Discussion). Because SRM 2775 did not pelletize, CNPGAA measurements were made on 500 mg powder samples wrapped in aluminum foil, while TNPAA measurements were made on 500 mg samples in 1 mm diameter Teflon vials, with 500 mg powder mixtures of urea and graphite matching the H mass fraction of the samples used as hydrogen standards. Additional elements were analyzed in SRM 1632 d using chlorine as the comparator element.

CNPGAA/TNPAA measurements for carbon were made on SRM 88b Dolomitic Limestone with calcium used as a comparator element. Pelletized 1500 mg aliquots wrapped in aluminum foil were used for CNPGAA measurement of C/Ca ratios, with similar sized aliquots of SRM 915b Calcium Carbonate (CaCO₃ mass fraction certified at 99.907 %) used as standards.

Pelletized 750 mg samples packaged in 1 mil thick Teflon film were used for TNP-GAA measurement of Ca with SRM 915b pellets used for standards.

Gamma-ray peaks in all spectra were integrated using commercial and in-house software. Table 1 lists gamma-rays used in the analysis for each element.

RESULTS AND DISCUSSION

Results for CNP-GAA/TNP-GAA measurements are given in Table 2. Element fractions for coals and coke are reported relative to dry mass, with drying performed according to instructions given by the Certificate of Analysis. Calcium and carbon mass fractions for dolomitic limestone were converted to CO₂ and CaO using appropriate conversion factors for comparison with certified values. Uncertainties were evaluated at the 95 % confidence level according to the guidelines in the NIST Technical Note 1297,⁷ based on uncertainties from sample and standards replication, peak integration, sample positioning in the beam, variability in neutron flux at the sample position, and moisture determination. PGAA values are in agreement within evaluated uncertainties with certified or reference values given on the certificate of analysis.

A survey of reference materials certified at NIST for carbon, sulfur, and nitrogen between 1991 and 2009 yields only a few contributions for value assignment from TNP-GAA alone (Table 3). For carbon, only one measurement was reported, carbon in 1632c Bituminous Coal with a relative expanded uncertainty of 5.2 %. Expanded uncertainties for nitrogen and sulfur PGAA values submitted for value assignment were mostly between 2 and 5 %, with sulfur in SRM 1648a being the exception. The magnitude of the expanded uncertainties likely reflects both poor counting statistics for samples as well as uncertainties in calibrating elemental sensitivities with neutron scattering power and geometry.

The use of element ratios measured by CNP-GAA in conjunction with calibration of a matrix element with good counting statistics by TNP-GAA, improves the measurement of these elements in several ways. First, because of the much greater sensitivity for these elements by CNP-GAA, carbon, nitrogen, and sulfur may be measured with improved counting statistics without the need for irradiations spanning many days. Second, the use of ratios with a comparator element eliminates the need to calibrate each element individually with H content

and target geometry, thus eliminating the need to prepare mixed standards matching every sample matrix. Only the comparator element need be calibrated, which for hydrogenous references materials (including agricultural and biological SRMs as well as fossil fuels), can usually be hydrogen itself, while element sensitivity ratios may be determined using pure substances or mixtures that contain the elements being measured but need not match the precise composition of the samples. For fuel oils it was shown that liquids with similar H fraction to samples could be used as hydrogen standards, with H sensitivity calibrated against mass. For powdered materials pressed into pellets, pellets prepared from a pure material or simple two component mixture of well measured H content with a hydrogen density approximately that of the sample make ideal calibrants. For pelletized samples and standards of the same diameter, the H count rate divided by pellet thickness serves as the crucial parameter. For SRM 1632d coal, standards of this parameter were prepared from a mixture of urea and graphite as described above, and H sensitivity (cps/mg) was calibrated against pellet thickness, with a linear relationship observed. In yet another example of the ratio method, sulfur was measured in SRM 1577c Bovine Liver using hydrogen as a comparator element. It was found that pelletized portions of SRM 920 D-Mannitol matched the H density of the standards, and were used to calibrate H sensitivity with pellet thickness. In this particular case, both ratios and absolute measurements were made by TNPGAA, with the sulfur sensitivity determined from the H calibration and the S/H sensitivity ratio measured using the previously mentioned mixed standards.

Using the ratio method, C, N, and S were measured in SRM 1632d bituminous coal with relative expanded uncertainties of less than 2 %, as was S in SRM 1623c fuel oil, and C in dolomitic limestone. The significantly higher expanded uncertainties observed in the measurement of these elements in the non-pelletized foundry coke and some of the fuel oils may have been due to the inability to achieve a consistent sample and standard geometry. The larger relative uncertainties determined for other elements measured in SRM 1632d are due to lack of replicate standards containing both elements being ratioed and the need to determine the ratio by more indirect methods. These measurements can be improved by more judicious choice of standards, their inclusion in this paper is merely to illustrate the utility of the method for measurement of a large number of elements.

Although TNP GAA by itself has not previously been used at NIST for value assignment of nitrogen at mass fractions below 3 % or for sulfur below 0.6 %, this work shows that it is possible to measure sulfur at levels close to 0.1 % with good reproducibility, while nitrogen values down to 0.3 % have previously been measured by CNP GAA.⁸ Table 4 lists detection limits for selected low Z nonmetals calculated using equations derived from the work of J. M. Jaklevic⁹ and L. A. Currie¹⁰ for both CNP GAA and TNP GAA. A 20-30 fold improvement in detection limit for CNP GAA over TNP GAA is observed, with other elements showing the same improvement.

Finally, the use of the combined method results in significant reduction in sample counting time over TNP GAA alone, while maintaining good counting statistics (≤ 1 %). Counting times for all samples for ratio measurement by CNP GAA were on the order of a day or less to achieve counting statistics of ≤ 1 % for all elements measured. Since TNP GAA was used only to measure the comparator element (usually H), counting statistics of < 0.5 % were generally obtained in less than half an hour for each sample. Thus, TNP GAA measurements of both SRM materials and standards could be completed with less than a weeks worth of counting. By contrast, it was found that use of TNP GAA alone for the same measurements required at least 3 to 5 days per sample to get adequate counting statistics for nitrogen and carbon. Thus it becomes easily possible to complete all measurements needed for certification of these elements in an SRM (samples, controls, standards) in one 6 week reactor cycle using CNP GAA/TNP GAA, while such measurements might require multiple cycles by TNP GAA alone.

The combined PGAA method has been used to provide C and Ca mass fractions for value assignment of SRM 88c Dolomitic Limestone and S and H values for SRM 1623d Sulfur in Residual Fuel Oil 0.2 %, with expanded uncertainties of < 1.5 % reported for all elements. The results are not given here, since certification of the SRMs has yet to be finalized. The results of these measurements and the ones reported here show that PGAA continues to be an important technique for providing data for certification of H, C, N, S, and other elements, with ongoing improvement in precision, accuracy, and detection limits.

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Table 1. Materials analyzed using the PGAA ratio method.

| SRM/Elements measured | Standards used | Element (s) measured in standard(s) using cold (CN) or thermal (TN) neutrons | Gamma-ray lines analyzed (keV) |
|---|--|--|--------------------------------|
| 88b Dolomitic Limestone | | | |
| CO ₂ | SRM 915b Calcium Carbonate | C/Ca (CN) | 3684 |
| CaO | SRM 915b Calcium Carbonate | Ca (TN) | 1942 |
| | | | |
| 1632d Trace Elements in Coal (Bituminous) | | | |
| H | urea/graphite mixtures | H (TN) | 2223 |
| C | SRM 912a Urea | C/H (CN) | 3684 |
| N | SRM 912a Urea | N/H (CN) | 10828 + EP* |
| S | urea/graphite /Na ₂ SO ₄ ; urea/graphite/SRM 143d L-cystine | S/H (CN) | 841 |
| Cl | urea/graphite/NaCl | Cl (TN) | 786/788 dblt |
| Fe | FeCl ₃ and FeCl ₂ | Fe/Cl (CN) | 7631/7645 dblt |
| Si | Si wafer, Ti foil, ti powder mixtures, NH ₄ Cl | Si/Cl (CN) Si/Ti*Ti/H * H/Cl | 3539 |
| Al | AlCl ₃ | Al/Cl (CN) | 1778 |
| K | KCl | K/Cl (CN) | 770 |
| Ti | Titanium powder/urea/graphite, NH ₄ Cl | Ti/Cl (Ti/H *H/Cl) | 1381 |
| B | urea/SRM 3107 Boron Standard Solution, NH ₄ Cl | B/Cl (CN) (B/H * H/Cl) | 478 |
| | | | |
| 2775 Foundry Coke | | | |
| H | urea/graphite mixture | H (TN) | 2223 |
| C | SRM 912a Urea | C/H (CN) | 3684 |
| N | SRM 912a Urea | N/H (CN) | 10828 + EP |
| S | urea/graphite /Na ₂ SO ₄ ; urea/graphite/SRM 143d L-cystine | S/H (CN) | 841 |
| | | | |
| 1623c Fuel Oil | | | |
| H | H ₂ O, CH ₃ OH | H (TN) | 2223 |
| S | urea/graphite /Na ₂ SO ₄ ; urea/graphite/SRM 143d L-cystine | S/H (CN) | 841 |
| | | | |
| 1577c Bovine Liver | | | |
| H | SRM | H (TN) | 2223 |
| S | urea/graphite /Na ₂ SO ₄ ; urea/graphite/SRM 143d L-cystine | S/H (TN) | 841 |

*Nitrogen count rate was calculated by adding the counts from the 10828 keV plus the double and single escape peaks at 10317 keV and 9806 keV with Compton Suppression turned off.

Table 2. Elements measured in SRMs using CNPGAA/TNPGAA with expanded uncertainties (*U*). Elemental mass fractions marked as * are in mg/kg; all others are in %. Certified and Reference values are denoted as C and R respectively.

| | n | PGAA value (<i>U</i>) | Relative <i>U</i> (%) | Certified or Reference Value (<i>U</i>) |
|--|----------|------------------------------|----------------------------------|--|
| 88b Dolomitic Limestone | 4 | | | |
| CO ₂ | | 46.55 (0.53) | 1.13 | 46.37 (0.12) ^C |
| CaO | | 29.97 (0.20) | 0.67 | 29.95 (0.05) ^C |
| 1632d Trace Elements in Coal (Bituminous) | 4 | | | |
| H | | 5.083 (0.047) | 0.92 | 5.10 (0.05) ^C |
| C | | 76.41 (1.12) | 1.47 | 76.88 (0.15) ^R |
| N | | 1.54 (0.03) | 1.95 | 1.59 (0.01) ^R |
| S | | 1.453 (0.024) | 1.65 | 1.462 (0.074) ^C |
| Cl | | 0.1135 (0.0032) | | 0.1145 (0.0011) ^C |
| Fe | | 0.737 (0.014) | | 0.7490 (0.0160) ^C |
| Si | | 1.73 (0.07) | | 1.65 (0.03) ^R |
| Al | | 0.918 (0.035) | | 0.912 (0.005) ^R |
| K | | 0.1122 (0.0020) | | 0.1094 (0.0026) ^C |
| Ti | | 476(10) * | | 477 (14) ^{*R} |
| B | | 59.6 (2.4) * | | 62 (1) ^{*R} |
| 2775 Foundry Coke | 4 | | | |
| H | | 0.410 (0.010) | 2.44 | 0.41 (0.06) ^R |
| C | | 91.79 (2.39) | 2.60 | 91.34 (0.49) ^R |
| N | | 1.155 (0.032) | 2.77 | 1.160 (0.05) ^R |
| S | | 0.583 (0.016) | 2.74 | 0.5816 (0.0051) ^C |
| 1623c Sulfur in Residual Fuel Oil 0.3 %; | S 4 | 0.3863 (0.0051) | 1.32 | 0.3806(0.0024) ^C |
| 1622e Sulfur in Residual Fuel Oil 2 %; | S 4 | 2.159 (0.072) [†] | 3.34 | 2.133 (0.067) ^C |
| 1619b Sulfur in Residual Fuel Oil 0.7 %; | S 4 | 0.7066 (0.0120) [†] | 1.69 | 0.6960 (0.0077) ^C |
| 1617 b Sulfur in Kerosene High Level; | S 4 | 0.1266 (0.0030) [†] | 2.37 | 0.1250 (0.0025) ^C |
| SRM 1577c Bovine Liver | | | | |
| S | 4 | 0.748 (0.016) | 2.14 | 0.749 (0.034) ^R |

[†]Previously reported [Reference 6]

Table 3. Historical (1991 to 2009) TNPAA measurements (with expanded uncertainties) made for value assignment of C, N, and S in reference materials. Relative uncertainties (%) for PGAA values are given in parentheses. The final certified or reference value is also given. All mass fractions are in %. Reference values for nitrogen (noted by R) are from PGAA only.

| Element/Material | PGAA Value \pm U (Relative % U) | Certified (except where noted) Value \pm U |
|--------------------------------|--------------------------------------|---|
| C | | |
| 1632c Bituminous Coal | 80.7 \pm 4.2 (5.2 %) | 77.45 \pm 0.25 |
| N | | |
| 2781 Domestic Sludge | 4.89 \pm 0.12 (2.45 %) | 4.18 \pm 0.16 |
| 695 Multi-Nutrient Fertilizer | 13.92 \pm 0.38 (2.76 %) | 13.9 \pm 0.4 ^R |
| 1577c Bovine Liver | 10.30 \pm 0.34 (3.30 %) | 10.30 \pm 0.34 ^R |
| 1570a Spinach Leaves | 6.06 \pm 0.20 (3.30 %) | 6.06 \pm 0.2 ^R |
| 1566b Oyster Tissue | 7.6 \pm 0.4 (5.30 %) | 7.6 \pm 0.4 ^R |
| S | | |
| 1632c Bituminous Coal | 1.41 \pm 0.04 (2.84 %) | 1.462 \pm 0.051 |
| 1566b Oyster Tissue | 0.65 \pm 0.03 (4.6 %) | 0.689 \pm 0.014 |
| 1577c Bovine Liver | 0.777 \pm 0.016 (2.06 %) | 0.749 \pm 0.034 |
| 1648a Urban Particulate Matter | 5.45 \pm 0.08 (1.47 %) | 5.51 \pm 0.036 |
| 1848 Lubricating Oil | 2.35 \pm 0.11 (4.6 %) | 2.327 \pm 0.0043 |

Table 4. Detection Limits for some low-Z nonmetals by CNPGAA and TNPAA. Limits are calculated for a 1 g sample or geological or biological material irradiated for 24 h.

| Element | Limit of Detection (μ g) | |
|---------|-------------------------------|-----------|
| | CNPGAA NGD | TNPAA VT5 |
| H | 0.5 | 15 |
| B | 0.003 | 0.068 |
| C | 1000 | 24000 |
| N | 35 | 1800 |
| S | 10 | 220 |
| P | 120 | 2100 |
| Cl | 10 | 220 |