

# Lessons Learned in the Interpretation of Mine Waste Static Testing Results

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## ABSTRACT

A mine waste geochemical characterization program is a fundamental component of the Environmental and Social Impact Assessment (ESIA) for a proposed mine. Typically, the primary objective of the geochemical characterization program is to characterize the acid rock drainage and metal leaching (ARD/ML) potential of mine materials (e.g., development rock, tailing and ore). Often, the laboratory testing program begins with static testing followed by kinetic testing, if deemed appropriate. Static testing is conducted to describe the bulk chemical characteristics of a material and evaluate the potential of a material to leach metals or generate acid. If static testing indicates an ARD/ML potential, kinetic testing is typically conducted to verify whether the various ARD/ML potentials identified will indeed be realized over time, to determine reaction rates, and to assess lag times to acid generation. Static and kinetic testing results often form the basis for the prediction of water qualities during operations and at closure.

This paper discusses the interpretation of results for industry standard static testing procedures. Laboratory testing examples are presented to demonstrate how static test results can be affected by the selection of a particular analytical method or the execution of the selected method. The examples presented include: (1) the potential for contamination from laboratory reagents to affect Net Acid Generation (NAG) test leachate concentrations; (2) the potential for filter selection to bias Synthetic Precipitation Leaching Procedure (SPLP) leachate pH values; and, (3) differences in sulfur and carbon determinations using different analytical methods.

This paper demonstrates the importance of a comprehensive understanding of the laboratory methods and the inclusion of data validation procedures in the development of a robust static testing data set for use in prediction of ARD/ML potential and water quality prediction.

**Keywords:** static, laboratory, NAG, SPLP, ABA, data validation

## INTRODUCTION

A mine waste geochemical characterization program is a fundamental component of the Environmental and Social Impact Assessment (ESIA) for a proposed mine. Typically, the primary objective of the geochemical characterization program is to characterize the acid rock drainage and metal leaching (ARD/ML) potential of mine materials (e.g., development rock, tailing and ore). Often, the laboratory testing program begins with static testing followed by kinetic testing, if deemed appropriate. Static testing is conducted to describe the bulk chemical characteristics of a material and evaluate the potential of a material to leach metals or generate acid. If static testing indicates an ARD/ML potential, kinetic testing is typically conducted to verify whether the various ARD/ML potentials identified will indeed be realized over time, to determine reaction rates, and to assess lag times to acid generation. Static and kinetic testing results often form the basis for the prediction of water qualities resulting from the interaction between mine waste materials and the ambient environment during operations and at closure.

Leach testing is conducted to characterize the metal leaching potential of a mine material. The results of leach tests are sensitive to the methodology used (e.g., solid to solution ratio, nature of the lixiviant, grain size reduction). Therefore, although leach tests provide an estimation of which metals are most likely to leach from a particular material, leachate metal concentrations will exhibit variability related to the specific test methodology used and may not be representative of field-scale conditions. Two examples of how leach test method implementation can affect test results are presented in this paper.

Acid base accounting (ABA) is the industry standard method used to provide an initial assessment of ARD potential of a mine material. The acid generation potential (AP) of a material is derived from a sulfur determination. The most environmentally conservative approach to calculate AP is to make the assumption that all sulfur in a sample is potentially reactive and therefore capable of generating acid; however, this ignores the fact that not all sulfur will contribute acidity. Total sulfur is often determined using a combustion method (e.g., Leco furnace) but acid digestion methods may also be used. Results from these methods are compared in this paper to show differences in calculated AP. The neutralization potential (NP) of a material is often estimated based on carbon analysis. Differences in carbon analysis results by method are also presented.

## STATIC TEST RESULTS AND POTENTIAL PITFALLS

### Net Acid Generation Leachate

The Net Acid Generation (NAG) test is an acid-base accounting test developed initially in Australia but now widely applied internationally. The NAG procedure uses a strong oxidant (hydrogen peroxide) to rapidly oxidize sulfide minerals in a crushed rock sample (AMIRA 2002). The NP of the sample then can be directly challenged by the acidity generated by rapidly oxidizing sulfides. If the sample has sufficient available NP, the alkalinity of the whole rock will not be entirely depleted, and the system is expected to have the capacity to remain circum-neutral. If there is inadequate available NP, then the pH of the test solution will fall below 4.5 and there will be net acidity rather than net alkalinity. In this case, a sample shows potential for acid generation.

The steps in the single-addition analytical procedure from AMIRA (2002) are summarized below:

- **Step 1:** Place 2.5 grams of a pulverized rock sample to a conical beaker.
- **Step 2:** Add 250 millilitres (mL) of 15% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)
- **Step 3:** Cover the beaker with a watchglass and place in a fume hood. Allow the sample to react until boiling or effervescence ceases.
- **Step 4:** Once the reaction is complete, place the beaker on a hot plate and heat until effervescence stops or a minimum of 2 hours.
- **Step 5:** Allow the sample to cool to room temperature. Add deionized water to increase the volume to 250 mL.
- **Step 5:** Measure the pH of the solution.
- **Step 6:** Titrate with sodium hydroxide (NaOH) to a final pH of 7.0.

Increasingly, comprehensive chemical analysis of NAG test leachate is conducted following Step 5 (i.e. prior to back titration). These results may then be used in mine water quality predictions as an indication of worst case or terminal water quality.

For quality assurance/quality control (QA/QC) purposes, it is critical that a blank sample be analysed in association with any NAG leachate analysis. The reagent grade hydrogen peroxide typically used by laboratories contains a number of impurities, including metals. Phosphorus is also present due to the use of phosphoric acid as a stabilizer. Other chemicals used for stabilization may also impart impurities (e.g., colloidal stannates, organophosphonates and colloidal silicates). The pH of hydrogen peroxide is variable due to the presence of stabilizing agents. Acids and bases used in pH adjustment of the hydrogen peroxide are another possible source of impurities. The NAG test method stipulates a target hydrogen peroxide pH between 4.5 and 6.0.

As an example, the specifications for a 30% reagent grade hydrogen peroxide, American Chemical Society (ACS) certified, are shown in Table 1 (Fisher Scientific 2014). An example analysis of a NAG blank for a test conducted with reagent grade hydrogen peroxide is shown in Table 2.

**Table 1** Example of 30% reagent grade hydrogen peroxide specifications

Parameter	Maximum Permissible Concentration (mg/L)
Iron (Fe)	0.5
Nitrate (NO <sub>3</sub> )	2
Sulfate (SO <sub>4</sub> )	5
Copper (Cu)	0.1
Nickel (Ni)	0.1
Ammonium (NH <sub>4</sub> )	5.
Chloride (Cl)	3
Heavy Metals (as Pb)	1
Phosphate (PO <sub>4</sub> )	2

**Table 2** NAG Blank Analysis Results

Param.	Conc.	Param.	Conc.	Param.	Conc.	Param.	Conc.
pH	5.24	Ag	0.00006	Cu	0.00358	Se	<0.00004
Alkalinity	1,600	Al	0.459	F	<0.06	Si	0.15
Cl	4.9	As	0.0005	Fe	0.206	Sn	10.7
SO <sub>4</sub>	5.0	B	0.0128	Hg	<0.00001	Sr	0.0285
P	45.9	Ba	0.00493	Li	0.000327	Ti	0.00237
Ca	5.44	Be	0.000011	Mn	0.0061	Tl	0.000025
Mg	1.43	Bi	<0.000007	Mo	0.00885	U	0.00018
Na	44.2	Cd	0.000425	Ni	0.0388	V	0.00001
K	0.579	Co	0.000878	Pb	0.00094	Zn	0.018
		Cr	0.0536	Sb	0.006	Zr	<0.002

Param = parameter

Conc. = concentration in mg/L for all parameters with the exception of pH

The NAG blank results indicate the presence of a number of metals at concentrations above their respective analytical reporting limits. For some metals/metalloids (e.g., antimony), the reported concentrations are of the same order of magnitude as the water quality standards against which leach test results are often compared (e.g., United States Environmental Protection Agency [USEPA] drinking water maximum contaminant level [MCL] [USEPA 2009]). Phosphorus was measured at a concentration of almost 50 mg/L. The hydrogen peroxide therefore is a likely source of metals and phosphorus. The concentrations of phosphorus and chloride measured in the blank are higher than their respective maximum permissible concentration in the reagent grade hydrogen peroxide. The results for other parameters (e.g., alkalinity and tin) demonstrate the importance of a blank in the interpretation of NAG leachate results.

To reduce the potential for the hydrogen peroxide to be a source of contamination, it is recommended that ultra-pure hydrogen peroxide be used in NAG testing when leachate analysis is performed. This change will result in a significant increase in the cost of laboratory analysis. The cost of reagent ACS grade hydrogen peroxide currently is approximately 15 US\$ per litre compared to 500 US\$ per litre for ultra-pure hydrogen peroxide. Regardless of the type of hydrogen peroxide used, it is recommended that a blank analysis always be performed in association with NAG leachate analyses.

### Synthetic Precipitation Leaching Procedure

The USEPA Synthetic Precipitation Leaching Procedure (SPLP) simulates the short-term interaction between meteoric water and a material (USEPA 1994). This test is frequently used in the mining industry to characterize the metal leaching potential of mine materials.

The SPLP test is conducted at a 20:1 solution to solid ratio. The lixiviant is prepared by the addition of a 60/40 weight percent mixture of sulfuric and nitric acids to reagent water to an end point pH of either 4.2 or 5.0, intended to be comparable to the pH of rainwater. The method calls for use of a pH 4.2 or 5.0 lixiviant for sites located east and west of the Mississippi River, respectively. Sample

preparation may include particle size reduction (<9.5 cm). Following 18 hours of reaction time, the leachate is filtered through a 0.6 to 0.8 µm glass fiber filter prior to chemical analysis.

Review of SPLP test results from multiple commercial laboratories has shown that an increase in leachate pH is sometimes observed following filtration. Example SPLP pH results for five waste rock samples tested using a pH 5.0 lixiviant are shown in Figure 1. These tests were conducted at a 4:1 solution to solid ratio instead of the standard 20:1 ratio. Leachate pH values were measured in the SPLP extraction vessel at the conclusion of testing (blue bars) and after filtration (green bars). The blank sample showed an increase in pH from 5.0, prior to filtration, to 6.2 after filtration. Significant increases (i.e. 10 to 20%) in pH were also observed for two of the five waste rock samples. The samples that demonstrated an increase in pH reported an initial value close to that of the lixiviant. As shown in Figure 2, these samples reported the lowest alkalinity and acidity concentrations and are therefore described as poorly buffered solutions. Poorly buffered solutions are the most susceptible to changes in pH following addition of an acid or base.

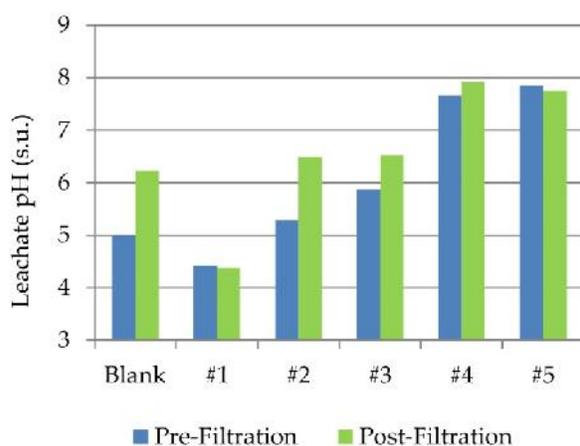


Figure 1 SPLP leachate pH results

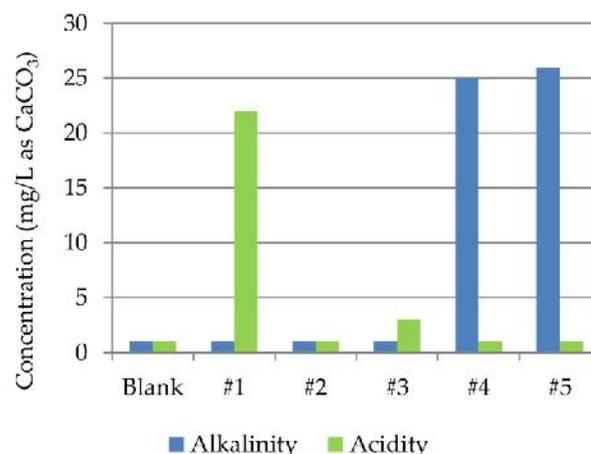


Figure 2 SPLP leachate alkalinity and acidity

Based on the results of additional laboratory testing, it was determined that improper filter preparation was the cause of the observed increase in pH. The potential for changes in the partial pressure of carbon dioxide in sample leachates was considered and discounted as the primary cause of the increase in pH.

The SPLP method stipulates that when evaluating the mobility of metals, filters shall be acid-washed and rinsed prior to use (USEPA 1994). Because the mobility of many metals is pH dependent, often decreasing as pH increases, a change in leachate pH has the potential to affect leachate metal concentrations. Therefore, use of a filter that does not impart a change in leachate pH is fundamental to the accurate determination of metal leaching.

Method specifications for SPLP filters include (USEPA 1994):

- Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8  $\mu\text{m}$ .
- Pre-filters must not be used.
- When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1 normal (N) nitric acid followed by three consecutive rinses with reagent water (a minimum of 1-liter per rinse is recommended).

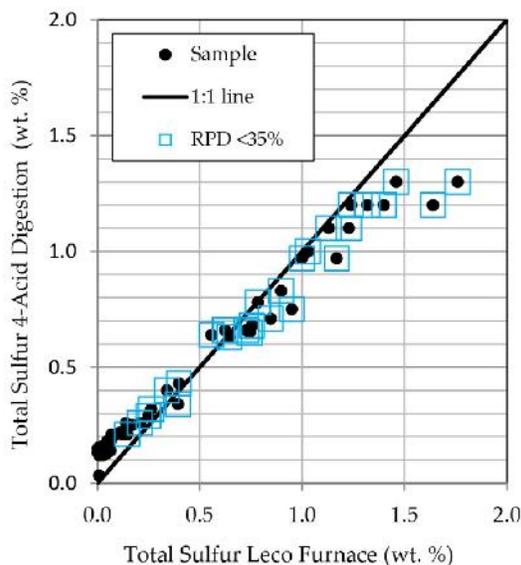
To evaluate the potential for filters to affect leachate pH, it is recommended that a method blank be performed in association with all SPLP tests. Although not stipulated in the SPLP method, it is further recommended that leachate pH be measured before and after the filtration step.

### Total Sulfur Analysis

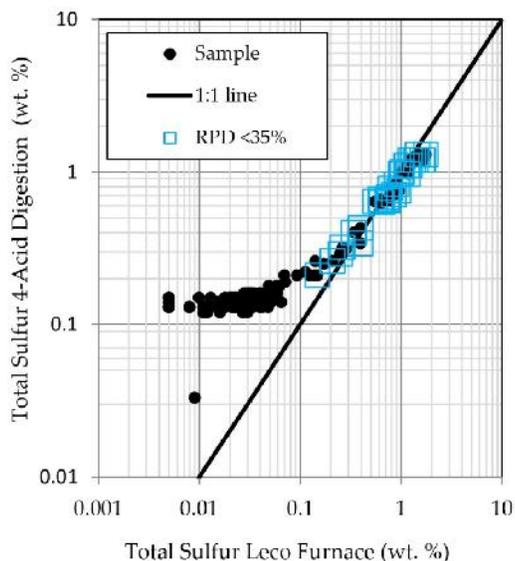
Accurate determination of total sulfur is an essential component of many mine waste management programs. Two common methods for total sulfur determination are combustion (i.e. Leco furnace) and strong acid digestion. Total sulfur determinations using these methods for samples from a magmatic sulfide deposit are compared in Figures 3 and 4 (both figures present the same data on a linear and logarithmic scale, respectively). Each analytical method is described below:

- **Sulfur by Combustion (ASTM 2009)** – Sulfur content is determined by the combustion of a dry and pulverized sample in an oxygen atmosphere. Sulfur in the sample is converted to sulfur dioxide gas. The amount of sulfur dioxide gas evolved is measured by infrared adsorption.
- **Sulfur by Acid Digestion (Rudolph 1979)** - Characterization of the elemental (including sulfur) composition of a sample is a two-step process that includes an acid digestion to release elements into the solution phase followed by analysis of the elements in the resulting digestion. The 4-acid digest used in this study was a mixture of hydrochloric (HCl), hydrofluoric (HF), nitric ( $\text{HNO}_3$ ) and perchloric ( $\text{HClO}_4$ ) acids. The digestion was analysed by inductively coupled plasma (ICP).

In Figures 3 and 4, sample results with relative percent difference (RPD) values between the two results less than 35% are identified. An RPD less than 35% represents acceptable precision for solid phase duplicate analysis (USEPA 2010). These figures show that, at sulfur values greater than approximately 0.15 wt.%, the two analyses yield similar results. Below this concentration threshold, total sulfur values determined by the 4-acid digestion method were consistently higher than values reported by Leco furnace. As shown in Figure 3, at low sulfur values, the combustion method returns values that range from 0.005 to 0.1 wt.%; however, the 4-acid digestion method yields results for these same samples that are consistently higher (i.e. generally in the range of 0.1 to 0.2 wt.%). The reporting limits (RL) for total sulfur by combustion and 4-acid digestion are the same (0.005 wt.%) according to the method descriptions. At total sulfur values greater than 1 wt.%, although the two methods yielded similar results (i.e. RPD <35%), total sulfur by combustion consistently yielded higher values than the 4-acid digest method. This trend is likely attributable to loss of sulfur by volatilization with the 4-acid digest method. Based on the assumption that the Leco furnace results are more accurate, acid potential estimated from total sulfur determined by 4-acid digest would result in a biased high estimate of acid potential at low total sulfur concentrations and a biased low estimate of acid potential at high total sulfur concentrations. Use of mineralogical results is recommended to verify that sulfur determinations provide accurate estimates of AP.



**Figure 3** Total sulfur by Leco versus 4-acid digestion (linear scale)



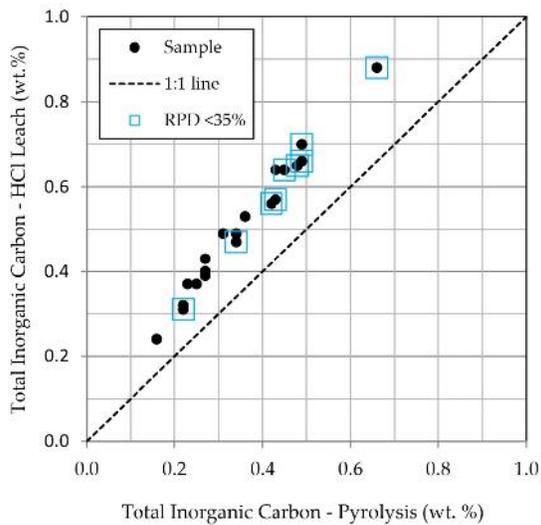
**Figure 4** Total sulfur by Leco versus 4-acid digestion (logarithmic scale)

### Carbon Analysis

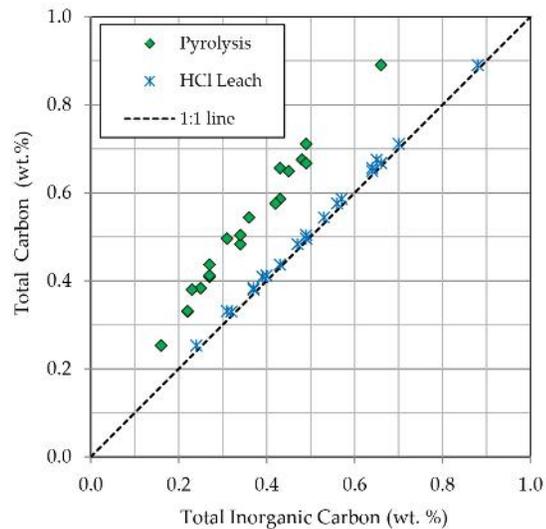
The American Society for Testing Materials method (ASTM E1915-09) for total inorganic carbon (TIC) analysis provides two options: acid leach or pyrolysis (ASTM 2009). For both methods, total carbon (TC) is determined by the combustion of a dry and pulverized sample in an oxygen atmosphere. Carbon in the sample is converted to carbon dioxide gas. The amount of carbon dioxide gas evolved is measured by infrared adsorption. For the acid leach option, TIC analysis is conducted following the method described for TC; however, the sample is treated with hydrochloric acid (HCl) prior to analysis to remove the inorganic carbon fraction. TIC is then determined by difference (i.e. TC minus residual carbon following an acid leach). The pyrolysis method does not include a pre-treatment step. Instead, the sample is combusted at 550 °C to promote volatilization of organic carbon. The residual carbon (residue) is reported as TIC. Because siderite [FeCO<sub>3</sub>] may decompose below 550 °C, the pyrolysis method may underestimate the TIC content of a sample when siderite is present (ASTM 2009).

TIC analysis results for 20 gold mine tailing samples are shown in Figure 5. For these samples, TIC values determined by HCl leach consistently yielded higher concentrations than TIC determined by pyrolysis. As shown in Figure 6, TIC by HCl leach was essentially equal to TC. TIC determined by pyrolysis indicated the presence of an organic carbon fraction (i.e. organic carbon equal to the difference between TC and TIC).

Mineralogical analysis by X-ray diffraction (XRD) indicated that the dominant carbonate mineral in all tailing samples was calcite [CaCO<sub>3</sub>], with concentrations ranging from 1.2 to 5.8 wt.%. Siderite was identified in six samples at concentrations of <1 wt.%. TIC values determined by the acid leach and pyrolysis methods are compared to TIC calculated from mineralogy in Figure 7. Compared to the mineralogy results, TIC by acid leach generally overestimates TIC and TIC by pyrolysis often underestimates TIC. The presence of siderite does not appear to affect this trend.

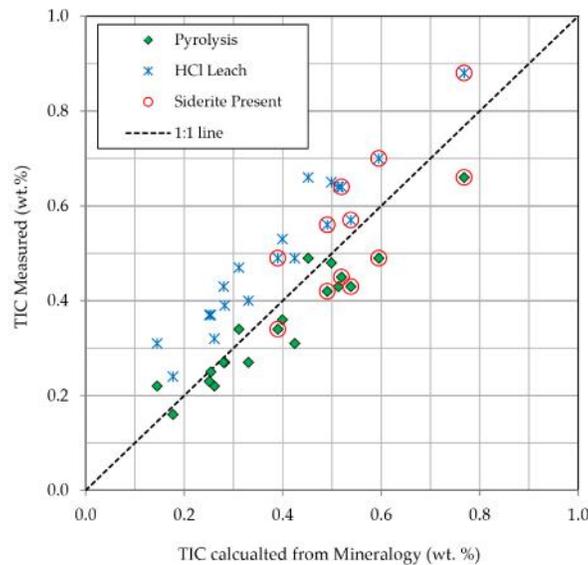


**Figure 5** Total inorganic carbon by two methods carbon



**Figure 6** Total inorganic carbon versus total carbon

The average AP of the 20 tailing samples calculated from sulfide sulfur was 61 kg CaCO<sub>3</sub>/t, whereas the average NP determined from calcite was 31 kg CaCO<sub>3</sub>/t. The average difference in NP determined from TIC by the two methods was 13 kg CaCO<sub>3</sub>/t, roughly one third of total NP. For a few samples, the difference in calculated NP is significant as the difference resulted in a change in the ARD classification of the sample as determined by neutralization potential ratio (NPR). Therefore, for these samples, even a small difference in estimated NP based on TIC is considered significant. Use of mineralogical results is recommended to verify that TIC determinations provide accurate estimates of NP.



**Figure 7** Comparison of total inorganic carbon by three methods

## SUMMARY AND CONCLUSION

The examples presented in this paper demonstrate the importance of a comprehensive understanding of the laboratory methods and the inclusion of data validation procedures in the development of a robust static testing data set for use in water quality predictions. Development of QA/QC procedures is required to evaluate the accuracy and precision of the analytical results prior to use in predictions.

As demonstrated by the NAG and SPLP examples, inclusion of a method blank is recommended for QA purposes. Method blank results should be used to evaluate laboratory contamination and confirm the target lixiviant pH. Although not specified in the SPLP method, measurement of leachate pH before and after filtration is recommended. When NAG leachate analysis is conducted, use of ultra-pure hydrogen peroxide is recommended.

Acid base accounting is the industry standard method to provide a preliminary indication of a material's ARD potential. As demonstrated by the examples presented in this paper, the analytical method selected for sulfur and carbon determinations may affect the results, and therefore the estimates of AP and NP. For the total sulfur determination example presented in this paper, total sulfur determined by Leco furnace is considered more accurate than total sulfur determined by 4-acid digest. For both sulfur and carbon determinations, use of mineralogical analysis results is recommended to verify that total sulfur and TIC determinations provide accurate estimates of AP and NP, respectively.

## REFERENCES

- AMIRA International Ltd. (AMIRA) (2002) *ARD Test Handbook – Project P387A Prediction and Kinetic Control of Acid Rock Drainage (Appendix C)*, May, pp. D1– D5.
- American Society of Testing Materials (ASTM). 2009. Standard Test Methods for Analysis of Metal Bearing Ores and Related Materials by Combustion Infrared Adsorption Spectrometry. E 1915-09.
- Fisher Scientific (2014) Hydrogen Peroxide, 30% (Certified ACS), Fisher Chemical Specifications, <http://www.fishersci.com/>.
- Rudolf, B. (Ed.) (1979) *A Handbook of Decomposition Methods in Analytical Chemistry*, Halsted Press, Div. Wiley & Sons, New York.
- United States Environmental Protection Agency (USEPA) (1994) *Method 1312 – Synthetic Precipitation Leaching Procedure (Revision 0)*, September.
- USEPA (2009) National Primary Drinking Water Regulations, EPA 816-F-09-004, May.
- USEPA (2010) USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review – Final, EPA 540-R-10-011, January.