

(R) Determination of Trace Elements in High Temperature Alloys

1. SCOPE:

This SAE Aerospace Recommended Practice (ARP) describes procedures for solution and solid graphite furnace atomic absorption spectrometric determination of lead, bismuth, selenium, tellurium, and thallium in nickel and cobalt high temperature alloys. Other analytical methods are able to provide the required accuracy and are mentioned herein.

2. APPLICABLE DOCUMENTS:

The following publication forms a part of this specification to the extent specified herein. The latest issue of SAE Publications shall apply.

2.1 SAE Publications:

Available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001.

AMS 2280 Trace Element Control, Nickel Alloy Castings

2.2 The following literature is cited as background on the development of the analytical procedures described herein:

2.2.1 Background Correction Techniques:

Slavin, W., Carnick, G. R., "CRC Critical Rev. Anal. Chem." 19 (1988) 95-134

2.2.2 Solution GFAAS Method:

Welcher, G. G., Kriege, O. H., Marks, J. Y., "Anal. Chem." 46 (1974) 1227-1231

Sotera, J. J., Cristiano, L. C., Conley, M. K., Kahn, H. L., "Anal. Chem." 55 (1983) 204-208

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2.2.3 Solid GFAAS Method:

Marks, J. Y., Welcher, G. G., Spellman, R. J., "Applied Spectroscopy" 31 (1977) 9-11

Irwin, R., Mikkelson, A., Michel, R. G., Dougherty, J. P., Preli, F. R., "Spectrochim Acta, Part B" 45B (1990) 903-915

3. DISCUSSION:

A variety of spectroscopic and spectrometric techniques have been found to be satisfactory for determining trace quantities of deleterious elements at levels prescribed by AMS 2280. Graphite furnace atomic absorption spectrometry (GFAAS) is currently the most widely practiced technique for this application. The acid dissolution GFAAS procedure is well suited to routine bulk analysis and the solid GFAAS method can be used for rapid single sample or spatial profile applications. Procedures for both methods are detailed herein. Other methods are available that also provide acceptable results. These methods are listed in Section 7.

4. INSTRUMENTATION SPECIFICATIONS AND PARAMETERS:

4.1 Equipment:

The following procedures require the use of an atomic absorption spectrometer and a graphite furnace sampling device. The spectrometer must also be capable of performing background correction during the analysis. Surface equipment is available from a variety of manufacturers.

4.2 Operating Parameters:

Specific parameters concerning the operation of atomic absorption equipment are available from the various manufacturers. The measurements are usually carried out at the wavelengths shown in Table 1 using electrodeless discharge lamps (EDLs) or hollow cathode lamps (HCLs):

TABLE 1 - Wavelength Parameters

Element	Wavelength (nm)
Selenium	196.0
Tellurium	214.3
Bismuth	223.1
Lead	283.3
Thallium	276.9

4.2.1 Note that alternative wavelengths may sometimes be necessary if matrix atomic absorption occurs at the recommended wavelengths.

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4.2.2 Optimum graphite furnace operating parameters must be determined for each element to be analyzed, given a particular instrument manufacturer, background correction scheme, and alloy composition. The furnace cycle is nominally comprised of a drying step, an intermediate "char" step and an atomization step. The temperature and duration of the dry step is selected to ensure that the sample (if liquid) does not splatter during subsequent furnace heating. The "char" temperature and duration is determined empirically. The temperature and duration of this cycle is chosen to reduce matrix effects on the analytical signal. The selected conditions should give rise to the optimum signal to noise ratio. The atomization temperature can be determined in a similar fashion. Best results are generally obtained by using the maximum furnace heat-up rate for the atomization step. All determinations should be carried out using pyrolytically coated graphite tubes with a solid pyrolytic graphite platform installed.

### 4.3 Background Correction Methods:

Several methods of background correction have been found to be acceptable for the analysis of trace elements in high temperature alloys. Zeeman background correction and the so-called Smith-Hiefjte" background correction schemes have been used successfully. Dueterium arc background correction was widely used in the past and is still acceptable.

## 5. STANDARDS AND CONTROLS:

Instrument calibration can be accomplished using synthetically prepared standard solutions that match the matrix of the samples to be analyzed, bracket the upper and lower limits of suspected analyte concentration, and contain the same amount of acid as the samples. Only spectroscopically pure or certified reagent grade chemicals of known composition should be used. If available, instrument calibration may be performed using solid standards or solutions prepared from alloy-matched solid standards. Control samples, if available, can be analyzed along with the samples to validate the procedure. For example, National Institute of Standards and Technology (NIST) standards 897, 898, and 899 contain known levels of lead, bismuth, selenium, tellurium, and thallium in a nickel alloy matrix. Solution preparation procedures for analyte stock solutions, calibration standards, and control samples are described herein.

### 5.1 Analyte Stock Solutions:

Lead, bismuth, tellurium, selenium, and thallium solutions (1.00 mg/mL) are prepared by dissolving the appropriate amount of high purity metal in dilute nitric acid. Certified stock solutions are also available from a number of suppliers.

### 5.2 Calibration Standards (Solution):

Standards can be prepared by combining a solution of pure alloy with know amounts of analyte elements. Solution that contain 1 ppm or less of the analyte elements should be prepared daily. Alternatively, the analyte elements can be added to an alloy matrix solution prepared from pure metal solutions. The metal alloy matrix solution should be prepared such that the elements will remain in solution. The total metal concentration should be 1.00 g/50 mL to be consistent with the sample concentration.

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5.2.1 For particular analyses the use of matrix matched standards may not be necessary. Techniques have been developed that utilize a calibration standard containing the analyte and a “matrix-modifier” element. Care must be taken when using this method to ensure that the analyte absorption behavior is identical in the matrix-modified sample and the calibration standards.

### 5.3 Calibration Standards (Solid):

The solid standards must have a composition similar to the alloy to be analyzed, and must have known content of trace elements at concentrations similar to those in the samples. If ingots are used, retain one ingot for a baseline comparison. Remelt the remaining material and cast one ingot with no additions. To the remaining melt or melts, make additions of high purity metal of the trace elements of concern to produce a series of standards containing up to two times the maximum permitted amount of each trace element. The solid standards must be checked for composition and homogeneity, preferably by interlaboratory round robin testing, before being used as standards.

### 5.4 Control Solutions:

Control solutions should be prepared along with the samples, using the same dissolution procedures (see 6.1.1). The control solutions should be analyzed with the samples, and the resultant analyte values should be within the limits specified on the certificate of analysis. In the event that the results fall outside of the certificate limits, the procedure must be repeated. New samples, controls, or standards must be prepared as appropriate.

## 6. ANALYTICAL PROCEDURES:

### 6.1 Graphite Furnace Atomic Absorption Spectrometry - Solution Method:

This procedure is recommended for analysis of materials which are coarse-grained or where the trace elements may otherwise be segregated. Use of a larger sample size minimizes such affects.

#### 6.1.1 Sample Discussion:

##### 6.1.1.1 Microwave Oven Digestion Method:

Weigh, to an accuracy of 0.001 g, 1.00 g of chips, (prepared as in 6.2.1) from the material to be analyzed. Transfer chips to a polytetrafluoroethylene (PTFE) microwave vessel designed for sample digestion. Appropriate microwave vessels can be sealed and have pressure relief valves built in. Observe all safety procedures provided by the equipment manufacturer. Choose an acid mixture that will dissolve the sample. For most samples the following procedure is adequate: add approximately 2.5 mL nitric acid, 0.6 mL hydrofluoric acid, and 7.0 mL distilled deionized water. Seal vessel and place in microwave oven to dissolve chips. Choose microwave oven conditions such that the pressure capacity of the PTFE vessel is not exceeded. When dissolution is complete, cool, open vessel, and transfer the content to a 50 mL volumetric flask. Dilute to volume with water.

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- 6.1.1.2 Open Hot Plate Digestion Method: Weigh sample as in 6.1.1.1. Transfer the chips to a 250 mL PTFE beaker and dissolve in a 10 mL of a 1:1:1 mixture of nitric acid, hydrofluoric acid, and distilled deionized water. Alternatively, a mixture of 2 mL hydrofluoric acid, 2 mL nitric acid, and 15 mL water has been found to be effective in dissolving nickel alloy samples. Warm as necessary to dissolve chips. When dissolution is complete, reduce the volume to approximately 5 mL by evaporation on the hot plate. Add approximately 20 mL water and heat to dissolve all salts. Cool, quantitatively transfer to a 50 mL plastic volumetric flask, and dilute to volume with water.
- 6.1.2 Furnace Parameters: Furnace time and temperature conditions should be selected as described in 4.2. The standard and sample aliquot should be chosen to provide optimum signal to noise ratio and to ensure that the analysis occurs in the linear portion of the calibration curve. Aliquots of 0.010 to 0.050 mL are generally used; follow the equipment manufacturer recommended guidelines. The precision of the analysis is improved by using an automatic sampling device.
- 6.1.3 Data Collection, Calibration, and Data Reduction: The background corrected integrated absorbance, or peak area, should be measured for each standard, sample, and control solution. At least two atomizations should be performed for each solution. The concentration of the analyte should be plotted against peak area for all of the standards. Most modern GFAAS instruments perform this calculation automatically. For best results, a linear calibration graph should be used. If the calibration graph is not linear, then the instrument parameters, or the sample volume should be adjusted, and data collection should be repeated. The sample and control concentrations are determined by comparing the measured peak area signal to the calibration graph. The concentration of the analyte in the original alloy sample is determined by multiplying the measured concentration by the appropriate dilution factor and dividing by the sample weight.
- 6.2 Graphite Furnace Atomic Absorption Spectrometry - Solid Chip Method:
- Because of the very small sample size used for this method, its use is most appropriate for analyzing fine-grained, chemically homogeneous materials. Analysis of multiple samples must be performed to obtain results which accurately reflect the concentration of trace elements in the alloy being analyzed.
- 6.2.1 Preparation of Chips: Chips must be milled from the solid specimen using tools and techniques that will not contaminate the millings. The use of abrasives to prepare chips should be avoided. A representative sample of alloy must be obtained. Generally 5 g of millings is sufficient. The machining conditions must be selected to provide chips with mass of 0.1 to 5 mg. An analytical microbalance capable of weighing a chip with an accuracy of 0.01 mg is required.
- 6.2.2 Furnace Parameters: Furnace conditions should be selected as described in 4.2, except that the need for a dry step is not necessary for the solid sample. Some instrument manufacturers offer solid sampling accessories that use a cup rather than a platform to contain the sample. After repeated use, the solid sample tends to build up inside of the furnace cup or platform, in which case the cup or platform must be replaced. The material can subsequently be removed by dissolving it from the graphite, and the cup or platform may be reused.