# Compositional Analysis by Spark Discharge in Argon - Optical Emission Spectroscopy (SDAR-OES)

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## 1 INTRODUCTION

The concentrations of selected elements in metallic objects can serve to chemically characterize their source. The concentrations of the elements intentionally added to an alloy are controlled by manufacturers to impart specific metallurgical properties required for a given product. Intentionally added elements are commonly specified to fall within a particular concentration range for a given alloy. Other elements are specified at maximum levels which the manufacturer may not exceed but which may otherwise vary considerably. Spark Discharge in Argon-Optical Emission Spectroscopy (SDAR-OES) is a destructive technique that can detect such variations in elemental concentrations, and thus provide means for identifying the alloy designation of a product, differentiating among the same alloy produced by different manufacturers, and distinguishing among specific production runs made by a single manufacturer.

## 2 SCOPE

This document applies to case working personnel using SDAR-OES in support of metallurgy examinations. It supplements METAL-210 with procedures for using SDAR-OES to perform quantitative compositional analysis. Operational procedures for specific alloy classes or specimen sizes are detailed in supplemental technical procedures.

## 3 SPECIMENS

Specimen preparation method, spark stand components, and arc-spark protocol are specific for the alloy class being analyzed. This procedure can be used for the analysis of metal alloy classes for which the instrument has been validated. Specimens must be large enough to completely cover the analysis area to permit their examination by the method outlined here. The surface to be analyzed must also be flat with any nonmetallic debris and scale removed.

## 4 EQUIPMENT

- SpectroLab LAS01spectrometer
- Spectro iCAL standard
- Standardization materials provided by the instrument manufacturer
- Specimen preparation equipment specific to the alloy class being analyzed
- High purity argon
- One or more certified reference material(s) (CRMs) matrix-matched to the alloy class being tested
- Additional reference materials, as needed
- Spark stand insert (waveguide), tungsten electrode and wire brush dedicated to the alloy class being tested
- Small specimen spark stand plate with insert, 6 mm diameter opening (optional)
- Vacuum cleaner with precision nozzle attachment
- Lint-free wipes

## 5 STANDARDS AND CONTROLS

Manufacturer-provided standards are used for re-profiling the optical system (iCAL specimen) and calibration standardization (materials specific to the alloy class being analyzed.) Proper standardization is verified using one or more CRMs in the same alloy class. The specific CRMs are chosen by the operator to demonstrate adequate performance of the instrument (accuracy) for the elements of interest in a particular analysis. Additional reference materials may be used to further demonstrate instrument performance on a specific element within a similar matrix.

## 6 PROCEDURE

### 6.1 Prepare Specimens

Specimens measured by SDAR-OES must be flat and free of debris and scale over the entire analysis region. The method of specimen preparation for any specific alloy class is detailed in supplemental technical procedures. Typically, steels are ground on zirconium oxide abrasive paper, cast irons are abraded using a swing grinder with $Al_2O_3$ abrasive, and softer, non-ferrous materials are turned on a lathe. Other methods of preparation may be suitable, but quantitative analysis must be validated for any alternate preparation method.

A. For the iCAL optic re-profiling standard, follow the steel preparation technique.

B. Analyze the evidence using non-destructive means (e.g., X-ray fluorescence spectrometry). to determine the appropriate allow-class technical procedure and instrument software routine for SDAR-OES analysis.

C. For the evidence, standardization and verification materials, follow the preparation method for the appropriate alloy class.

### 6.2 Clean Instrument

A. Turn off power (“Source”) to the spark stand when opening stage plate and cabinet.

B. Assure that there is sufficient water in the system and that the air filter is not saturated with soot. Fill or exchange as necessary.

C. Inspect the spark stand components for soot accumulation. Vacuum if necessary.

D. When the spark stand components are changed in order to run a different alloy class, the spark stand must be thoroughly cleaned.

E. Prior to running the re-profiling program, run a ‘dummy’ specimen of the same alloy class (steel) to flush out any residual oxygen and nitrogen in the system. This is especially important if the instrument has just been cleaned. Repeat until the elemental readings are stable.

### 6.3 Re-profile Optic

A. Verify that the proper spark stand components for the re-profiling standard (electrode and spark stand insert) are installed in the spark source stand.

B. Run the iCAL routine on the manufacturer-supplied iCAL specimen to optimize alignment of the optics. A minimum of five measurements is recommended.

C. Print the re-profiling results and retain them in the log accompanying the instrument.

### 6.4 Standardize

A. Run the standardization routine within the appropriate method for the alloy class chosen based on the evidence to be analyzed. A minimum of five readings per standard is recommended.

B. Print the standardization results and retain them in the associated case file. Record the results of the standardization in the instrument log.

### 6.5 Perform Analysis

A. Verify accuracy with CRM(s) using the appropriate, standardized method for the selected alloy class. A minimum of five readings per standard is recommended.

   1. If the CRM results do not agree with the certified values, or if the relative standard deviations (RSDs) of the data exceed those given in the Limitations section, the instrument will be re-standardized, or re-profiled then re-standardized, to optimize performance.
   2. Additional matrix-matched reference materials may be analyzed to supplement the CRM demonstration of instrument performance.
   3. Print the CRM results and retain them in the associated case file.

B. Prepare an appropriately sized area on the evidentiary item(s). Assess the specimen surface.

   1. Assure removal of all scale, embedded debris, or corrosion product. Resurface the specimen if necessary and repeat the test sequence.
   2. Identify porosity that may make the specimen unsuitable for OES testing.

C. Follow the instrument-prompted sequence for specimen analysis. Take at least five measurements on each specimen.

D. Compare the RSD of each element of interest to those given in the Limitations section. If the RSDs are too high:

E. Check that the specimen surface is free from debris or porosity. If not, re-prepare the surface.

F. If the surface is adequately clean and RSDs are still higher than expected, make additional burns on each specimen to characterize inherent inhomogeneity of the material.

G. Save and print the concentration data from individual measurements as well as the average and standard deviation of the collected measurements.

H. Rerun one or more of the CRMs, taking a minimum of five measurements per CRM, to create pre- and post-test comparison(s) to determine if any instrument drift has occurred.

I. Print the post-test CRM results and retain them in the associated case file.

# 7 CALCULATIONS

## 7.1 Quantitative Analysis

The measured emission intensity of each element of interest is compared to the emission intensity of a selected matrix line and the system calibration curves. This data is used to determine the weight percentage of each of the elements present. Quantitation of the data is performed automatically by the system program and is not directly controlled by the user.

Reporting the quantitative data generated by the instrument requires estimation of measurement uncertainty, see section Measurement Uncertainty. Measurement uncertainties are not typically calculated when a conclusion is limited to describing general alloy categories of evidentiary materials.

## 7.2 Comparative Analysis

Where quantitative data from two specimens are being compared, a Welch's t-test of the sample means (i.e., the composition data sets for the specimens) is used for the comparison per METAL-210. Typically, five or more measurements per specimen are used for performing comparisons.

# 8 ACCEPTANCE CRITERIA

## 8.1 Instrument Performance

- Adequate function of the SpectroLab LAS01 will be demonstrated on CRMs and recorded in the case notes. Criteria to demonstrate adequate function are dependent on alloy-base and analysis port size and are detailed listed in the appropriate specific technical procedure.

- The instrumental conditions (i.e., argon flow rate, spark voltage, spark duration, and spark sequence) are set by the instrument manufacturer and are not normally modified by FBI Laboratory personnel. If service of the instrument requires modification of these parameters, the verification sequence will be performed to demonstrate adequate performance on CRMs.

## 8.2 Quantitative Analysis Conclusions

Quantitative elemental composition results are limited to the specimens tested. Variation of composition of a source product may be able to be estimated based on production method and alloy, but such extrapolation must be clearly reported as opinion and supported by sound bases.

## 8.3 Comparative Analysis Conclusions

The average weight concentrations (wt %) of a given element in two specimens are inter-compared using a Welch's t-test comparison of sample means. The concentrations are deemed to be "analytically indistinguishable" if the absolute t-value for the test of the two specimens is less than the preselected critical t-value. This procedure is repeated for each of the elements present in the specimen. Critical t-values are chosen so that an $\alpha = 0.05$ can be achieved for the overall analysis of the two specimens. Only elements above the LOQ are considered in calculating the "$\alpha^*$" used for individual comparisons: $\alpha^* = \alpha / r$, where "r" is the number of elements present above the quantitation limit and $\alpha$ represents the approximate cumulative probability of calling two specimens analytically distinguishable when they are not.

For example, suppose 15 elements are above the LOQ, then choosing ($t_{0.9966} = t_{critical}$) yields an $\alpha = 0.05$. This means there is a 5.0% chance of incorrectly rejecting a match between any two specimens when one actually exists. Note that repetitive means testing requires a relatively high critical value of t. In contrast, for a $t_{0.99}$, $\alpha = 0.14$ leading to a relatively high rate of false rejection (14%).

Segregation, surface depletion and microstructural banding may also need to be considered in evaluating alloy sources. Constituents that do not completely solutionize are especially prone to inhomogeneous distribution. Consequently, these may potentially exhibit unusually high t-test values. Because these effects depend on the prior processing history, generalizations often cannot be applied. The examiner may make a determination that two specimens are associated to a given degree based on inspection of the analytic data and considerations of the possible sources of compositional variation in the material.

## 9 MEASUREMENT UNCERTAINTY

Quantitative data from this procedure are generally used for comparative purposes as detailed in the Calculations section. Expanded measurement uncertainty should not be used for these inter-comparisons because it increases the probability two samples will appear to be analytically indistinguishable and therefore increases the likelihood of type II errors (false inclusion). Instead, the variances associated with the samples and with data acquisition are accommodated by the statistical comparison.

When quantitative data are compared to a particular specification or when quantitative elemental compositions are reported, estimate the measurement uncertainty per METAL-210. Measurement uncertainty associated with a particular element can vary depending on alloy class, concentration of the element of interest, and the concentrations of other elements present in the alloy, so uncertainties will be calculated on a case-by-case basis.

## 10 LIMITATIONS

### 10.1 Limits of Quantitation

The estimated limits of quantitation (LOQ) have been determined for each alloy class validated and are listed in the specific alloy class technical procedures. In general, these values have been found to correlate well with those observed in practice using CRMs (where these are available). However, some day-to-day variation is expected and values approaching the LOQ are best regarded as qualitative unless a CRM is available to confirm the specific elemental LOQ of interest in a particular instrumental run. Data below the LOQ are to be used only in a qualitative fashion due to the inherent uncertainty associated with them. For example, the absence of manganese in a steel analysis would be an important qualitative result due to the ubiquitous presence of this element in steels.

### 10.2 Relative Standard Deviation

The RSD ranges in Table 2 are used to provide guidance during testing. (Refer to section Perform Analysis.) Insoluble elements will frequently give higher than expected RSDs due to their inherently inhomogeneous distribution in a given specimen.

**Table 2: Typical Relative Standard Deviations for SDAR-OES Testing**

| Elemental Concentration (wt %) | Acceptable RSD |
|---|---|
| 0.1 - 100 | 5% |
| 0.01 - 0.1 | 15% |
| LOQ - 0.01 | 30% |

## 11 SAFETY

- Review pertinent Safety Data Sheets (SDS) prior to machining and testing samples. Analyze the composition of an unknown metal sample by non-destructive means (e.g., x-ray fluorescence analysis) prior to SDAR-OES analysis. If additional guidance is required, contact the Laboratory Health and Safety Group.
- Wear appropriate eye protection when preparing specimens and cleaning and operating the SDAR-OES instrument.
- Wear a lab coat and gloves when cleaning the instrument and changing the air filter.

## 12 REFERENCES

- METAL-210, Examinations for Association and Origin, Chemistry Unit, latest revision

## 13 REVISION HISTORY

| Revision | Issued | Changes |
|---|---|---|
| 02 | 09/15/2022 | Revised to comply with new formatting requirements. Relocated information from Introduction to Principle section. Distributed information from previous Instrumental Conditions and Decision Criteria sections into new Acceptance Criteria section. Informational references removed. |
| 03 | 08/15/2024 | Revised to accommodate replacement instrument. Made METAL-400 dependent on METAL-210 and removed redundant content throughout. Removed Principle section and relocated content to training materials. |