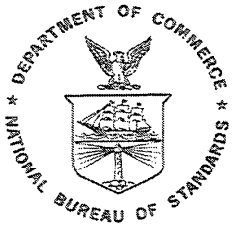

NBS SPECIAL PUBLICATION 260-70

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Standard Reference Materials:

PREPARATION AND CHARACTERIZATION OF AN IRON-CHROMIUM-NICKEL ALLOY FOR MICROANALYSIS: SRM 479a

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PREPARATION AND CHARACTERIZATION OF AN IRON-CHROMIUM-NICKEL ALLOY FOR MICROANALYSIS: SRM 479a

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PREFACE

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George A. Uriano, Chief
Office of Standard Reference Materials

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ABSTRACT

An alloy of weight fraction 0.710 iron, 0.181 chromium, and 0.109 nickel was characterized at the micrometer level of spatial resolution by means of electron probe microanalysis. This alloy, designated SRM 479a, is of suitable homogeneity for use as a standard in microanalytical techniques. There is no statistically significant variation in composition within specimens or from specimen to specimen. SRM 479a is supplied as a disk about 4.5 mm diameter by 0.8 mm thick.

Key Words: austenitic stainless steel; electron probe microanalysis; Fe-Cr-Ni alloy; homogeneity testing; Standard Reference Material.

I. INTRODUCTION

The National Bureau of Standards maintains a continuing program to provide standards suitable for quantitative microanalytical methods such as electron probe microanalysis (EPMA), spark source mass spectrometry, and laser probe analysis. Several standard materials have already been certified under this program [1-4][4]. This report describes the methods and results of homogeneity characterization of an austenitic Fe-Cr-Ni alloy designated SRM 479a. This alloy was produced to provide a reissue of a similar Fe-Cr-Ni alloy, SRM 479 [4]. Suitable thermomechanical processing treatments led to a material of acceptable homogeneity for reference material use in microanalytical methods of analysis. The material preparation and the results of quantitative electron probe microanalysis of the constituent elements are presented in this report.

II. ALLOY PREPARATION

The alloy was melted by the nonconsumable electrode technique [5] in an arc furnace using appropriate amounts of the raw material in the form of chips and small pieces. A reducing gas atmosphere consisting of 5 percent hydrogen in argon was maintained within the furnace at a pressure of about 0.3 atmospheres. This gas mixture was used to prevent the formation of oxide inclusions during melting of the alloy. A raw material charge of approximately 128 grams was melted using a non-consumable tungsten electrode. Each of three hemispherical buttons was melted eight times, four on each side, and then allowed to solidify in a depression

[4]Figures in brackets indicate references at the end of this paper.

in the water-cooled, copper-base plate. Finally, the three hemispherical buttons were placed together over another depression in the base plate having a rectangular cross-section of about 15 cm x 1 cm x 1 cm, and consolidated by melting into a single rod. The purities of the raw materials used were: Ni - 99.99 percent, Cr - 99.99 percent, and Fe - 99.9 percent (Ferrovac E). The target composition was 10.6 percent Ni, 18.8 percent Cr, and 70.6 percent Fe.

The ingot was annealed for 1 hour at 1120°C within a sealed quartz tube containing helium at a pressure of 0.3 atmospheres. The ingot was then swaged to about 60 percent reduction in diameter, sealed again in quartz, and homogenized for 5 days at 1120°C. Two subsequent swaging and annealing steps produced the final round rod of 4.5 mm diameter x 32 cm long. At each step the rod ends were cropped and the surface etched deeply in a 20 percent nitric acid plus 3 percent hydrofluoric acid solution. No lubrication was used during the mechanical processing. Each heat treatment was concluded by quenching the sealed ingot into water. Five disks, 1 mm thick, were cut from the final rod at each end and at the 1/4, 1/2, and 3/4 positions. These disks were used for electron microprobe characterization of the material.

III. CHEMICAL ANALYSIS

Chemical analysis was performed on representative portions of the final rod. The samples were dissolved in a mixture of hydrochloric and nitric acids. Sulfuric acid was added after digestion and the samples fumed to remove nitric acid. The samples were then diluted. Nickel was determined spectrophotometrically by a dimethylglyoxime procedure. Chromium was determined by potentiometric titration of chromium with ferrous ammonium sulfate. The average of eight measurements for nickel content was 0.109, with a

standard deviation of 0.0012 weight fraction. The average of eight measurements for chromium content was 0.181, with a standard deviation of 0.001 weight fraction. The amount of iron by difference was 0.710 weight fraction.

SRM 479a is issued as a disk, approximately 0.8 mm thick x 4.5 mm diameter, in the as-cut condition after diamond blade slicing. The typical microstructure found on metallographically polished and also etched[5] transverse surfaces is shown in figures 1 and 2. The as-polished surfaces (figure 1) indicate the appearance of the specimens as they might be used for electron probe microanalyses. Some small second phase particles were found near the outer edge of the specimen disks studied. Figure 2 shows an example of an etched surface, indicating the grain size present. Some small pits and voids that were not completely removed in the processing treatments can be seen. Inclusions were rarely detected in the central portions of the specimens examined.

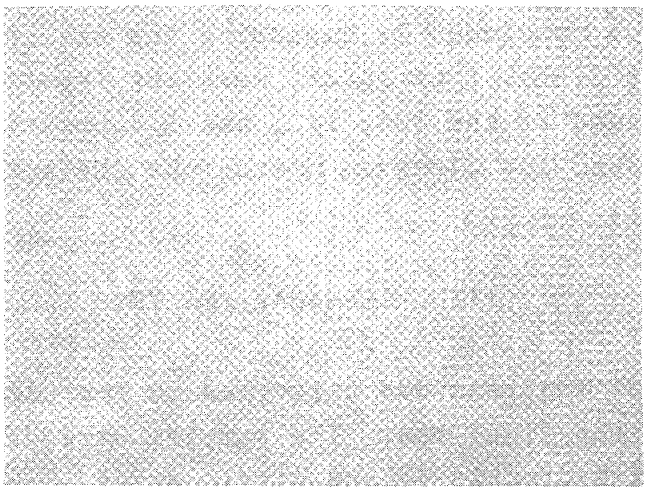

Figure 1a. Metallographically polished surface of one disk specimen, unetched. M = 160X.

[5] 20mL HCl; 20 mL glycerine; 5 mL HNO_3; swab for 1 minute at 23°C.

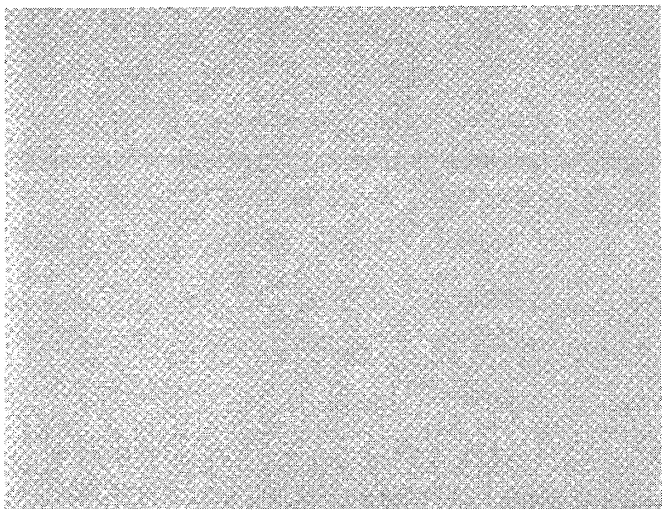

Figure 1b. Metallographically polished surface of one disk specimen, unetched, a different area. M = 640X.

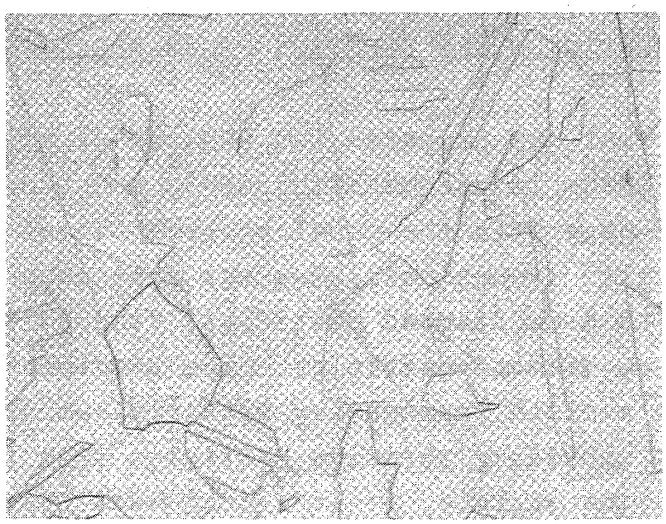

Figure 2a. Metallographically polished and etched surface of one disk specimen showing grain structure present. M = 160X.

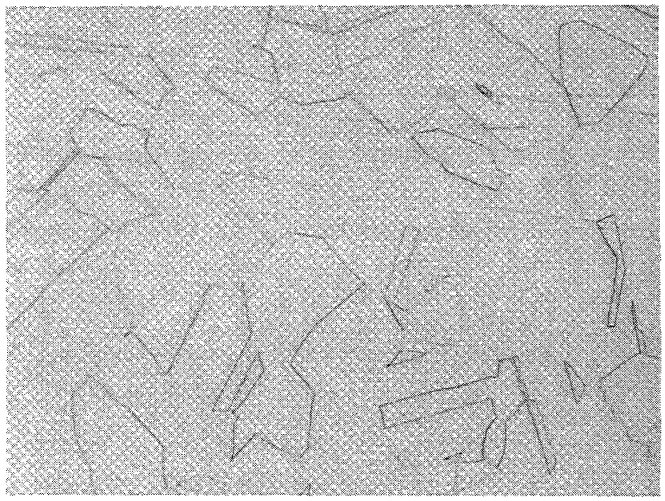

Figure 2b. Metallographically polished and etched surface of one disk specimen showing grain structure present, a different area. M = 160X.

IV. PREPARATION FOR ELECTRON PROBE MICROANALYSIS

This material was prepared for EPMA by grinding the five disk specimens in one metallographic mount on water-lubricated SiC papers in the usual progression of 80, 220, 400, and 600 grit. Rough polishing was done on a cloth impregnated with 6-μm diamond particles; fine polishing was done with 1/4-μm diamond particles. The specimen was finished using a cloth impregnated with 0.05-μm Al_2O_3. In order to avoid embedding abrasive particles from the polishing steps into the surface, it is recommended that two or more cycles of polishing and etching be carried out as the final steps. Unetched specimens were carbon-coated and analyzed with EPMA. Pure element standard specimens were subsequently placed in the same mount as the Fe-Cr-Ni specimens for quantitative EPMA.

V. HOMOGENEITY CHARACTERIZATION

The tests described below were designed to evaluate specimen microhomogeneity, or composition fluctuations from micrometer to micrometer within the specimen, and to evaluate macrohomogeneity, or composition differences between specimens taken from different positions along the rod length. Testing was done with an NBS electron microprobe at an excitation potential of 20 kV. The probe emergence angle was 52.5°. A point beam (about 1-μm diameter) was used. Three wavelength spectrometers with LiF crystals and sealed or flow proportional counters were used to detect the Kα x-rays of iron, nickel, and chromium. The specimen current was about 4×10^{-8} A. The highest count rate observed was 25,000 counts per second for pure nickel. The shortest counting period used in these experiments was 10s. For the alloy, the total number of counts per 10s was about 25,000 for nickel, 25,000 for chromium, and 75,000 for iron.

Since the analysis of the first SRM 479, a new microhomogeneity testing procedure has been developed at NBS. This method was used to check the transverse microhomogeneity of the five specimens. The new procedure, which is described in much greater detail in a recent publication [6], uses a periodic integrator based entirely on digital operations. With a stepping motor on the stage, the specimen is moved automatically under the electron beam in steps of 1 to 10 micrometers. X-ray counts are accumulated at each point for a preselected time period (usually 10 s), and the total number of counts are then shown on a fast strip chart recorder as an analog signal which remains unchanged during the next counting period. The signal can be digitally multiplied by any appropriate factor or a bias can be applied to digitally subtract any desired count rate from the signal display.

The resulting visual display of specimen homogeneity on the micrometer scale can be quickly obtained. An example is shown in figure 3.

This periodic integrator trace is typical of those obtained for all five SRM 479a specimens. Each specimen was moved in 5-μm steps under a 1-μm (approximate diameter) electron beam. Counting periods were 10 s. The three elements were simultaneously analyzed with LiF crystal spectrometers. Double-headed arrows to the right of the traces indicate the theoretical ±3-sigma limits about the average number of counts per counting period, $\bar{N}$, for the trace. Sigma, σ, equal to $\sqrt{\bar{N}}$, is an unbiased estimate of the standard deviation, according to Poisson counting statistics. The ±3-sigma region provides a 99.7 percent confidence limit. Deviations outside this range indicate inhomogeneities, assuming that no serious instrumental fluctuations are present.

To the left of the figure is a time-resolved trace made with a stationary 20 x 20-μm scanning raster. If there are no serious systematic instrumental errors associated with the testing procedure, this signal should lie within the ±3-sigma limits, as in fact it does. Variations within the ±3-sigma limits are due only to the expected statistical fluctuations. For a truly homogeneous specimen, assuming a concentration large enough to produce a signal above background level, the trace for the moving specimen should be similar to that of the stationary specimen. This, in fact, occurs here.

To test the transverse microhomogeneity of each of the five specimens, two traces such as these, normal to one another and crossing near the center of the specimen, were prepared. Each trace was 500 to 600 μm in length. Initially the traces were made with steps of 1-μm intervals. No significant concentration fluctuations were observed at this spatial resolution. In order to cover more of the specimen,

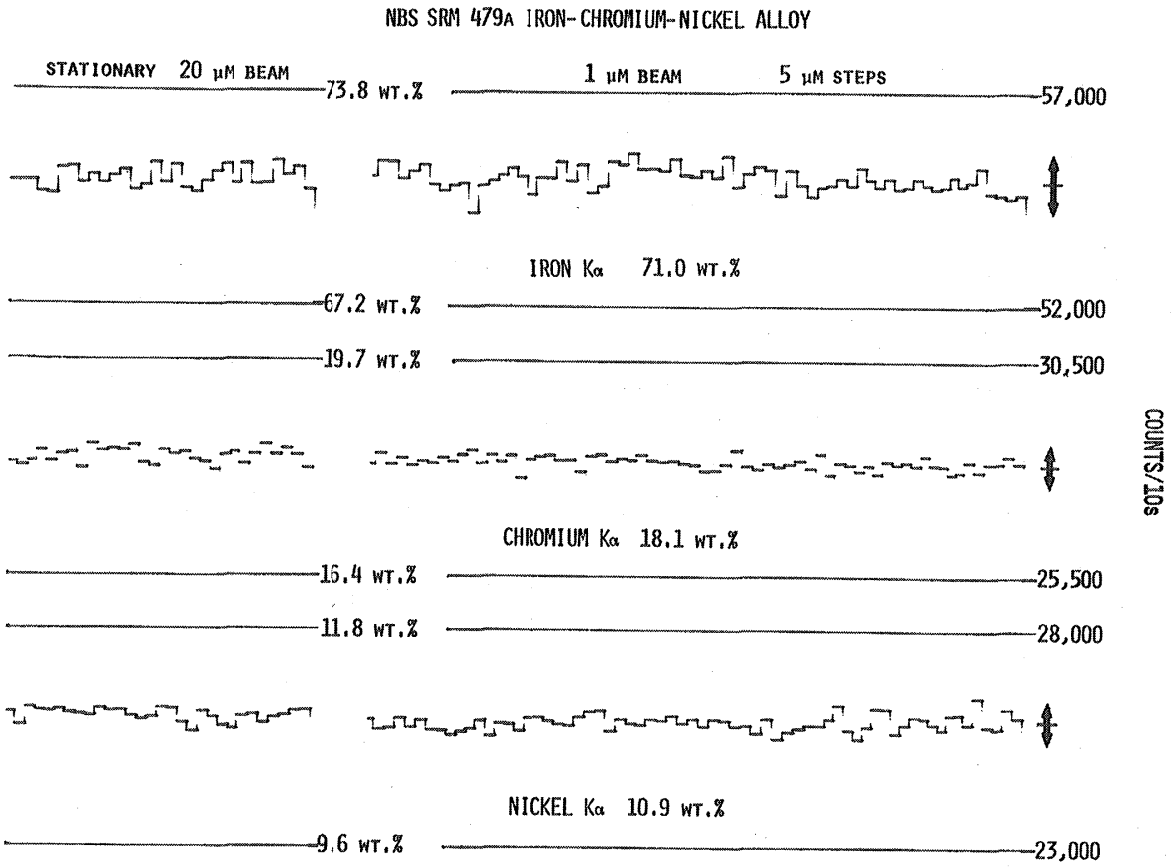

Figure 3. Periodic integrator homogeneity traces of iron, chromium, and nickel simultaneously recorded from NBS SRM 479a. (excitation potential = 20 kV, specimen current = 4.2×10^{-8}A). In the traces on the right, the sample was advanced in 5-μm steps under a 1-μm electron beam after each 10-second counting period. To the left, the sample was not moved during repeated 10-second counting periods with a 20 x 20-μm scanning raster. The double-headed arrows to the right represent a range of $\pm 3\sqrt{\bar{N}}$ around the average number of counts per 10 seconds, $\bar{N}$, for the entire trace.

subsequent traces were made with 5-μm steps. No significant deviations beyond the ±3-sigma limits were observed in any of the traces.

In addition to the visual traces, a statistical evaluation was made on another homogeneity trace of each specimen. The same experimental parameters were used for these traces except that data readings were taken twice on each point. The equations used in the statistical evaluation are explained in the reference cited previously [6]. From the duplicate samplings of each point, the statistical analysis separates the components of the standard deviation. A "within" standard deviation, σ_W, represents the precision of repetitive counting, i.e., the error due only to counting statistics. A "between" standard deviation, σ_B, represents the difference between points. A comparison of these two standard deviations in weight percent for the five samples is in Table 1. In no case is σ_B significantly greater than σ_W, therefore indicating that the total error is due more to the measurement error than to specimen inhomogeneity. These conclusions, of course, are based on the assumption that there are no systematic instrumental errors present. No evidence of this, such as instrument drift, etc., was observed.

The expression of these errors in weight percent as they appear in Table 1 required the conversion of net counts (background-corrected) to concentration. The conversion can be determined without a calibration plot if there is a linear relationship between the net counts and concentration which passes through the origin. This linear relationship was, in fact, validated for the three elements, iron, chromium, and nickel, in SRM 479a.

Five mounted polished cross-sections of NBS steels, SRM's 442, 443, 444, 446, and 447, were randomly sampled with a 20 x 20-μm scanning raster at a 20 kV excitation potential and a specimen current of 4×10^{-8}A. The large scanning

Table 1. Comparison of Statistical Data from Homogeneity Tests (wt. %)

		Homogeneity Trace		Comparison with Random Sampling	
		σ_W	σ_B	σ_{RS}	$\sqrt{\sigma_W^2+\sigma_B^2}$
I	Ni	.07	.07	.09	.10
	Cr	.13	0	.11	.13
	Fe	.27	.06	.49	.28
II	Ni	.08	.04	.10	.09
	Cr	.12	.06	.15	.13
	Fe	.23	.19	.47	.30
III	Ni	.08	0	.07	.08
	Cr	.10	.07	.10	.12
	Fe	.22	.10	.26	.24
IV	Ni	.07	.06	.08	.09
	Cr	.12	.07	.11	.14
	Fe	.26	.28	.29	.38
V	Ni	.07	.01	.08	.07
	Cr	.13	.05	.11	.14
	Fe	.30	.24	.28	.38

raster was used because the microhomogeneity has not been established in these SRM's.

The concentration range for nickel in the five SRM's is 9.4 to 13.3 weight percent, and for chromium it is 16.1 to 23.7 weight percent. The iron concentrations range from 61.8 to 70.5 weight percent. This was slightly below the certified composition of 71.0 weight percent for SRM 479a, but no sudden changes from linearity would be expected at slightly higher concentrations. In all plots of net counts vs. concentration the line fell at or near the origin; small deviations from the origin would probably contribute little

to error calculations as the change in slope would not be large. All subsequent error calculations were made with the above assumptions.

A random sampling test was also done to evaluate specimen microhomogeneity. Fifty randomly selected points were sampled once on each specimen, and x-ray counts were accumulated for 20 s on each point. The results of this test are also listed in Table 1. One standard deviation, σ_{RS}, calculated from the 50 points is expressed here in weight percent. These values of σ_{RS} agree favorably with the combined components of variance, $\sqrt{\sigma_W^2 + \sigma_B^2}$.

A macrohomogeneity test, designed to evaluate differences between specimens, was done on all five samples. Two different operators were used for three experiments. The specimens were analyzed in a different order in each experiment and six random samplings were made twice on each specimen in each experiment, giving a total of 12 random samplings per specimen per experiment. Counting periods were 20 s.

Three contributions to the errors found in these experiments were estimated. These are σ_S^2, the variance between the different specimens, σ_B^2, the variance within specimens on the micrometer scale, and σ_E^2, the variance of a single measurement error. The estimated values of these variance components in weight percent as determined from the three experiments for all specimens are:

	σ_S^2	σ_B^2	σ_E^2
Iron	0.5863	0.0638	0.0335
Chromium	0.0311	0.0028	0.0070
Nickel	0.0147	0.0016	0.0025

The between specimen component, σ_S^2, is almost 10 times greater than the within specimen component, σ_B^2; i.e., the macrohomogeneity or homogeneity along the rod length is not as good as the microhomogeneity of a single specimen.

During this work the test results consistently showed a lower total number of counts for all elements in one end specimen, which suggests the presence of unanalyzed elements such as carbon on oxygen. Since only the center portion of the rod was to be used for the SRM issue, the results obtained from this specimen were excluded from subsequent data evaluations. The following variance components were then obtained (in weight percent):

	Excluding Sample 1		
	σ_S^2	σ_B^2	σ_E^2
Iron	0.2231	0.0671	0.0335
Chromium	0.0265	0.0034	0.0071
Nickel	0.0061	0.0006	0.0025

As expected, the most significant change from exclusion of sample 1 has occurred in the between specimen component, σ_S^2.

The components of variance can be combined for an estimate of one standard deviation (1-sigma) of a single measurement, σ_P. This is given by:

$$\sigma_P = \sqrt{\sigma_S^2 + \sigma_B^2 + \sigma_E^2}$$

In weight percent 1-sigma for a single determination is:

Iron	0.57
Chromium	0.19
Nickel	0.10

Assuming similar experimental conditions to those used in these homogeneity studies, the average of 16 randomly chosen points on a single specimen should, with 99 percent probability, lie within the uncertainty interval given by $\pm 3\sigma_{\overline{P}}$:

Iron	71.0 ±1.47
Chromium	18.1 ±0.49
Nickel	10.9 ±0.24

This uncertainty, $\pm 3\sigma_{\overline{P}}$, is calculated from the estimates of the variance components according to the equation

$$\sigma_{\bar{p}} = \frac{\sigma_S^2}{n_S} + \frac{\sigma_B^2}{n_S n_B} + \frac{\sigma_E^2}{n_S n_B n_E}$$

The uncertainty estimates above for SRM 479a are somewhat larger than the 99 percent confidence intervals reported for SRM 479 [4]. The values (in weight percent) reported for SRM 479 were iron ±0.80, chromium ±0.20, and nickel ±0.12. These values were calculated from a 1.5 percent coefficient of variation determined from homogeneity tests on five specimens of SRM 479.

The difference in the uncertainty intervals for the two SRM's is due to the absence of the between specimen component, σ_S, for SRM 479. The homogeneity tests on SRM 479 [4] showed no obvious differences between specimens.

When the current homogeneity studies on SRM 479a were being done, only one specimen of SRM 479 was available for observation. The periodic ratemeter traces indicated that the one available specimen was slightly less homogeneous than any single specimen of SRM 479a. If this is the case, there is a possibility that specimen-to-specimen differences (along the rod length) that we now see in SRM 479a were undetected in SRM 479 because of the greater heterogeneity observed within each specimen.

Table 2 compares the two specimens. Using the 1.5 percent coefficient of variation assigned to the microhomogeneity of SRM 479, a within-specimen variance term, $\sigma_B^2 + \sigma_E^2$, is calculated. The values of this term for all elements are greater for SRM 479 than for SRM 479a. These numbers again suggest that the microhomogeneity of a single specimen of SRM 479a is better than for SRM 479. The standard deviation (1-sigma) of a single measurement is also lower for the newer SRM in spite of the addition of the large variance component associated with the differences between specimens, σ_S^2. The 99 percent confidence intervals were calculated for both SRM's for two different experiments.

Table 2. Comparison of SRM 479 and SRM 479a.

						EXPERIMENT A: 16 measurements on one specimen $n_S=1$, $n_B=16$, $n_E=1$		EXPERIMENT B: 2 measurements on each of 8 specimens $n_S=8$, $n_B=2$, $n_E=1$	
		$\hat{P}_o$	σ_S^2	$\sigma_B^2+\sigma_E^2$ [a]	SD of single measurement σ_P [b]	SD of average: $\sigma_{\bar{P}}$ [c]	99% confidence interval [d]	SD of average: $\sigma_{\bar{P}}$ [c]	99% confidence interval [d]
Iron	479	71.0	0	1.1342	1.07	0.27	71.0 ±0.80	0.27	71.0 ±0.80
	479a	71.0	0.2231	0.1006	0.5689	0.4790	71.0 ±1.437	0.1849	71.0 ±0.555
Chromium	479	18.3	0	0.0754	0.27	0.07	18.3 ±0.20	0.07	18.3 ±0.20
	479a	18.1	0.0265	0.0105	0.1923	0.1649	18.1 ±0.495	0.0630	18.1 ±0.189
Nickel	479	10.7	0	0.0258	0.16	0.04	10.7 ±0.12	0.04	10.7 ±0.12
	479a	10.9	0.0061	0.0032	0.0965	0.0796	10.9 ±0.239	0.0311	10.9 ±0.093

(a) Computed as $(0.015 \times \hat{P}_o)^2$, for SRM 479.

(b) $\sigma_P = \sqrt{\sigma_S^2 + \sigma_B^2 + \sigma_E^2}$

(c) $\sigma_{\bar{P}} = \sqrt{\frac{\sigma_S^2}{n_S} + \frac{\sigma_B^2}{n_S n_B} + \frac{\sigma_E^2}{n_S n_B n_E}}$

(d) $\hat{P}_o \pm 3\sigma_{\bar{P}}$

In experiment A, one specimen was randomly sampled 16 times, while in experiment B, two random samplings were made on each of eight specimens. The second type of experiment shows a marked improvement in $\sigma_{\overline{p}}$, the standard deviation of the average, and thus in the 99 percent confidence interval. One implication of these results is that if the 99 percent confidence intervals for SRM 479a in experiment A are not low enough, the only way to reduce these values is to increase the number of specimens of SRM 479a sampled.

VI. QUANTITATIVE ELECTRON PROBE MICROANALYSIS

The specimens from the 1/4, 1/2, and 3/4 positions as well as from the one acceptable end were quantitatively analyzed with the electron microprobe. Two different NBS electron microprobes were used as well as both wavelength dispersive (WDS) and energy dispersive (EDS) spectrometers. All analyses were conducted at an excitation potential of 20 kV.

WDS analyses were done on both instruments with three LiF crystal spectrometers and proportional counters. A point beam (1 μm or less diameter) was used, and counting periods were 40 s. The take-off angle for instrument 1 is 52.5° and for instrument 2 it is 40°. The specimen current measured on an SRM 479a specimen was about 2×10^{-8} A. Standards were read before and after taking data from the SRM 479a specimens. When needed, standards were read frequently during the analyses to assure that there was minimal current drift (less than 1 percent). Several (four to six) randomly selected points were read on each standard and SRM specimen.

Dead time corrections were made with the equation

$$N = \frac{N'}{1 - N'\tau}$$

where N' is the observed count rate in counts per second, N

is the true count rate in counts per second, and τ is the dead time in seconds (See ref. [7] for a discussion of this equation). For instrument 1 the dead time is 3 μs and for instrument 2 it is 1 μs. The highest count rate observed at the specimen current used was 14,000 counts/s for pure nickel on instrument 1.

An on-line correction procedure, FRAME [8], was used to calculate the concentrations from the data of instrument 1. Another correction procedure, COR [9], was used for the data from instrument 2. Although these programs are slightly different, identical results were obtained when the same raw data was input for both. COR has an additional correction for fluorescence due to the x-ray continuum, which in these analyses did not significantly change the results.

EDS quantitative analyses were done on instrument 2. The beam current was about 6×10^{-9} A and a 10 x 10-μm scanning raster was used. The accumulation time was 200 s. Concentrations were calculated with the correction procedure FRAME C [10].

The results of the quantitative analyses are in Table 3. For each experiment the instrument used and the technique (WDS or EDS) are indicated. The first four experiments were done with pure element standards. A specimen from the original SRM 479 lot was used as the standard in the last five experiments. A large discrepancy occurs in the values obtained for chromium by the two different standardization procedures. At an excitation potential of 20 kV, the matrix correction procedure is apparently inadequate for chromium in this alloy when using pure element standards. Similar results were observed in the electron probe microanalysis of SRM 479 [4] with pure element standards where at 20 kV the calculated chromium concentration is considerably higher (19.2 wt%) than the certified concentration (18.3 wt %). More accurate results (better agreement with the certified values) were obtained when using the SRM 479 specimen as a

Table 3. Electron Probe Microanalysis of SRM 479a.

Pure Element Standards		Composition (weight percent)		
Instrument	Technique	Fe	Cr	Ni
#1	WDS	70.6	19.7	10.9
#1	WDS	70.6	19.5	10.8
#2	WDS	70.8	19.2	10.5
#2	EDS	70.8	19.4	10.4
		70.70(0.57)	19.45(0.28)	10.65(0.25)
SRM 479 Standard				
Instrument	Technique	Fe	Cr	Ni
#1	WDS	69.0	18.6	11.0
#1	WDS	71.0	17.9	11.0
#2	WDS	70.0	18.4	10.6
#2	WDS	70.4	17.9	10.6
#2	EDS	69.9	18.7	10.6
		70.06(0.90)	18.30(0.42)	10.76(0.23)
Certified Concentrations[a]				
SRM 479		71.0	18.3	10.7
SRM 479a		71.0	18.1	10.9

[a]Nickel and chromium were determined independently by wet chemical techniques and iron by difference.

standard where matrix correction procedures were minimal due to the similarity between the standard and unknown specimens. The errors cited are estimates of one standard deviation for a single measurement, including the variation between experiments as well as the variation due to macrohomogeneity, microhomogeneity, and measurement error.

VII. CONCLUSIONS

The ternary alloy consisting of 0.710 iron, 0.181 chromium, and 0.109 nickel, as determined by chemical analysis, is suitable for use as a microanalytical standard. This alloy, SRM 479a, has a chemical homogeneity expressed as a coefficient of variation of not more than 1.0 percent for each principal element present. The individual region for which this coefficient of variation is valid is a sphere of material approximately 1.5 μm in diameter. SRM 479 should be useful in any laboratory concerned with the quantitative microanalysis of stainless steels.

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APPENDIX

Let P_o be the true weight percent concentration of a particular element in the original alloy rod. Any single (micrometer level) measurement P in weight percent taken at a randomly selected point of a randomly selected specimen will deviate from P_o because of variation between specimens (macroheterogeneity), variation within specimens (micro-heterogeneity), and measurement error. Thus, the deviation $P - P_o$ may be viewed as a sum of "random effects":

$$P = P_o + S + B + E,$$

where,

$P_o + S$ = true weight percent concentration in the selected specimen;

$P_o + S + B$ = true (micrometer level) weight percent concentration at the selected point of the selected specimen; and

E = measurement error.

The "components of variance" σ_S^2, σ_B^2, σ_E^2 are the variances of the random effects S, B, E, respectively. The variance, σ_P^2, of the measurement P is given by

$$\sigma_P^2 = \sigma_S^2 + \sigma_B^2 + \sigma_E^2 \quad .$$

If n_E independent measurements are made at each of n_B randomly selected points of each of n_S randomly selected specimens, and if P_{ijk} denotes the k^{th} replicated measurement at point j of specimen i, then the grand average

$$\overline{P} = \frac{1}{n_E n_B n_S} \sum_{i=1}^{n_S} \sum_{j=1}^{n_B} \sum_{k=1}^{n_E} P_{ijk}$$

has variance

$$\sigma_{\overline{P}}^2 = \frac{\sigma_S^2}{n_S} + \frac{\sigma_B^2}{n_S n_B} + \frac{\sigma_E^2}{n_S n_B n_E} \quad .$$

Thus, the uncertainty in the average measurement $\overline{P}$ may be estimated from estimates of σ_S^2, σ_B^2, and σ_E^2. In

particular, an approximate 99 percent confidence interval for the mean (micrometer level) concentration is

$$\bar{P} \pm 3\left[\frac{\sigma_S^2}{n_S} + \frac{\sigma_B^2}{n_S n_B} + \frac{\sigma_E^2}{n_S n_B n_E}\right]^{1/2}$$

Estimates of σ_S^2, σ_B^2, σ_E^2 were obtained as follows. Let Y_{ijk} denote the k^{th} count measured by the NBS electron microprobe at point j of specimen i. And let D_{ijk} represent the background count associated with the measured count Y_{ijk}. Assuming a linear relationship between the number of counts above the background count and the (micrometer level) weight percent concentration, Y_{ijk} determines a weight percent measurement $P_{ijk}=(Y_{ijk}-D_{ijk})/C$ where the conversion factor C depends on experimental conditions (operating voltage, counting time period, etc.).

Let:

$\bar{D}$ = average background count,[6]

$\bar{Y}_{ij} = \frac{1}{n_E}\sum_{k=1}^{n_E} Y_{ijk}$ = average count at point j in specimen i,

$\bar{Y}_i = \frac{1}{n_B}\sum_{j=1}^{n_B} \bar{Y}_{ij}$ = average count in specimen i,

$\bar{Y} = \frac{1}{n_S}\sum_{i=1}^{n_S} \bar{Y}_i$ = grand average count,

[6]Since the background count is low, it is treated as independent of which specimen, or which point within a specimen is analyzed. Therefore, it is not read for every ijk. $\bar{D}$ is actually the average of five readings taken at the time of the experiment.

$$M_1 = n_B n_E \sum_{i=1}^{n_S} (\bar{Y}_i - \bar{\bar{Y}})^2 = \text{"between specimens sum of squares"},$$

$$M_2 = n_E \sum_{i=1}^{n_S} \sum_{j=1}^{n_B} (Y_{ij} - \bar{Y}_i)^2 = \text{"between points within specimens sum of squares"}.$$

Assuming Poisson variation for the background count and for replicated counts at each point of each specimen, it follows that

(i) $\bar{Y} - \bar{D}$ is an (unbiased) estimate of $C^2\sigma_E^2$;

(ii) $M_2/n_S(n_B-1) - \bar{D}$ is an (unbiased) estimate of $C^2(\sigma_E^2+n_E\sigma_B^2)$; and

(iii) $M_1/(n_S-1) - \bar{D}$ is an (unbiased) estimate of $C^2(\sigma_E^2+n_E\sigma_B^2+ n_B n_E\sigma_S^2)$.

The estimated components of variance are thus taken to be

$$\hat{\sigma}_E^2 = (\bar{Y} - \bar{D}) \Big/ \hat{C}^2, \tag{1}$$

$$\hat{\sigma}_B^2 = \left\{ \frac{M_2}{n_S(n_B - 1)} - \bar{Y} \right\} \Big/ n_e \hat{C}^2, \tag{2}$$

and

$$\hat{\sigma}_S^2 = \left\{ \frac{M_1}{n_S - 1} - \frac{M_s}{n_S(n_B - 1)} \right\} \Big/ n_B n_E \hat{C}^2, \tag{3}$$

where the conversion factor C is estimated by

$$\hat{C} = (\bar{Y} - \bar{D})/\hat{P}_o \tag{4}$$

with $\hat{P}_o$ equal to the certified weight percent concentration value determined by chemical analysis of the original alloy rod.

It is essential to the above computations that the conversion factor C remain constant throughout the experiment. Since current drift, etc., will induce changes in C, there are practical limitations on the number of measurements that may be taken in any one experiment. Hence, we

conducted three separate experiments (each with n_S=4, n_B=12, n_E=1), and equations (1)-(4) were used to obtain three estimates of each variance component; these were (weighted) averaged to yield the final estimates quoted in the certificate.

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