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STANDARDIZATION OF A SPECTROGRAPHIC METHOD
FOR THE DETERMINATION OF CONSTITUENTS IN LOW-ALLOY STEELS

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August 28, 1974

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Prepared for U.S. Atomic Energy Commission under contract no. W-7405-Eng-48

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STANDARDIZATION OF A SPECTROGRAPHIC METHOD
FOR THE DETERMINATION OF CONSTITUENTS IN LOW-ALLOY STEELS*†

ABSTRACT

A general method for analyzing low-alloy steels in a concentration range of 0.05% to 1.00% was developed. The method was standardized for the determination of Mo, Mn, Ni and Cr using iron as an internal standard. One of the principal advantages in using a solution method is that many problems of sample form and metallurgical history are eliminated.

INTRODUCTION

There are several advantages in using a solution A.C. spark spectrographic method for analyzing steel samples. Steel samples can be dissolved fairly rapidly and in sufficient quantities to allow a number of replicates to be run. The acid solutions appear to be stable and therefore can be stored for prolonged periods. With a good choice of line pairs and careful attention used in preparation of standards, excitation conditions, darkroom processing and treatment of data, satisfactory results can be achieved.

In this method, a steel sample is placed in solution and introduced into a cup reservoir around a graphite electrode. Figure 1 shows electrode and solution cup configuration.

The sample solution is excited with an interrupted A.C. spark and the emitted light is dispersed into a spectrum using a Jarrel-Ash 3.4 meter grating spectrograph. The spectrum is recorded on photographic plates. The plates are processed and suitable spectrum line pairs selected for analysis. The intensities of the line pairs are measured on a Jarrel-Ash densitometer interfaced to a time-shared computer¹.

* Work performed under the auspices of the Atomic Energy Commission.

† The author, a summer employee of Lawrence Livermore Laboratory, is a student at San Jose State University, San Jose, CA.

Figure 1. Sample and Electrodes

The computer measures a background adjacent to a line, scans an internal standard iron line and an analytical line of the operator's choice, converts the minimum transmittance to intensity and calculates an intensity ratio of the analytical to the internal standard line. The ratio thus obtained can be taken to a calibration curve of intensity ratio vs. concentration of substituent element plotted on logarithmic paper from which the concentration of the element of interest can then be determined.

METHOD

Preparation of Standard Solutions

Suitable standards of synthetic steel alloys can be prepared from stock 1.00% Ni, Cr, Mo, Mn and 2.00% iron solutions. To prepare the stock Ni, Cr, Mo, and Mn solutions, one gram of each metal in the form of chips, pellets or small pieces is weighed accurately and dissolved with 8M HNO_3 for Ni, Mo, Mn and with 4M HCL for Cr in 250 ml beakers. Adding distilled water and boiling is necessary to hasten the solution process. The solutions are then cooled and transferred to 100 ml volumetric flasks where they are brought to volume with distilled water. They are finally transferred into plastic bottles and stored.

The 2.00% iron solution is prepared by weighing out four grams of pure iron wire accurately and dissolving with 40 ml of 8M HNO_3 in a 400 ml beaker. 160 ml of 4M HCL are added and the solution is boiled for about ten minutes. It is then cooled and transferred to a 200 ml volumetric flask and brought to volume with distilled water.

The necessary standards are then prepared by pipetting specific volumes from bottles of the stock solutions into 150 ml beakers according to the schedule of Table 1A. Table 1B indicates the percentages by weight of a substituent element with respect to steel standard obtained by following Table 1A. The standard solutions are then boiled down slightly, cooled and transferred to 50 ml volumetric flasks where they are diluted to the volumetric mark with an acid solution consisting of one part 8M HNO_3 and three parts 4M HCL. The solutions are finally

Table 1A. Preparation of Standard Solutions

	standard			
	#1	#2	#3	#4
metal	ml of stock solutions			
Fe	48.4	49.1	49.1	48.4
Ni	0.05	0.10	0.20	1.00
Cr	1.00	0.20	0.10	0.05
Mo	1.00	0.20	0.10	0.05
Mn	0.05	0.10	0.20	1.00

Table 1B. Percentage of Metal Obtained

Fe	97.9	99.4	99.4	97.9
Ni	0.05	0.10	0.20	1.00
Cr	1.00	0.20	0.10	0.05
Mo	1.00	0.20	0.10	0.05
Mn	0.05	0.10	0.20	1.00

placed in plastic bottles until used. The standard solutions will be approximately 2.00% steel overall by solution, as will be the regular sample solutions.

Sample Preparation

Approximately one gram of steel sample is weighed. Ten ml of 8M HNO_3 are added to dissolve the sample in a 150 ml beaker. When solution is complete 40 ml of 4M HCL are added and the solution covered with a watchglass. The solution is boiled for about ten minutes.² The watchglass is removed and the solution boiled down slightly, allowed to cool, transferred to a 50 ml volumetric flask and diluted to the volumetric mark with an acid solution of one part 8M HNO_3 and three parts 4M HCL. This will yield a solution that is 2.00% steel overall by volume. It is best to transfer the sample solution into a plastic bottle, then cap and store until use.

Excitation, Processing and Analysis

The equipment and conditions used in producing the spectra are listed in the check-list, Table 2. The excitation used is an interrupted A.C. spark with four breaks per half-cycle monitored with an oscilloscope. An analytical gap of 2mm is used. The current is kept at 6 amps and the powerstat voltage at 200 volts.

A solution volume of one ml delivered with an Eppendorf pipet is transferred to the teflon cup of the lower electrode and allowed to stand in the cup for about 15 seconds prior to ignition. This is done

Table 2. Check-List.

Equipment

spectrograph	Jarrel-Ash 3.4 m
optics	spherical
grating	#75 (blazed at 7500A) at 6200A
slit size	25 μ x 3mm
filters	two-step 100/60 T neutral density, 7-54 Corning color filter

Excitation and Exposure Conditions⁴

excitation	interrupted A.C. spark
powerstat voltage	200 volts
primary resistance	setting #6
Inductance	155 μ H
secondary resistance	residual
capacitance	0.10 μ F
breaks/half cycle	4
spark current	6.0 amps
analytical gap	2 mm
pre-burn	5 seconds
exposure	50 seconds
charge	2.00% steel in solution
emulsion	SA #1
electrodes	Ultra-Carbon type 105U and Ultra-Carbon type 6011

to insure that the electrode is well-soaked with solution before the spark is started. After a run is completed, the interior of the excitation stand including the electrode holders is cleaned of any spattered solution with a sponge and paper tissue. New solution electrodes and counter-electrodes are used each time a run is made.

The spectra are recorded on 2" x 10" glass plates with a Kodak SA #1 photographic emulsion. The plates are processed according to ASTM practices³. The densitometry is performed on a modified Jarrell-Ash model 23-102SP recording comparator-densitometer interfaced with a PDP-7 computer described earlier. The concentration range used for analysis in this method is from 0.05% to 1.00% for all four elements Mo, Mn, Ni and Cr using the following analytical line pairs of Table 3. The roman numeral, I, indicates a neutral atom and the, II, a singly-ionized atom.

Table 3. Analytical and I.S. Line Pairs

Mn I	2794.8 ⁰ A	Fe I	2788.1 ⁰ A
Cr I	3040.8	Fe I	3055.3
Ni I	3012.0	Fe I	3016.2
Mo II	2816.2	Fe II	2788.1

RESULTS AND DISCUSSION

In developing the method a variety of experimental conditions were tried. Sample and standard concentrations, slit size, grating and the particular lines analyzed were modified throughout the process

of improving and standardizing the method. Effort was aimed at setting up good intensity ratio vs. concentration curves with the synthetic standards. In the final part of method development, two NBS standards were analyzed as unknowns to test the method.

The results and statistics of the standards are given in Table 4. The replicates of an element concentration series were averaged to produce an average series of four mean ratios as listed in the table. The average series of each element was used to construct the standard intensity ratio-concentration curves. The curves plotted from the tabulated data are shown in Figures 2, 3, 4 and 5.

Inspection of Table 4 reveals low precision as indicated by the high coefficient of variation values obtained. One reason for this may be that the line intensities vary from one spectrum to another. Intensities were not as reproducible as desired. The larger variations in line intensities at the extreme concentrations of standards and the lower reliability in measuring intensities accurately at these concentrations would contribute to the high variation values obtained. This might indicate that the concentration range covered may have been too broad for analysis with just one pair of lines for each element.

The results and statistics of the two NBS standards analyzed as unknown samples are given in Table 5. These results and statistics are based on five replicate determinations except in the case of standard 818A for Cr. Precision for the two NBS standards, 812A and 818A, was

quite satisfactory. The highest coefficient of variation value, 7, occurred in the above case for which only four replicate determinations were obtained. The accuracy, however, was not quite as satisfactory as can be seen from the percent difference between the observed concentrations and the true NBS concentrations. The loss in accuracy is mostly attributed to the calibration curves themselves.

In all cases, the observed concentrations were found to be lower than their true value. The observed concentration for Mn of standard 812A was found to be lower than the true NBS value by a percent difference of 21.8%. The calibration curve for the determination of Mn is flatter than it should be. It was found that interference due to iron lines at 2794.7A and 2795.0A occurred on the Mn line at 2794.8A. This may have been the cause for the poorer Mn calibration curve and thus for the large percent error obtained.

CONCLUSION

The objective of this work was to develop a rapid, economical spectrographic method for the analysis of low-alloy steels that would yield reasonable accuracy and precision. The described method uses a simple solution A.C. spark excitation. Dissolution of the samples is fast and the solutions are stable thus allowing prolonged storage. In addition, excitation, production of the spectrum and computer-assisted densitometry are all fairly rapid. Once calibration curves have been prepared, a sample can be processed and analyzed in a short period of time.

Good precision and accuracy will depend, for the most part, on rigorous control of photographic (emulsion and processing) and excitation conditions. Also, new line pairs at the extreme concentrations should be selected, especially for Mo and Cr, and any line used in analysis must be checked to insure that it is free from interference effects. The need for more experimentation to improve the statistics of the calibration curves or to generate new curves is indicated. With more time devoted to this objective, the method developed here should prove to be valuable in analyzing low-alloy steels.

ACKNOWLEDGEMENTS

The author is grateful to William Morris and Edgar Peck in answering and assisting with technical questions and problems in standardizing the technique.

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Table 4. Results and Statistics of Synthetic Standards

	number of determinations	mean ratio	standard deviation	coefficient of variation
	n	$\bar{X}$	S_d	v
Mo	6	2.939	0.47	16
	10	0.630	0.03	5
	10	0.294	0.07	24
	9	0.118	0.02	20
Ni	9	3.304	0.55	16
	10	1.218	0.12	10
	10	0.704	0.036	5
	10	0.456	0.023	5
Cr	9	3.625	0.45	12
	10	0.890	0.074	8
	10	0.432	0.089	21
	9	0.252	0.065	26
Mn	9	2.018	0.140	7
	10	0.985	0.058	6
	10	0.777	0.065	8
	9	0.606	0.085	14

LOGARITHMIC 2 X 2 CYCLES AL 0543

Figure 2. Intensity ratio vs. conc.

9. Ni

Figure 4. Intensity ratio vs. conc.

Figure 4. Intensity ratio vs. conc.

Figure 5. Intensity ratio vs. conc.

Table 5. Results and statistics of
NBS standards

	mean ratio, $\bar{X}$	S_d	ν	% from curves	% NBS	% difference
NBS standard #812A						
Mo	0.579	0.026	4	0.18	0.18	0.00
Cr	1.975	0.065	3	0.50	0.55	9.1
Ni	2.161	0.076	4	0.51	0.56	8.9
Mn	1.744	0.035	2	0.68	0.37	21.8
NBS standard #818A						
Mo	0.658	0.014	2	0.20	0.21	4.8
Cr	3.398	0.240	7	0.103	0.125	17.6
Ni	0.741	0.033	4	0.90	1.02	11.5
Mn	1.525	0.064	4	0.50	0.52	3.8

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