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Y-1543
Chemistry

**SPARK SOURCE MASS SPECTROGRAPHIC
ANALYSIS OF STEELS AND NICKEL
ALLOYS (U)**

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT** **Contract W-7405 eng 26**

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Date Issued: July 6, 1966

Report Number Y-1543

Chemistry
TID-4500

UNION CARBIDE CORPORATION
Nuclear Division

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Contract W-7405-eng-26
With the US Atomic Energy Commission

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OF STEELS AND NICKEL ALLOYS (U)

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RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Oak Ridge, Tennessee

Report Number Y-1543

Chemistry

TID-4500

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ABSTRACT

Spark source mass spectrography has been utilized for the determination of boron in steels and nickel alloys. Both visual and microphotometric methods of interpreting data have been developed. The reproducibility of the microphotometer technique has been calculated from standard samples and the visual technique has been compared with conventional methods.

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INTRODUCTION

Laboratories are experiencing an increased need for determining analytically the boron content of steel and nickel alloys due to the $B-10nLi-7$ reaction which may lead to helium embrittlement of the alloys when exposed to high temperatures and neutron fluxes. Many alloys of this type are used in reactor assemblies.

Spark source mass spectrography has some advantages as a technique for determining the boron content in steel and nickel alloys. The sensitivity of the instrument can detect boron at the one part-per-billion level without difficulty. In addition, the samples do not have to be dissolved or chemically altered. The only preparation, after cutting, is the etching of the surface in electronic-grade acids. Another advantage of the technique is that estimations may be made on any element desired. However, the technique has one possible disadvantage—a small sample size may make results sensitive to inhomogeneities in the sample. This condition can be minimized by a careful analysis of the plates and duplicate exposures of questionable samples. This inhomogeneity does not seem to be as prevalent as might be expected.

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SUMMARY

The spark source technique of analysis provides a versatile method for analyzing alloys. Detection limits are in the range of one part per billion, and the method provides good reproducibility and accuracy.

An Associated Electrical Industries spark source mass spectrograph has been utilized for the analysis. Two methods have been used to interpret the photographic plates: a microphotometer and visual estimation. Both techniques of interpretation have been applied to known standards and unknown samples. Photographic detection of positive ions is accomplished by standard Ilford Q-II photographic plates.

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ANALYTICAL METHOD

METHODS OF DATA INTERPRETATION

Since the data are obtained on a photographic plate, two methods of data interpretation are immediately available. The visual-estimation method is quite simple and can be performed quickly; however, at times, precision is not very good. This method can be summarized by the following expression:

$$PS = \frac{E_{\min}}{E_{\max}} \times \frac{\% X}{100} \times \frac{\% I_{\text{std}}}{100} \times 10^6, \quad (1)$$

where:

$E_{\min}$ represents the minimum detectable exposure for a chosen internal standard isotope,

$E_{\max}$ the longest exposure on the plate,

$\% X$ the atom percent of the element chosen as the standard,

$\% I_{\text{std}}$ the isotopic abundance of the internal standard isotope, and

PS the plate sensitivity in ppm atomic.

Then:

$$C_i = PS \times \frac{E_{\max}}{E_{\text{det}}} \times \frac{100}{\% I_i}, \quad (2)$$

where:

C_i represents the concentration of the impurity element in ppm atomic,

E_{det} the minimum exposure at which the impurity can be detected, and

$\% I_i$ the isotopic abundance of the impurity isotope.

This method lacks reproducibility for several reasons, and values are somewhat dependent on the personnel interpreting the data. Experienced personnel obtain very good results with this technique.

The second method of data interpretation is somewhat more complex but provides better precision and perhaps better accuracy. This method requires a microphotometric measurement of the light transmission and subsequent conversion of this percent transmission to light intensity by an analog computer. The relative intensity is then integrated, if needed. The concentration of an impurity in a sample is then:

$$C_i = \frac{E_s}{E_i} \times \frac{X}{100} \times \frac{I_s}{I_i} \times \frac{S_s}{S_i} \times \frac{A_i}{A_s} \times 10^6, \quad (3)$$

where:

E_s represents the relative intensity of the standard line,

E_i the relative intensity of the impurity line,

X the atomic percent concentration of the standard,

I_s the isotopic abundance of the standard isotope,

I_i the isotopic abundance of the impurity isotope,

S_s the relative sensitivity of the standard,

S_i the relative sensitivity of the impurity ion,

A_s the relative area of the standard line, and

A_i the relative area of the impurity line.

In actual practice, if the area terms are necessary, the area of the intensity curve is integrated and the $E_s/E_i \times A_i/A_s$ factors become one as an integrated relative intensity.

Precision for this method is significantly better than for the visual method of interpretation; ie, visual estimation is usually $\pm 50 - 100\%$ while the microphotometer range is ± 3 to 40% .

EXPERIMENTAL PROCEDURE

Sample Preparation

The samples, either metal wires, rods, or plates, were machined or cut into rods 1/16 to 1/8 inch in diameter by 1/2 to 3/4 inch in length.

The samples were degreased in methyl chloroform followed by two rinses in Mallinkrodt Transist AR acetone. Between acetone washes the samples were rinsed in running deionized water. After the samples were degreased, they were etched three times (1 1/2 minutes) in aqua regia made from Transist AR hydrochloric and nitric acids. Between etches and after the last etch, the samples were rinsed in running deionized water. Next, the samples were loaded wet into the source of the mass spectrometer and evacuated to approximately 5×10^{-7} torr. After cleaning was initiated, the samples were handled with tantalum forceps in Teflon beakers to minimize contamination.

Each sample was presparked to about the equivalent of a 1×10^{-8} coulomb exposure to remove surface contamination. An Ilford Q-II plate was then exposed in a series of graded exposures so that the shortest exposure was approximately 1×10^{-13} coulomb and the longest about 1×10^{-8} coulomb. This exposure schedule was found to be sufficient to provide detection limits in the 0.1 to 0.4 ppm atomic (0.02 to 0.08 ppm weight) range. National Bureau of Standards steels were alternated every second or third run with the samples.

The Q-II plates were developed at 20° C, three minutes in Kodak D-19, short stopped in dilute acetic acid, fixed in Kodak Rapid Fixer, washed for ten minutes in water, and then rinsed again in distilled water. Nitrogen burst agitation is employed on all tanks. The plates were dried for ten minutes in circulating air at 38° C.

Plate Reading

Plates are read by visual estimation on the modified microfilm reader shown in Figure 1. If microphotometric determination is desired, the plates are scanned on the Jarrell Ash 24-310 microphotometer. Transmission data are converted to intensity by a 23-515 Jarrell Ash H and D analog computer which has a previously determined plate calibration curve installed in the instrument. The output of the intensity recorder is integrated on an Infotronics Model CRS-1 integrator and amplifier when necessary. The system is schematically outlined in Figure 2.

Results and Data

Some 200 samples of steels and alloys have been analyzed for their boron content and for some other elements. This number of samples has provided adequate opportunity for cross checks with other analytical methods and the analysis of standard samples.

These samples represented many material types and concentration ranges. Table 1 presents the boron level as analytically determined for each material type.

Most of the data have been obtained by visual estimation; however, cross-check information has been accumulated when possible. In Table 2, spark-source mass

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Figure 1. A MODIFIED MICROFILM READER USED TO READ PLATES BY VISUAL ESTIMATION.

Figure 2. OUTLINE OF THE MICROPHOTOMETER SYSTEM.

spectrographic data are compared with chemical results obtained for the same series of steel samples using colorimetric methods.

When higher levels of boron were encountered in INOR-8 samples, a direct-reading emission spectrograph (1.5-meter grating instrument) was used to obtain comparison values. The results of this comparison are summarized in Table 3.

To ascertain the effects of inhomogeneity on the analysis of steels and to determine if any type of analysis provided a biased answer, a series of Type 304 stainless steel samples were analyzed by four different laboratories. The results are summarized in Table 4.

Table 1
SUMMARY OF BORON ANALYSES FOR
VARIOUS MATERIAL TYPES

Material Type	Boron Level (ppm by wt)
Aluminum	5 or less
Chromium	< 0.1
Graphite	10 - < 1.0
Hastelloy X	4 - 20
Incoloy	2 - 7
Inconel	5 - 25
INOR-8	1 - 120
Iron	< 1
Manganese	< 1
Molybdenum	< 1.0
Nickel	< 1
Uranium	0.2 - 0.1
Waspalloy	40
304 SS	0.3 - 70
308 SS	1 - 50
316 SS	2 - 25

Table 2
COMPARISON OF SPARK-SOURCE MASS SPECTROGRAPHIC
METHOD TO THE COLORIMETRIC METHOD

Sample Number	Analytical Method	
	Colorimetric (ppm by wt)	Spark Source Mass Spectrograph (ppm by wt)
1	4.1	2.6
2	3.7	2.7
3	5.0	2.3
4	5.2	7.0
5	4.4	4.2
6	1.9	1.8
7	2.5	2.5
8	2.5	2.5
9	7.0	4.2

Table 3
COMPARISON OF THE SPARK SOURCE MASS SPECTROGRAPHIC
METHOD TO THE DIRECT-EMISSION SPECTROGRAPHIC METHOD

Sample Number	Analytical Method	
	Spark Source Mass Spectrograph (ppm by wt)	Quantometer (ppm by wt)
1	20	10
2	20	10
3	6	7
4	100	120
5	120	80

Table 4
SUMMARY OF BORON ANALYSIS FROM STAINLESS STEEL

Sample Location	Emission Spectrograph	Boron Concentration per Type ⁽¹⁾ (ppm by wt)		Wet Chemistry
		Spark Source Spec 1	Spark Source Spec 2 ⁽²⁾	
1 (top)	1.3, 1.3	1.0	1.0, 1.6	3.1, 4.0
2	0.8, 1.4	1.0	1.4, 2.0	0.2, 2.6
3	-	-	1.2, 1.4	-
4 (bottom)	-	2.0	-	0.4

(1) These comparison data were provided by W. R. Martin of the Oak Ridge National Laboratory.

(2) Y-12 Laboratory.

To provide an indication of the precision and accuracy of the method, a series of three National Bureau of Standards samples were analyzed for their boron content. These standards were treated just as unknowns and the data obtained by visual estimation. The results, presented in Table 5, were accumulated over a period of several months.

Table 5
SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSES OF
NBS STANDARD SAMPLES FOR BORON CONTENT

Sample Number	NBS Value (ppm by wt)	Spark Source Mass Spectrograph (ppm by wt)
NBS 442	5	5.5 ± 1.8
NBS 443	12	10 ± 5
NBS 444	33	30 ± 15

The data just presented were obtained by visual estimation alone and, as such, lack precision better than about $\pm 50\%$ of the value. As better precision is desirable, a series of standard samples have been analyzed and measured with the microphotometer system.

Preliminary curves and emulsion calibration curves were obtained from the ratios of Sn-117 to Sn-119. This particular calibration curve was placed in the H and D computer and all plates discussed were analyzed with the same curve in the instrument.

National Bureau of Standard Sample 443 was taken as a standard and measured for nine elements. From the observed concentration of these elements, a sensitivity factor was calculated, as shown in Table 6.

Next, NBS Samples 442 and 444 were read for the same nine elements using the same calibration curve. The raw data were then corrected for the sensitivity factors calculated in Table 6.

Table 6
SENSITIVITY FACTORS DETERMINED IN STEELS

Element	Found ⁽¹⁾	NBS Value ⁽¹⁾	Sensitivity Factor ⁽²⁾
B	0.0071	0.0061	0.859
Co	0.0790	0.1120	1.416
Cr	20.6000	19.6900	0.956 ⁽²⁾
Cu	0.1200	0.1200	1.000
Mn	2.4800	3.4000	1.371
Mo	0.0500	0.0660	1.320
Nb	0.0260	0.0290	1.116
Ni	5.2300	8.8600	1.520
Ti	0.0078	0.0034	0.436
V			0.707 ⁽³⁾

(1) Values are atom percent. NBS values were calculated from certificates.

(2) Except for chromium, all sensitivity factors were determined using the copper concentration as the standard. Chromium sensitivity was determined using the iron concentration as a standard.

(3) Used previous sensitivity factor.

The precision data in Table 7 are calculated from no fewer than four data points and no more than ten data points. The error calculated assumes there is no error in the NBS values.

Table 7
PRECISION DATA FROM THE SPARK-SOURCE MASS SPECTROGRAPHIC
ANALYSES OF NBS STANDARD STEELS

Element	Found ⁽¹⁾		Percent Relative Standard Deviation ⁽²⁾		NBS Value ⁽¹⁾		Percent Deviation from NBS Value	
	NBS 442	NBS 444	NBS 442	NBS 444	NBS 442	NBS 444	NBS 442	NBS 444
B	0.0028	0.184	32.0	43.1	0.0025	0.0167	+ 12.0	+ 10.2
Co	0.109	0.186	16.0	6.1	0.122	0.2	- 10.8	- 7.0
Cr	18.76	19.31	5.6	9.8	17.2	21.71	- 9.2	- 11.0
Mn	2.49	3.84	5.8	27.2	2.89	4.45	- 13.8	- 13.7
Mo	0.077	0.137	22.5	32.2	0.069	0.13	+ 11.0	+ 5.2
Nb	0.023	0.113	24.4	17.2	0.019	0.118	+ 20.0	- 4.1
Ni	8.370	9.43	1.03	20.1	9.3	9.47	- 10.0	- 0.4
Ti	0.0026	0.0182	48.5	9.5	0.0022	0.021	+ 18.2	- 13.3
V	0.048	0.118	8.4	6.8	0.034	0.13	+ 43.5	- 9.2

(1) In atom percent.

$$(2) \text{ Relative Standard Deviation} = \frac{\sqrt{\frac{[EX^2]_n - [EX]^2}{n(n-1)}}}{\text{Mean}} \times 100.$$

The average relative standard deviation for NBS Sample 442 was 16.5%; for Sample 444 it was 19.1%.

To observe more elements at different concentration levels, the same technique was applied to NBS Samples 461 and 462. This plate was interpreted with the same curves as for the previous NBS samples. The data are summarized in Table 8.

Table 8
SPARK-SOURCE MASS SPECTROGRAPHIC ANALYSES
OF AN NBS MILD STEEL
(NBS Sample 462)

Element	Found(1)	Percent Relative Standard Deviation	NBS Value(1)	Percent Deviation from NBS Value
Ag	< 0.0003		< 0.0002	
As	0.046	23.0	0.034	+ 35.3
Bi	0.0014	28.6	0.025	- 44.0
Co	0.122	8.2	0.102	+ 19.6
Cr	0.87	3.1	0.78	+ 11.0
Mn	0.88	2.4	0.94	- 6.4
Mo	0.04	11.2	0.046	- 13.0
Nb	0.066	10.1	0.057	+ 15.8
Ni	0.73	12.5	0.658	+ 12.3
Pb	0.0020	50.0	0.0015	+ 33.3
Sn	0.030	42.9	0.03	+ 1.3
Ti	0.059	19.8	0.042	+ 40.0
U	0.032	32.8	0.035	- 15.1
V	0.082	10.6	0.063	+ 30.0
W	0.0086	19.8	0.016	- 46.2

(1) In atom percent.

CONCLUSIONS

Spark-source mass spectrometry provides a capability for measuring impurities in steels and nickel alloys to concentrations less than one part per million. In addition, the technique provides quantitative data over a concentration range of 20 to 0.0005% when standard samples are available.

Notes:

1. Points represent the values obtained by the Y-12 Plant.
2. The bars represent the range of values obtained by other laboratories.

PPM

1.000

0.100

0.010

0.001

Attachment I. COMPARISON OF VALUES OBTAINED FROM AN ANALYSIS OF A NBS-SUPPLIED, HIGH-PURITY ZINC SAMPLE.

(Y-1543)

Attachment II

**COMPARISON OF DATA OBTAINED FROM SPARK SOURCE MASS SPECTRO-
GRAPHIC ANALYSIS OF A HIGH-PURITY BERYLLIUM SAMPLE**
(All Values in ppm)

Element	Y-12	ORNL	Element	Y-12	ORNL
Ag	< 0.01	< 0.02	N	1	1
Al	< 0.05	0.10	Na	0.02	0.03
As	< 0.005	< 0.01	Nb	< 0.005	< 0.01
Au	< 0.005	< 0.01	Nd	< 0.04	< 0.04
B	< 0.006	< 0.01	Ni	< 0.007	< 0.02
Ba	< 0.005	< 0.01	O	100	30
Be	M	M	Os	< 0.02	< 0.02
Bi	< 0.005	< 0.01	P	< 0.02	< 0.01
Br	0.1	< 0.02	Pb	< 0.01	< 0.02
C	35	30	Pd	< 0.03	< 0.04
Ca	0.005	< 0.01	Pr	< 0.01	< 0.01
Cd	0.11	< 0.03	Pt	< 0.02	< 0.03
Ce	< 0.01	< 0.01	Pu	< 0.01	
Cl	20	0.10	Rb	< 0.005	< 0.01
Co	< 0.015	< 0.01	Re	< 0.01	< 0.02
Cr	0.007-0.02	< 0.01	Rh	< 0.005	< 0.01
Cs	< 0.005	< 0.01	Ru	< 0.02	< 0.03
Cu	0.07	0.01	S	< 0.10	< 0.10
Dy	< 0.01	< 0.04	Sb	< 0.01	< 0.02
Er	< 0.02	< 0.03	Sc	< 0.015	< 0.10
Eu	< 0.01	< 0.02	Se	< 0.01	< 0.02
F	< 0.50	3	Si	< 0.15	< 1
Fe	0.04	0.01	Sm	< 0.04	< 0.04
Ga	< 0.03	< 0.02	Sn	< 0.02	< 0.03
Gd	< 0.01	< 0.04	Sr	< 0.01	< 0.01
Ge	< 0.02	< 0.03	Ta	< 1	< 0.01
Hf	< 0.01	< 0.03	Tb	< 0.01	< 0.01
Hg	< 0.01	< 0.03	Te	< 0.01	< 0.03
Ho	< 0.01	< 0.01	Th	< 0.02	< 0.01
I	< 0.01	< 0.01	Ti	0.015	< 0.01
In	0.015	< 0.01	Tl	< 0.01	< 0.01
Ir	< 0.01	< 0.02	Tm	< 0.01	< 0.01
K	0.015-0.05	< 0.01	U	< 0.015	0.03
La	< 0.01	< 0.01	V	0.005	< 0.01
Li	0.05	< 0.10	W	< 0.01	< 0.03
Lu	< 0.01	< 0.01	Y	< 0.005	< 0.01
Mg	< 0.03	< 0.01	Yb	< 0.01	< 0.03
Mn	0.05-0.15	0.10	Zn	0.02-0.07	< 0.02
Mo	< 0.02	< 0.04	Zr	< 0.02	< 0.06