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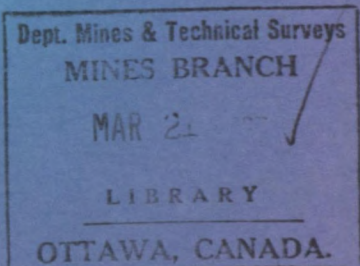
DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

*EXPERIMENTAL ALLOY ANALYSIS
BY X-RAY SPECTROSCOPY*

D. J. REED

MINERAL SCIENCES DIVISION

Reprinted from the Canadian Spectroscopy
January 1967, Vol. 12, Issue No. 1, pp.6-9.



Reprint Series RS 33

Price 25 cents

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ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada

1967

Experimental Alloy Analysis by X-Ray Spectroscopy**

by D. J. REED*

Résumé

Par suite du manque d'échantillons étalons pour certaines analyses spéciales par spectrométrie des rayons-X, il en est résulté un usage croissant d'étalons synthétiques pour la détermination des constituants mineurs dans les alliages expérimentaux. Dans nos laboratoires, ces étalons synthétiques ont servi à la préparation d'étalons secondaires pour l'analyse des aciers doux.

Pour les constituants majeurs, l'emploi de solutions évaporées sur papier-filtre a donné des résultats imprévus. Les éléments majeurs d'un alliage ont été déterminés à partir de rapports obtenus sous des conditions d'excitation semblables à celles utilisées lorsqu'un seul étalon était disponible. On a examiné des techniques à base d'ordinateurs pour la détermination des constituants majeurs et mineurs quand il existe un nombre convenable d'étalons.

Abstract

The lack of standards for non-routine X-ray spectrography has resulted in the use of synthetic standards for the determination of minor constituents in experimental alloys at the Mineral Sciences Division of the Mines Branch. For mild steels secondary Mines Branch standards have been developed with the aid of these synthetic standards.

For major constituents the use of solutions dried on filter papers has produced some unexpected results. Major elements in an alloy have been determined from ratios obtained under conditions of equivalent excitation when only a single standard was at hand.

Computer techniques have been examined for the determination of both major and minor constituents when a suitable number of standards were available.

Introduction

In the Mineral Sciences Division of the Mines Branch samples for X-ray analysis are examined as received, if possible. When it has been necessary to change the form of the sample, no chemical separation has been made. Elements have been determined at, or below, their original concentration.

A standard Norelco 100 kV spectrograph was used for most of the alloy analyses reported, although a 60 kV instrument was used for the early work. The pulse height analyzer unit in the counting panel was modified to give a baseline of 150V in addition to the original 60V one.

For trace analysis, the sensitivity might have been increased by collimation coarser than the 0.005 in. used and, for specific analyses, filters might have helped; but, with a wide variety of samples for diverse determinations and a small number in any set, constant alteration of the equipment was not practical.

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**Presented at the Fifth National Meeting of the Society for Applied Spectroscopy, Chicago, June 13-17, 1966.

Determination of Minor Constituents

Synthetic standards have proved useful for a number of alloy analyses when appropriate standards were not available. Mild steels have been analysed for zirconium⁽¹⁾, niobium⁽²⁾ and hafnium^(3, 4) in the range 0.001 to 0.3% using such standards. The elements were added to the steel singly and originally, for niobium and zirconium, in amounts less than 0.1%. NBS low alloy steel standards were not satisfactory for these samples as there was an insufficient number in the appropriate concentration range.

The synthetic standards were prepared by dissolving electrolytic iron, with additions of the appropriate metals to give the desired concentration, in hydrochloric and fluoboric acids. The solutions were taken to dryness and the residues ground to pass 200 mesh. Portions of the samples were treated similarly for comparison with the standards.

The steel samples were submitted as discs two inches in diameter. After repeated analysis of the corresponding powders under varying conditions, a value was assigned to an appropriate selection of these discs as secondary standards. The range was extended as sample variation permitted.

Both niobium and zirconium radiation are subject to high background counts as they occur where the continuum slopes towards its maximum value. Synthetic standard backgrounds were determined by extrapolation from counts at three or four points on the continuum. For secondary standards, it was found that the means of background counts taken $\pm 0.70^\circ 2\theta$ from the characteristic peak was satisfactory. This was shown by the small intercept of the regression line for NbK α at 80kV which had the equation: $Y = 0.00007466X - 0.00026$. The standard error of prediction in this case was $\pm 0.0005\%$ niobium.

Steel samples were counted at 80 or 90 kV. These potentials increased the continuum height significantly and their use could conceivably increase the background more than the characteristic radiation. The use of high potentials was tested by taking counts on two zirconium-containing steels at varying kV's. The peak-to-background ratios obtained, listed in Table 1,

improved with increasing potential so the use of high potentials was advantageous.

Table 1 — The Effect of kv on ZrK α Peak-to-Background Ratios in Mild Steels

kv	Ratio	
	0.082% Zr	0.320% Zr
40.....	1.60	3.24
50.....	1.65	3.61
60.....	1.75	3.88
70.....	1.84	4.08
80.....	1.86	4.22
90.....	1.96	4.28

Once secondary standards were available, samples were analyzed against them as a matter of convenience. The establishment of additional secondary standards as sample variation permitted soon extended their range beyond that of the synthetic standards. Concern was felt that any primary error could thus have been compounded. Therefore, Mines Branch standards were compared with NBS ones once their composition ranges coincided. Niobium counts on the two groups combined to give a reference line having a correlation coefficient of + 0.9993. The effect on the background counts of the equivalent or greater amount of niobium present in all NBS standards containing zirconium resulted in a poorer correlation for the combined zirconium standards (+ 0.9900.) These correlation coefficients were considered evidence that only insignificant error could be present in the values assigned to the secondary standards.

NBS standards were too small for the 1- $\frac{3}{8}$ in. diameter radiation ports of the sample holders so a platinum mask with a port 1 in. in diameter was made to support them. Secondary zirconium standards gave the lines shown in Figure 1 which illustrate the effect of exposed area and of applied potential. Both variables affect the results significantly. The intercept of the lines is due to zirconium in the aluminum holder used.

With the 100kV spectrograph both K and L radiation could be used for the determination of hafnium in mild steels. L radiation has a low background, but suffers interference from the WL lines from the X-ray tube. K radiation has a high background, but no tungsten interference because WK lines do not appear in the tube continuum even at 100kV, although they are fluoresced from a sample once the critical potential is exceeded. HfK (n = 1) radiation occurs near the continuum maximum and at low concentrations is masked by it; however, second order K radiation can be used for mild steel analysis.

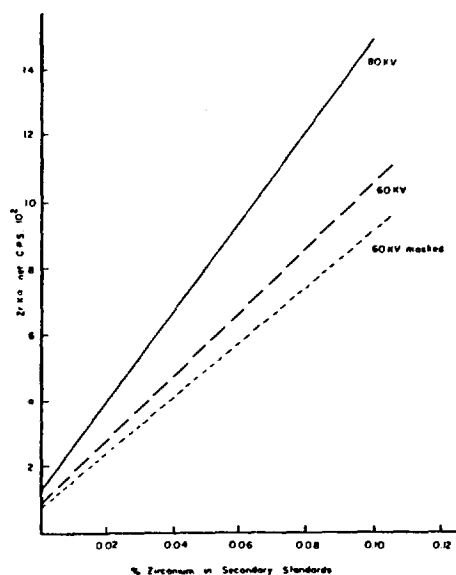


Figure 1 - The Effect of Exposed Area and Applied Potential on ZrK α Counts.

Hafnium samples were analyzed against synthetic standards using L radiation. Neutron activation ratios were also determined for interest. The results given in Table 2 demonstrate that the analytical results agree with neutron activation ratios. K and L counts on the sample discs are included to show comparative sensitivity.

Table 2 — Hafnium in Mild Steels

	% Hf*	Neutron Ratio	Net cps on discs	
			L α (n = 1)	K α (n = 2)
A.....	0.200	1.00	332	240
B.....	0.154	0.75	242	174
C.....	0.080	0.42	132	103
D.....	0.035	0.17	60	28

*synthetic standards.

Synthetic standards have also been used for the determination of hafnium in niobium and elements added to stainless steels not exceeding the 2% level. The effect of pulse height analysis on the determination of hafnium in niobium may be of interest. Shown in Table 3 are regression characteristics of lines from counts made with 6V baseline to eliminate noise and with baseline and channel settings to pass only escape peak energies or main peak energies. Both total and net counts have been used. Total counts gave high but constant backgrounds as "a" and 0% counts show. The use of the pulse height analyzer reduced the error as the main peak results show.

Table 3 -- Hf in Nb: Regression Characteristics for Second Order HfK α Radiation. $Y = a + bX$

	a	b	error	0% Hf cps	
				calc.	obs.
6V net.....	- 0.015	0.007397	± 0.39	20	20
6V total.....	- 8.46	0.006911	± 0.32	1224	1252
EP* net.....	- 3.31	0.052676	± 0.55	63	63
EP* total.....	-35.59	0.043791	± 0.54	813	828
MP ^o net.....	- 0.19	0.007694	± 0.24	25	20
MP ^o total.....	- 1.78	0.007208	± 0.24	245	245

*escape peak. ^omain peak.

The escape peak counts increased both the error and the intercept and the use of such counts cannot be recommended unless interfering radiation makes it necessary.

Determination of Major Constituents

In the determination of major components of alloys, inter-element effects are often significant and must be compensated for.

Solutions

Solutions on filter paper have been advocated as a means of eliminating enhancement and absorption effects^(5,6,7,8). At the Mines Branch it was found that the only way to prevent migration of the ions with the leading edge of the solution was to immerse the filter papers in the solution, then dry them on blotters. This had proved satisfactory for the determination of tin in complex ores using 5 cm Whatman 541 paper⁽⁹⁾.

The possibility of using mixtures of solutions of pure metals in this way as standards, when there were no other standards available, was attractive and was investigated. While the method was not practical due to inter-element effects, the unexpected results obtained using solutions of iron, cobalt, nickel and chromium are of interest.

Table 4 -- The Effect of Iron on CoK α Net Counts Using Solutions on Filter Papers. N = 6

	Al Backing			
	1 paper	3 papers	6 papers	1 paper
Blank.....	763 ± 5	831 ± 5	889 ± 6	128 ± 4
Co.....	1707 ± 105	4061 ± 72	5950 ± 63	1624 ± 81
Fe.....	5	25	34	9
Co + Fe.....	1799	4281	6255	1732

Using solutions of pure metals at concentrations of 0.5 mg/ml in 1:10 nitric acid on filter paper, iron was found to enhance cobalt. The results are presented in Table 4. Fe radiation should not have sufficient energy to excite cobalt because the cobalt absorption edge is to the high

energy side of FeK β . That the enhancement observed is not due to FeK β which occurs near CoK α on the 2 θ scale is proved by the counts on iron alone. Iron made an insignificant contribution to the cobalt counts. As Table 5 shows, chromium enhances FeK α , but should absorb it, and nickel, which would be expected to enhance iron, does not. At first it was thought that this might be partly a transmission effect due to reflection of the X-rays from the aluminum disc used to hold the papers flat, but the same effect is observed with no backing. It is interesting to compare these deviations with those Marti⁽¹⁰⁾ found in his influence factors.

Table 5 -- The Effect of Neighbouring Elements on FeK α Net Counts Using Solutions on Filter Papers. N = 8

	Al Backing			
	1 paper	3 papers	6 papers	1 paper
Blank.....	790 ± 10	794 ± 8	805 ± 6	156 ± 7
Fe.....	1111 ± 38	2403 ± 57	3362 ± 56	1042 ± 59
Cr.....	3	11	11	5
Fe + Cr.....	1192	2578	3554	1112
Co.....	-3	3	3	5
Fe + Co.....	1148	2514	3458	1044
Ni.....	0	7	11	8
Fe + Ni.....	1116	2420	3354	1010

To give an idea of the sensitivity using solutions on filter papers: the exposed area on which the above counts were made absorbed 47 μ g of the metals.

Equivalent Excitation

When insufficient standards are at hand, comparison with pure elements⁽¹¹⁾ or with a single standard⁽¹²⁾ using simple ratios has been reported. At the Mines Branch a single standard has been found satisfactory for three to five component alloys when combined with equivalent excitation⁽¹³⁾ and the use of the count ratios of each component to the matrix⁽¹⁴⁾. With the wide variation in the critical potential of elements, application of a single exciting potential to an alloy usually results in significantly unequal excitation of the constituents. For comparable excitation, the critical potential of each element must be exceeded to the same degree by using a small multiple of each, within the limit of the kV output of the equipment. Results have been obtained using 2, 2.5 and 3 times the potential. From the ratios of the counts, simple formulae have been derived from simultaneous equations solved by Gauss' method⁽¹⁵⁾.

The analysis of steel samples using two standards showed that equivalent excitation gave

better results than constant kV. Reproducibility of results was best when three was the multiple of the critical potential used. Table 6 presents the percent recovery when the standard steels were analyzed against each other using both constant kV and equivalent excitation. Results were calculated by the formulae and by simple ratios. Acceptable recovery was achieved using the formulae and three times the critical potential.

Table 6 — Percent Recovery of Steel Components Using Different Excitation and Calculation

	6318			6832		
	Cr	Mn	Ni	Cr	Mn	Ni
Ratios						
3CP*	113.1	110.3	111.4	88.4	91.1	90.6
5CP*	99.3	92.9	108.8	100.7	107.3	91.6
30kV	130.7	110.0	138.0	76.5	89.7	72.4
Formulae						
3CP*	100.5	100.6	100.8	99.4	100.0	99.1
5CP*	92.6	88.4	101.6	107.7	116.1	98.4
30kV	111.8	95.5	118.0	87.5	102.9	82.9

*critical potential.

Copper, tin and lead alloys have also been analyzed in this way with acceptable results⁽¹⁴⁾. The use of constant kVA was tried for several alloys but did not improve results.

Computer Methods

A number of methods for mathematical treatment of counts to overcome interelement effect have been devised that may be used when sufficient standards are available^(10,16,17,18,19,20). The Mineral Sciences Division has investigated two of the more recent methods.

The method of Lucas-Tooth and Price⁽²¹⁾ requires $n + 2$ standards where n is the number of elements to be determined. The standards must cover the concentration range of the samples — results cannot be extrapolated. Calculations are based on the equation

$$P_{nm} = \alpha_n + I_{nm} (k_{no} + \sum_x k_{nx} I_{xm}),$$

where P and I are the percentage and X-ray in-

tensity respectively of the n th element in the m th alloy. The α and k 's are constants derived empirically from counts on the standards. Interelement k 's are usually small and effective only when the intensity is high.

This formulation was satisfactory for the analysis of lead alloys⁽²²⁾ and adequate for the determination of seven components in stainless steels⁽²³⁾ but did not have sufficient accuracy for high temperature alloys with nine components⁽²⁴⁾. These alloys were used to test the Traill-Lachance solution for interelement effects^(25, 26, 27) which may be derived from the Beatty-Brissey formulation⁽¹⁶⁾. The Traill-Lachance basic equation

$$R_A = \frac{I_A}{I(A)} = \frac{C_A}{1 + C_B \alpha_{AB} + C_C \alpha_{AC} + \dots + C_N \alpha_{AN}}$$

uses the relative intensity of the X-radiation of an element in a mixture. I_A is the net intensity of the X-ray line A from a sample or standard. $I(A)$ is the net intensity of the line A from pure element A. The C 's are weight fractions of respective elements in the sample. The α 's may be calculated from n simultaneous equations. Therefore only n standards are necessary. Results may be extrapolated beyond the standard range. The α 's may also be calculated from mass absorption coefficients, but are better if derived empirically because of the difficulty of calculating effective absorption coefficients for polychromatic radiation.

The Traill-Lachance equations were applied to high temperature alloys for nine elements with a wide range of concentrations. Comparison of the percent recovery of components present in concentrations greater than 1% showed that these equations gave no better results than the earlier approach.

In the high temperature alloys used components were present in amounts from 0 to 80%, with the major component iron, nickel or cobalt. Such a concentration range is a severe test for any interelement correction formula. If these alloys were grouped to give smaller ranges of composition and the same major component, it is probable that both formulations would give as satisfactory results as they have for stainless steel and other alloys.

(Reference on page 27)

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