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ABSTRACT

A summation of the normalised relative intensities of selected spectrum lines of the major components of an alloy is used as an internal standard for the emission spectrographic analysis of a group of alloys. The procedure depends on the sum of the concentrations of the major components being constant but does not rely on prior knowledge of these concentrations. The usefulness of the technique is demonstrated in the analysis of stainless steels, using argon spark excitation with point-to-plane geometry. In principle, the technique should be applicable to other alloy systems.

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ALLOYS; EMISSION SPECTROGRAPHY; STAINLESS STEELS

CONTENTS

1. INTRODUCTION

The emission spectrographic analysis of multicomponent alloys, using a photographic plate as a detector, has a number of advantages over the use of direct reading spectrometers. The photographic plate is a permanent record of the sample spectrum and permits both rapid qualitative identification and semi-quantitative analysis of the alloy by visual examination. Quantitative analysis of all elements may also be carried out with photometric measurements of appropriate spectrum lines of the elements. Direct readers lack the versatility necessary to analyse different alloys because of the limited number of lines that can be programmed on the focal plane.

To obtain adequate precision with a photographic spectrograph, it is necessary to use an internal standard to cope with variations in exposure, the plate sensitivity and excitation conditions. The most suitable internal standard is the major component of the alloy; however, because constant time exposures must necessarily be employed, the variable concentration of the major component complicates its use as an internal standard. A procedure for internal standardisation based on such a component has been described [ASTM 1964]; this method utilises the concentration ratios of the analysis element to the internal standard element and requires all elements which significantly contribute to the composition of the alloy to be determined. The concentration of the internal standard can then be determined and the concentrations of the other elements calculated.

Another procedure which uses a variable internal standard for analysing ferrous alloys relies on an estimate of the internal standard (iron) concentration [Arrak 1963]. This estimate is made from prior knowledge of the type of alloy and allows a corrected iron internal standard intensity to be used in determining the concentrations of all other elements. If the iron value, obtained by difference, is significantly different from the estimated value, a new estimate has to be made and the element concentrations redetermined. This procedure is repeated until the assumed and calculated values agree.

These methods have the disadvantage of requiring analysis for all elements which contribute to the composition of the alloy or prior knowledge of the concentration of the internal standard element.

The procedure described here does not require a knowledge of the major component concentrations but assumes that their sum is constant. A total internal standard is derived from the sum of the relative intensities of selected spectrum lines of these major components. The relative intensities are normalised so that their sum represents the total intensity of the major components.

The procedure has been tested on stainless steel alloys having widely varying major component concentrations. It permits the determination of all constituents including iron.

2. BASIS

The basis of the total intensity internal standard procedure is that, for a multicomponent system, the sum of the concentrations of the major components is constant. For n major components

$$\sum_{i=1}^{n} C_i = \text{constant} \quad ,$$

where C_i is the concentration of element i.

In a three-component system

$$C_1 + C_2 + C_3 = C_T = \text{constant} \quad , \tag{1}$$

where C_T is the total concentration of the three components.

The relationship between intensity and concentration is given by

$$I = \alpha C^{\gamma} \quad , \tag{2}$$

where I is the intensity measured on some arbitrary scale, α is a constant for a given set of conditions and γ is the slope. This equation can be rewritten as

$$C = \left(\frac{I}{\alpha}\right)^{1/\gamma} \quad . \tag{3}$$

For the individual components therefore, we have:

$$C_1 = \left(\frac{I_1}{\alpha_1}\right)^{1/\gamma_1} \quad , \quad C_2 = \left(\frac{I_2}{\alpha_2}\right)^{1/\gamma_2} \quad \text{and } C_3 = \left(\frac{I_3}{\alpha_3}\right)^{1/\gamma_3} \quad .$$

If the relative intensity values I_1, I_2 and I_3 of the three components corresponding to C_1, C_2 and C_3 are all normalised to a single intensity scale with respect to element 1, then it follows that

$$(I_1)^{1/\gamma_1} + (I_2^{*})^{1/\gamma_2} + (I_3^{*})^{1/\gamma_1} = (I_T)^{1/\gamma_1} = \text{constant} \quad , \tag{4}$$

where I_2^* and I_3^* are the normalised relative intensity values of I_2 and I_3 for the concentration components C_2 and C_3, respectively. Alternatively, this can be expressed as

$$(I_1)^{1/\gamma_1} + (k_1 I_2)^{1/\gamma_1} + (k_2 I_3)^{1/\gamma_1} = (I_T)^{1/\gamma_1} \quad , \tag{5}$$

where

$$k_1 = \frac{I_2^*}{I_2} \quad \text{and} \quad k_2 = \frac{I_3^*}{I_3} \quad .$$

The single value I_T which is obtained for each exposure is used as the internal standard.

In practice, the normalising factors k_1 and k_2, together with the slopes, are determined from constant time intensity-concentration plots of the individual components using an appropriate set of standards.

The constancy of the normalising factors and, therefore, the best accuracy of the procedure in analysing unknown samples, will occur only when the intensity-concentration plots for the individual components are parallel. This can be seen from the fact that the normalising factors can be expressed as

$$k_1 = \frac{I_2^*}{I_2} = \frac{\alpha_1}{\alpha_2} C_2^{\gamma_1 - \gamma_2} \quad \text{and} \quad k_2 = \frac{I_3^*}{I_3} = \frac{\alpha_1}{\alpha_3} C_3^{\gamma_1 - \gamma_3} \quad .$$

It is only under this condition of parallelism that the normalising factors will be constant for all possible combinations of major component concentrations.

When the curves are not parallel, errors will occur since normalising factors are dependent on major component concentrations.

3. EXPERIMENTAL

The spectrograph and its operating conditions are given in Table 1. The surface of the sample was prepared using a smooth flat file.

Analytical spectrum lines are given in Table 2. The composite internal standard used for Fe, Cr, Mo and Ti is based on the intensities of Fe 315.421 nm, Cr 315.221 nm and Ni 310.155 nm. The internal standard for Ni and Si is based on Fe 309.997 nm, Cr 315.221 nm and Ni 310.155 nm.

Percentage transmittance data were obtained with a microdensitometer and converted to relative intensity values by means of a Hurter and Driffield calibration curve, obtained from an exposure using a 7-step rotating sector.

To facilitate the determination of the normalising factors, the setting up of working curves and the processing of results, a number of computer programs were written using the ACL-NOVA system [Sanger 1972]. The standards used were National Bureau of Standards (NBS) Reference Materials Nos. 845-850.

The basic steps used for data acquisition are as follows:

(a) Mean relative intensities of the selected lines used in the total internal standard are calculated from 10 exposures of each standard. These are plotted against their respective element concentrations.

(b) Regression lines are obtained with a standard, weighted non-linear least squares procedure. The slopes and intercepts of the regression lines are calculated.

(c) From these regression lines, the normalising factors are calculated at any nickel or chromium concentration. Typical concentrations chosen for nickel and chromium are 10% and 20% respectively. Each normalising factor is obtained at any desired concentration by taking the ratio of the iron intensity value to the intensity value of the nickel or chromium.

(d) The normalising factors, together with the slope of the normalising component curve, are then used to obtain I_T (from Equation (5)) for each exposure.

(e) Working curves are then set up for each element by calculating the mean ratio of the relative intensity of the analytical line to the total internal standard intensity I_T. Each working curve is a regression line determined from these ratios.

(f) Relative intensities for samples are treated in a similar manner, using the normalising factors determined in step (c). The mean ratios are substituted into the appropriate regression line working curve to provide the final concentration.

(g) Error analysis of the final concentration is undertaken using a statistical approach (See Appendix A).

4. RESULTS

The intensity-concentration plots for Fe 315.421 nm, Cr 315.221 nm and Ni 310.155 nm are shown in Figure 1. The degree by which the regression lines deviate from parallelism is given by their slopes which, under experimental conditions, are 0.81, 0.74 and 0.74 for Fe, Cr and Ni, respectively. In practice, it has been found difficult to select lines which are parallel. In view of this, an error in the results may arise if the normalising factors are chosen at inappropriate concentrations for an unknown sample alloy. The extent of this error will be shown later.

Working curves using k factors derived from the combinations of 315.421 nm, Cr 315.221 nm and Ni 310.155 nm lines and Fe 309.997 nm, Cr 315.221 nm and Ni 310.155 nm lines are shown in Figures 2 and 3. These have been used to analyse a set of stainless steels which had previously been analysed by wet chemical methods. The results are shown in Table 3. In general, there is satisfactory agreement between the results except for silicon which appears to be low at around 0.5% concentration. The reason for this is not known. However, these results agreed with those obtained using the ASTM [1964] method on the same data, indicating that the disagreement was not a function of the total intensity method described. It may be that, for silicon, using these conditions, metallurgical history effects are responsible for the discrepancy.

To investigate the effect of deviation from parallelism in the intensity-concentration plots of the Fe 315.421 nm, Cr 315.221 nm and Ni 310.155 nm lines, and its subsequent effect on the results, two typical stainless steel samples were analysed using a wide range of normalising factors corresponding to different concentration levels of chromium and nickel. The results are shown in Table 4. The variation of results is insignificant since it lies within the experimental error (95% confidence level) of the method. Furthermore, the results illustrate that a wide range of normalising factors can be tolerated, indicating that it is not necessary to have any prior knowledge of the concentration of the major components.

To test the validity of the procedure further, three sets of certified standards were used to obtain a calibration for manganese in steels. The standards chosen were the NBS steels Nos. 845-850 normally used for obtaining working curves, together with NBS steels Nos. 442-444 having relatively high manganese content and British Chemical Standards (BCS) low alloy steels Nos 1/1-8/1. The low alloy steels contain sufficiently small quantities of other components as to make their presence of minor concern. Thus, for these standards, iron can be used as the internal standard, I_T, thus allowing an assessment of the total intensity standard to be made. The results are shown in Figure 4 and illustrate the validity of the total intensity internal standard procedure by the single calibration.

The precision of the method was assessed from replicate exposures of standards, and the relative standard deviation of the ratios of relative intensities was in the range 0.5 to 4 per cent. The overall error in the determination of element concentrations depends not only on the error in the analytical ratio but also on that introduced by the use of the working curve regression line. Since, in this case, the working curve regression lines are non-linear, special treatment of the data is essential to determine the overall error. This treatment is given in Appendix A.

5. DISCUSSION

The procedure is based on the assumption that:

- the sum of the concentrations of the major components is constant, and
- the normalising factors are constant at all concentration levels.

The data presented show that this is not the case. For the NBS standards used to obtain working curves, the sum of the concentrations of iron, chromium and nickel ranged from 94.9% to 98.7%. Also, the intensity-concentration plots used to establish the normalising factors were not parallel. However, the results obtained for the chemically analysed samples were satisfactory and only a small error was introduced by using normalising constants corresponding to a wide range of selected chromium and nickel concentrations. In fact, quite good agreement was obtained for the AISI 431 and AISI 420 steels (see Table 3), even though the normalising factors were those corresponding to 20% chromium and 10% nickel. This indicates that deviations from the proposed criteria can be tolerated.

The total internal standard was derived from a combination of neutral atom and ion lines. The lines were chosen on the basis of their freedom from spectral interference and suitable intensities at the conditions described. It was anticipated that changes in excitation index from exposure to exposures might cause variations in the normalising factor which would then affect the total intensity. However, it was found that the excitation index based on the observation of the ratio of FeII 315.421 nm/ FeI 309.997 nm, showed little variation over a range of exposures; consequently, it had an insignificant effect on the analytical results.

The internal standard based on FeI, NiI and CrII was used for nickel and silicon. Nickel results with this internal standard were in slightly better agreement with the chemical values than those obtained with the FeII-NiI-CrII combination, whereas no significant difference was observed in the silicon results. In the case of nickel, it would appear that the close matching of the excitation potentials of the lines is responsible for the improved agreement.

The successful application of this procedure depends largely on the use of argon as the shield gas and the resultant black burn characteristics of the exposure. Arrak [1963] showed that linear intensity-concentration curves for various ferrous alloys can be obtained using this procedure because it minimises metallurgical history effects. Our own experience verifies this and we find that this procedure provides greater reproducibility between exposures, and this leads to higher precision.

6. CONCLUSION

The method described here has been found suitable for analysing stainless steels with good precision and the results are in satisfactory agreement with those obtained by chemical analysis. An attractive feature of the method is its independence of the major component concentration. Once established, the procedure is very rapid by comparison with other techniques.

Its successful application to other alloy systems would depend on the basic condition that the sum of the major component concentrations is constant.

7. ACKNOWLEDGEMENT

We wish to acknowledge the assistance of Dr. P.L. Sanger in the derivation of the non-linear regression equations.

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APPENDIX A

DERIVATION OF ERROR EQUATIONS FOR NON-LINEAR REGRESSION WORKING CURVES

Consider the ratio of two independent variables [Hamilton 1964]

$$r = y/x \quad . \tag{A1}$$

It can be shown that the square of the relative error of a ratio is approximately equal to the sum of the squares of the relative errors of the numerator and denominator provided there is almost no probability that either x or y is near zero and that $\sigma^2(x) << \mu_x^2$. That is

$$\left(\frac{\sigma(r)}{\mu_r}\right)^2 \approx \left(\frac{\sigma(x)}{\mu_x}\right)^2 + \left(\frac{\sigma(y)}{\mu_y}\right)^2 \quad . \tag{A2}$$

Consider the case

$$I = \alpha c^{\gamma}$$

where I is the measured dependent variable (intensity or analytical ratio),

α and γ are constants for a given set of conditions, and

c is the independent concentration variable.

Then $$\ell n\ I = \ell n\ \alpha + \gamma\ \ell n\ c \tag{A3}$$

or $$\ell n\ c = \frac{(\ell n\ I - \ell n\ \alpha)}{\gamma} \quad . \tag{A4}$$

Making the assumption

$$\sigma_{\ell n\ c} \approx \frac{1}{2}\ \ell n \left\{(c + \sigma_c) - \ell n\ (c - \sigma_c)\right\} \tag{A5}$$

that is $$2\ \sigma_{\ell n\ c} \approx \left\{\ell n \left(\frac{c + \sigma_c}{c - \sigma_c}\right)\right\} \quad ,$$

then $$\sigma_c \approx c\left\{\frac{\exp\ (2\ \sigma_{\ell n\ c}) - 1}{\exp\ (2\ \sigma_{\ell n\ c}) + 1}\right\} \quad . \tag{A6}$$

Alternatively

$$\sigma_{\ell n\ c} \approx \frac{1}{2}\left\{\ell n\ \frac{\left(1 + \frac{\sigma_c}{c}\right)}{\left(1 - \frac{\sigma_c}{c}\right)}\right\} .$$

Thus $$\sigma_{\ell n\ c} \approx \frac{1}{2}\left\{\ell n\ \frac{\left[1 + \frac{2\sigma_c}{c} + \frac{\sigma_c{}^2}{c^2}\right]}{\left[1 - \left(\frac{\sigma_c}{c}\right)^2\right]}\right\} .$$

If $$\left(\frac{\sigma_c}{c}\right)^2 << 1 ,$$

$$\sigma_{\ell n\ c} \approx \frac{1}{2}\ \ell n\left(1 + \frac{2\sigma_c}{c}\right) . \tag{A7}$$

Therefore

$$2\ \frac{\sigma_c}{c} + 1 = \exp\ (2\ \sigma_{\ell n\ c}) ,$$

i.e. $$\sigma_c = \frac{c}{2}\left\{\exp\ (2\ \sigma_{\ell n\ c}) - 1\right\} .$$

Applying Equation (A2) to (A4)

$$\left(\frac{\sigma_{\ell n\ c}}{\ell n\ c}\right)^2 \approx \left\{\frac{\sigma_{\ (\ell n\ I\ -\ \ell n\ \alpha)}}{(\ell n\ I\ -\ \ell n\ \alpha)}\right\}^2 + \left\{\frac{\sigma_\gamma}{\gamma}\right\}^2 ,$$

thus

$$\left(\frac{\sigma_{\ell n\ c}}{\ell n\ c}\right)^2 \approx \left\{\frac{\sigma^2{}_{\ell n\ I} + \sigma^2{}_{\ell n\ \alpha}}{(\ell n\ I\ -\ \ell n\ \alpha)^2}\right\} + \left\{\frac{\sigma_\gamma}{\gamma}\right\}^2 . \tag{A8}$$

From Equation (A7), we have

$$\sigma_{\ell n\ I} \approx \frac{1}{2}\ \ell n\ \left(1 + \frac{2\sigma_I}{I}\right) , \tag{A9}$$

and

$$\sigma_{\ell n\ \alpha} \approx \frac{1}{2}\,\ell n\left(1 + \frac{2\sigma_\alpha}{\alpha}\right) \quad . \tag{A10}$$

Substituting Equations (A9) and (A10) into (A8), we have

$$\left(\frac{\sigma_{\ell n\ c}}{\ell n\ c}\right)^2 \approx \left\{\frac{\left[\frac{1}{2}\,\ell n\left(1 + \frac{2\sigma_I}{I}\right)\right]^2 + \left[\frac{1}{2}\,\ell n\left(1 + \frac{2\sigma_\alpha}{\alpha}\right)\right]^2}{[\ell n\ I - \ell n\ \alpha]^2}\right\} + \left\{\frac{\sigma_\gamma}{\gamma}\right\}^2 ;$$

that is

$$\sigma_{\ell n\ c} = \ell n\ c\sqrt{\frac{\left[\frac{1}{2}\,\ell n\left(1 + \frac{2\sigma_I}{I}\right)\right]^2 + \left[\frac{1}{2}\,\ell n\left(1 + \frac{2\sigma_\alpha}{\alpha}\right)\right]^2}{[\ell n\ I - \ell n\ \alpha]^2} + \left[\frac{\sigma_\gamma}{\gamma}\right]^2} \quad , \tag{A11}$$

where σ_I is the standard deviation of the sample analytical ratio calculated from replicate exposures.

For a given set of data values, the constants α and γ can be readily obtained from standard weighted non-linear regression package programs (ACL-NOVA computer non-linear weighted least squares library routine (NLRPW)).

The estimation of the error in the final concentration is obtained from Equations (A6) and (A11).

TABLE 1

APPARATUS AND SPECTROGRAPHIC OPERATING CONDITIONS

Spectrograph	Large quartz prism, Littrow mount (Hilger & Watts, Model E478)
Wavelength region	240-330 nm
Source-to-slit distance	35.5 cm
Slit	0.02 x 2 mm
Analytical gap	2 mm
Pre-exposure	10 s
Exposure	20 s
Source	15 kV condensed spark; L = 0.06 mH, C = 0.005 μF tandem gap setting 3 mm. (Hilger and Watts, Model FS131)
Electrodes	Lower: ASTM C-4 (National AGKSP grade graphite) Upper: Sample
Inert gas chamber	Delrin chamber Spex Cat. No. 3310
Argon flow rate	7 ℓ $\min^{-1}$
Emulsion	Ilford N30
Developing conditions	4 min 1:1 Kodak D19B (continuous agitation), fixed 4 min in Ilford Hypam Rapid Fixer with chrome alum hardener. Tank temperature 20°C
Emulsion calibration	Rotating 7-step sector, step ratio 0.5
Densitometry	Jarrell-Ash Model JA2105 microdensitometer

TABLE 2

ANALYTICAL SPECTRUM LINES

Element	Wavelength (nm)	Excitation Potential (eV)*
Fe II	315.4206	7.66
Cr II	315.221	8.28
Ni I	310.1554	4.09
Fe I	309.9968	4.89
Mo II	281.6153	6.04
Mn II	293.305	5.38
Ti II	326.1596	5.01
Si I	251.6109	4.93

*From Moore [1945]

TABLE 3

COMPARISON OF SPECTROGRAPHIC AND CHEMICAL RESULTS ON VARIOUS STAINLESS STEELS

Type	% Cr		% Ni		% Mn		% Ti		% Mo		% Si		% Fe	
AISI	Spectro[†]	Chem[§]	Spectro	Chem	Spectro	Chem	Spectro	Chem	Spectro	Chem	Spectro	Chem	Spectro	Chem[*]
321	17.5 ± 0.7	17.9	10.1 ± 0.3	10.2	0.77 ± 0.02	0.87	0.52 ± 0.05	0.50	-	-	0.55 ± 0.03	0.68	69.8 ± 0.9	70
321	18.1 ± 0.8	17.9	8.7 ± 0.2	9.2	1.17 ± 0.04	1.28	0.40 ± 0.08	0.36	-	-	0.52 ± 0.03	0.60	69.8 ± 1.5	71
316	18.7 ± 0.7	18.6	11.1 ± 0.3	11.3	0.77 ± 0.02	0.77	-	-	2.34 ± 0.13	2.02	0.59 ± 0.03	0.73	67.5 ± 0.8	67
310	25.7 ± 0.8	25.4	23.2 ± 1.0	22.4	0.93 ± 0.04	0.89	-	-	-	-	0.43 ± 0.03	0.54	54.8 ± 1.6	51
431	16.3 ± 0.4	16.9	2.2 ± 0.1	2.8	0.57 ± 0.05	0.55	-	-	-	-	0.18 ± 0.02	0.15	76.8 ± 1.2	80
420	13.0 ± 0.7	13.4	-	-	0.28 ± 0.02	0.28	-	-	-	-	0.17 ± 0.02	0.16	82.4 ± 0.9	86

[*] % Fe calculated by difference

[†] Limits are quoted for 1.96 x σ (95% confidence level)

[§] Precision of chemical analysis is ± 3%

TABLE 4

EFFECT OF VARIATION OF NORMALISING FACTORS ON ANALYTICAL RESULTS

Ni-Cr concentrations (%) used for determining normalising factors	% Fe	% Cr	% Ni	% Mn	% Ti	% Mo	% Si
Sample: AISI 321							
5-10	72.1	18.3	10.1	0.80	0.55	-	0.54
5-20	70.7	17.8	9.8	0.78	0.53	-	0.52
5-40	69.2	17.3	9.5	0.76	0.52	-	0.51
10-10	71.2	18.0	9.9	0.79	0.54	-	0.53
20-10	70.1	17.6	9.7	0.77	0.52	-	0.51
20-20	68.8	17.2	9.4	0.76	0.51	-	0.50
20-40	67.4	16.7	9.2	0.74	0.50	-	0.49
10-20[†]	69.8	17.5	9.6	0.77	0.52	-	0.51
Chem. value	70	17.9	10.2	0.87	0.50	-	0.68
Max. deviation[§]	2.4	0.8	0.5	0.03	0.03	-	0.03
% Max. error	3.4	4.6	5.2	3.9	5.8	-	5.9
% Exp. error[*]	4.3	6.4	7.1	7.0	18.5	-	14.6
Sample: AISI 316							
5-10	70.7	19.6	12.3	0.82	-	2.46	0.63
5-20	68.5	19.0	11.8	0.80	-	2.41	0.61
5-40	67.1	18.5	11.4	0.78	-	2.32	0.59
10-10	68.9	19.2	11.9	0.81	-	2.41	0.62
10-40	66.1	18.1	11.2	0.77	-	2.27	0.58
20-10	67.8	18.8	11.6	0.79	-	2.36	0.60
20-20	66.4	18.2	11.3	0.77	-	2.29	0.58
20-40	65.1	17.7	11.0	0.75	-	2.22	0.56
10-20[†]	67.5	18.7	11.6	0.79	-	2.34	0.60
Chem. value	67	18.6	11.3	0.77	-	2.02	0.73
Max. range	2.5	1.0	0.7	0.04	-	0.12	0.04
% Max. error	3.7	5.3	6.0	5.1	-	5.1	6.7
% Exp. error[*]	4.3	6.5	7.2	6.9	-	12.0	13.0

[*] Experimental error is taken at the 95% confidence level (1.96 x σ). This error is calculated from Equations (A1) and (A2) in Appendix A. It also includes the error in the analytical ratio.

[†] Appropriate subdivision level for this sample.

[§] Maximum deviation from mean value obtained using the most appropriate normalising factors.

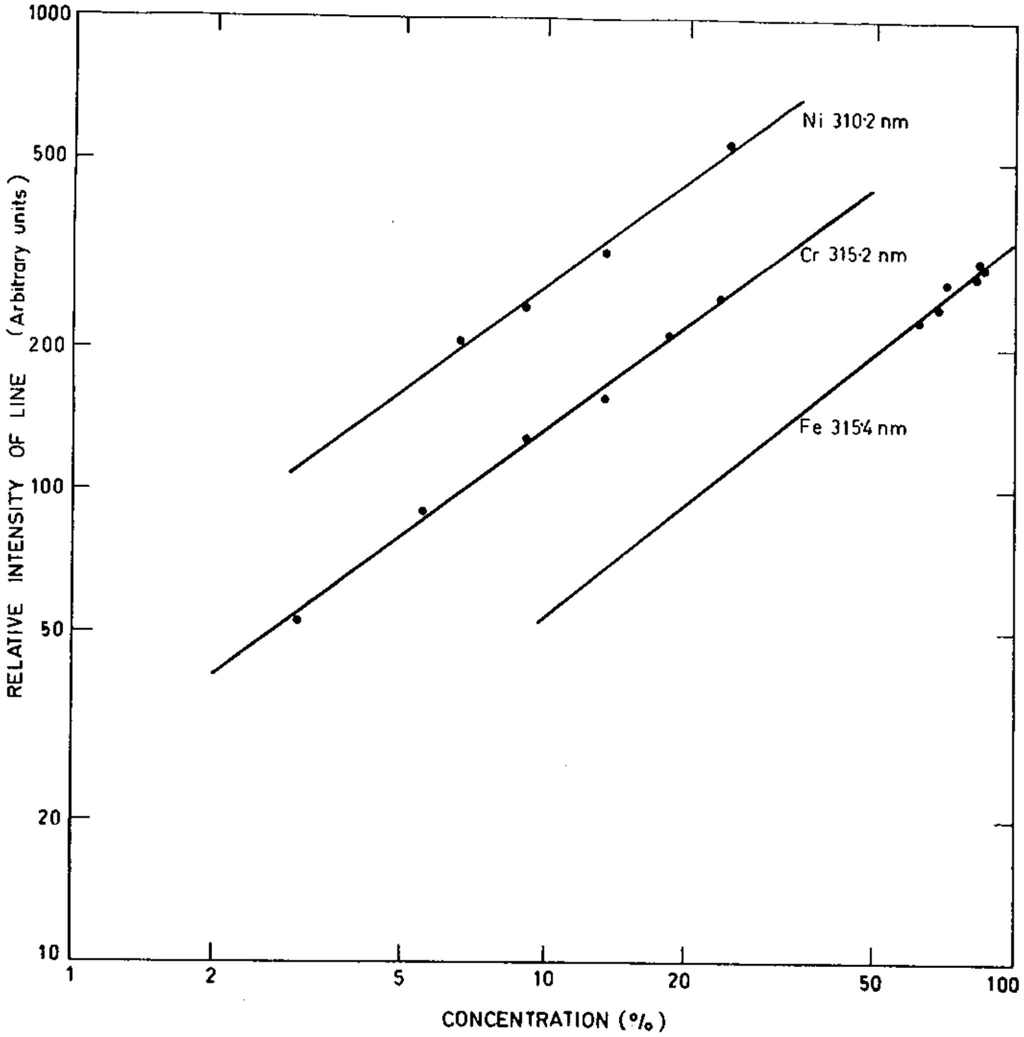

FIGURE 1. INTENSITY-CONCENTRATION CURVES USED FOR OBTAINING NORMALISING FACTORS

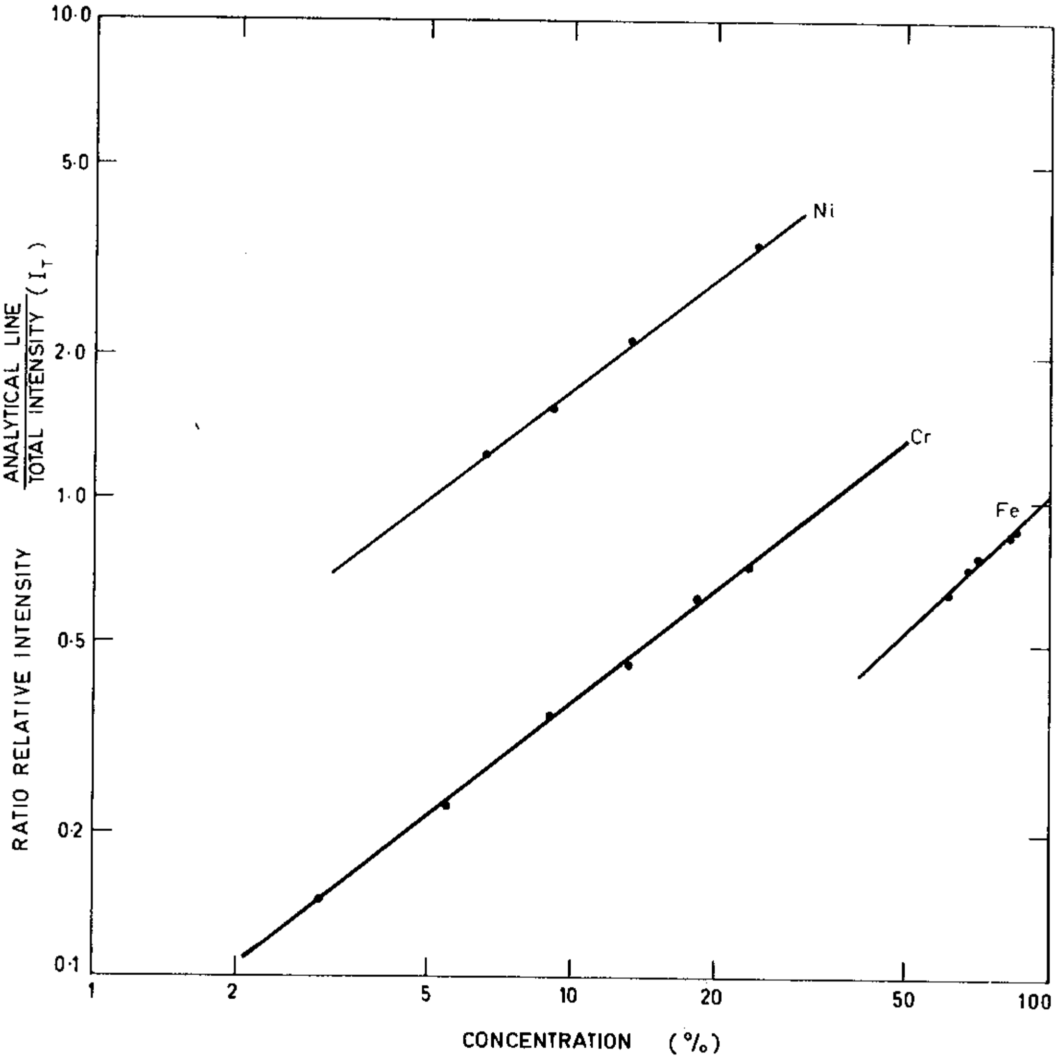

FIGURE 2. WORKING CURVES FOR IRON, CHROMIUM AND NICKEL

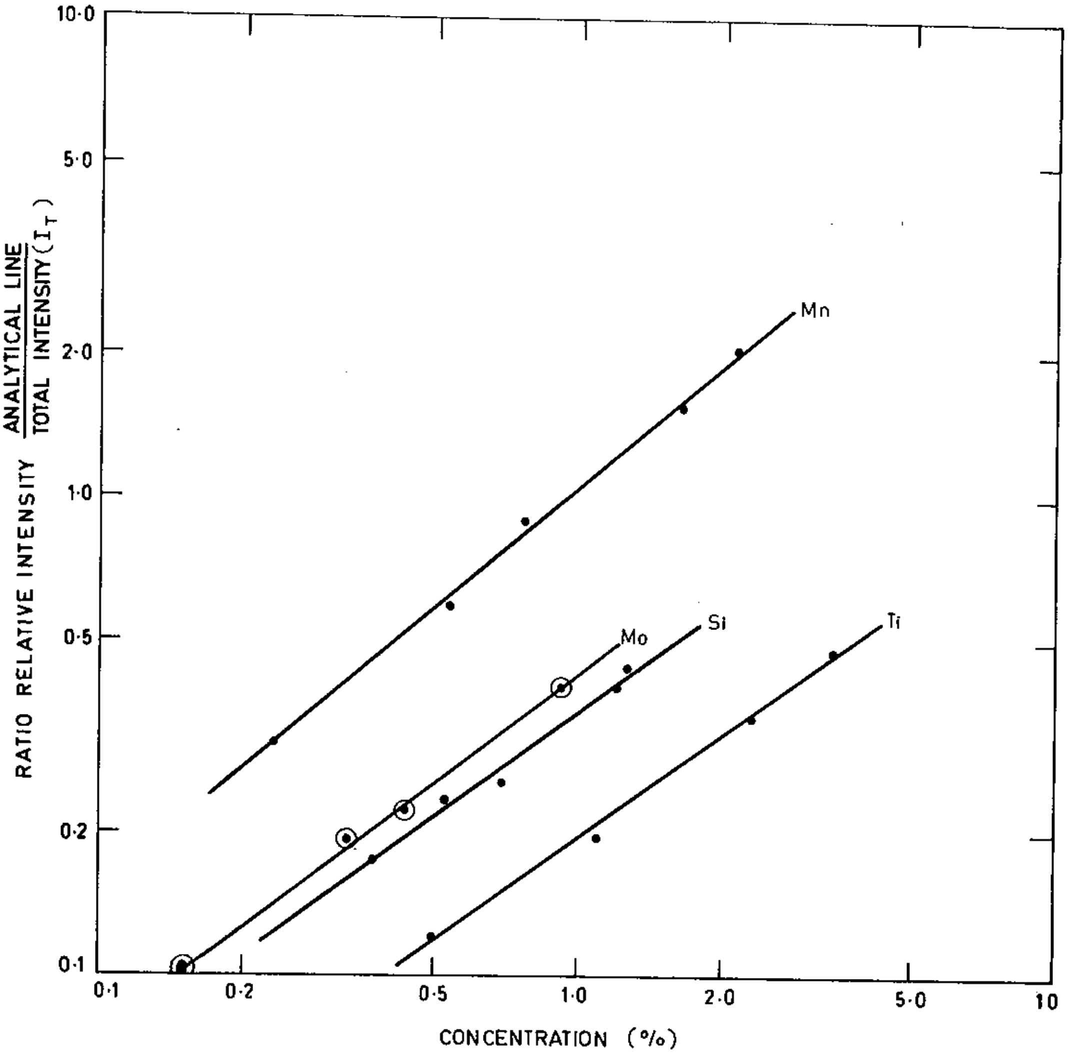

FIGURE 3. WORKING CURVES FOR TITANIUM, SILICON, MOLYBDENUM AND MANGANESE

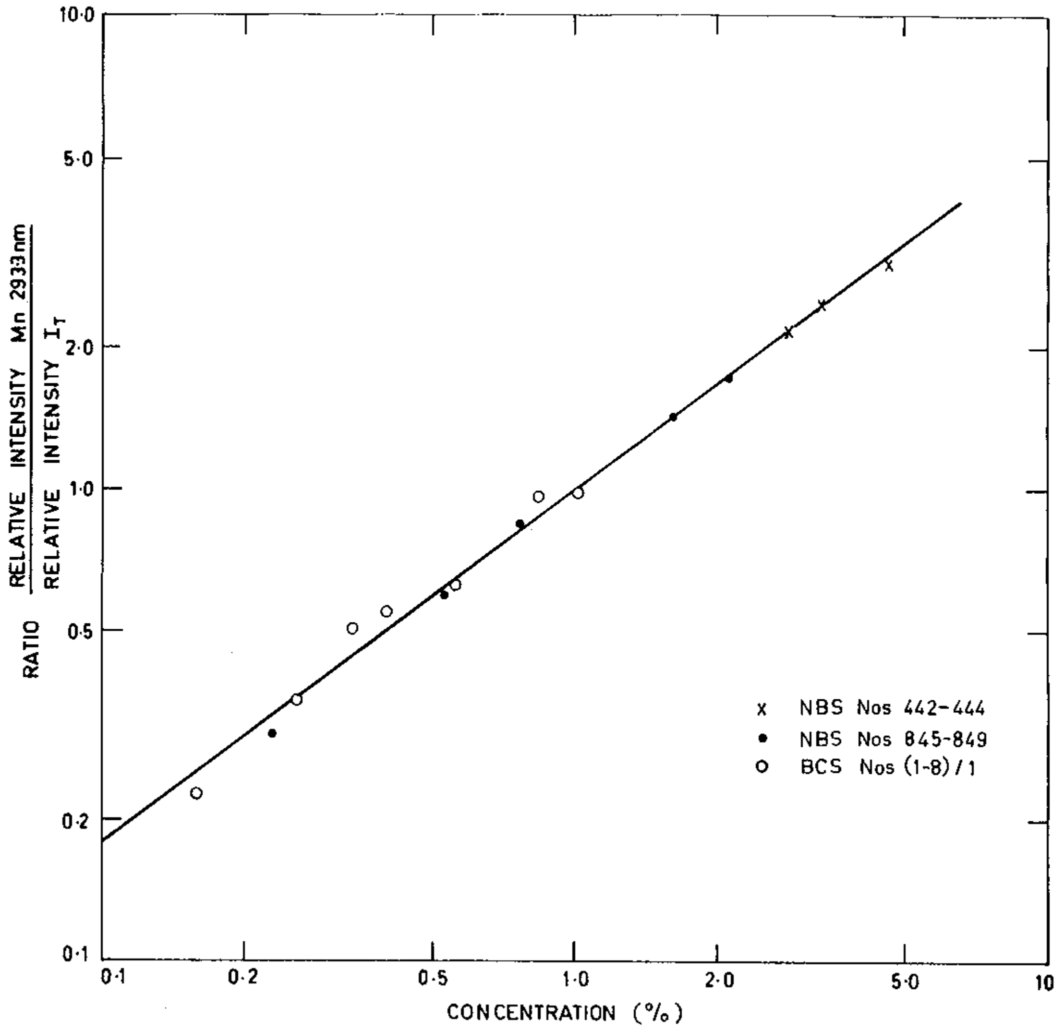

FIGURE 4. WORKING CURVE FOR MANGANESE USING STAINLESS STEEL AND LOW ALLOY STEEL STANDARDS