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Evaluation of Spectrochemical Data Using Digital Techniques

Abstract: This paper describes how a digital computer was used in combination with an emission spectrometer to determine chemical compositions of some steels. A mathematical model describing the relations between the composition and the intensities of the spectral lines was derived and experimentally tested. Both overlapping and matrix effects were considered. The computer was also used to calibrate the instrument.

Introduction

Quantitative chemical analysis, based on the measurement of electromagnetic radiation from a sample whose atoms have been excited, originates from experiments performed by Kirchhoff and Bunsen in the middle of the 19th century. Optical emission spectroscopy was used. More recently the same principles have led to x-ray fluorescence chemical analysis. This paper deals with optical emission spectroscopy and shows how a digital computer was used in some experiments to establish a relationship between composition and spectral line intensity.

Chemical analysis based on emission spectroscopy has developed into an elaborate technique. Two major difficulties encountered have been the instability of the spectroscopic light source, which leads to a large statistical error or poor precision, and matrix effects, which introduce systematic errors or poor accuracy. In order to discuss the nature of these problems and some previous work, we will give a short introduction to fundamental concepts.

Spectrochemical analysis is based on the fact that the light intensity of a spectral line is related to the composition of the sample. Ideally the intensity of each line depends on only one particular constituent of the sample, and as a first approximation this simplification is generally acceptable. In addition the light intensity also depends on the *excitation conditions*. Because of the inherent instability of the two excitation processes most commonly employed (arc and spark discharge), the recorded intensities generally fluctuate heavily. In order to smooth out the fluctuations, simultaneous integration of all the observed lines is applied with respect to time. Division by the integration time will give the intensity average of each line. If the integration time is kept constant from run to run, this division need not be carried out explicitly. When the integration time is kept constant, the outcomes of repeated measurements will still differ from run to run, primarily because of varying excitation conditions.

Whether integration is applied or not, it is often observed that the fluctuations of two different line intensities are close to being proportional, i.e., the two signals recorded are strongly correlated. The two lines then form an *homologous pair*.[1] This means that in an idealized case their intensity ratio does not vary, either with excitation condition or time. When the condition of homologous pairs is approximated, it is possible to counteract the effects of light source instabilities by applying the method of relative intensities (using an internal standard), which will now be outlined.

A reference line is chosen corresponding to the internal standard, some specific constituent of the sample. Generally the major constituent is selected as the internal standard. First, let us assume that the concentration of the standard does not differ from sample to sample such as in the case of Fe in carbon steel. The time of integration is then determined in such a way that the integral of this reference line reaches a preset value, the reference level. Thus the effect of the correlated noise is eliminated and repeated measurements will now give results having far less spread. The remaining spread is due to uncorrelated noise, e.g., from intensity fluctuations of scattered light in the spectrometer and thermal noise in the multipliers.

If the concentration of the internal standard varies,

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such as in the case of Fe in stainless steels, the method has to be modified. The reference level should be such that if the samples contain a constituent whose concentration (as opposed to that of the internal standard) is constant from sample to sample, the intensity integral corresponding to this constituent should remain the same. If this condition is fulfilled, the integral corresponding to the internal standard will vary with the concentration of the standard. The graph of this relation is called the correction curve of the internal standard. Conversely, this curve will now give the reference level for an arbitrary sample if it is assumed that its content of the internal standard can be estimated. When this technique is used, the times of integration will no longer be constant but will instead be randomly distributed around a mean. It should be mentioned that if the time of integration is kept constant and equal to this mean, the correction curve of the internal standard can be obtained through averaging repeated measurements of each sample.

Once the intensity integrals corresponding to the constituents of the sample have been determined, the concentrations are normally evaluated from working curves relating the intensity to the concentration of each constituent. However, this method may in some cases lead to considerable errors. Such a working curve, for example, might only hold true for classes of samples having a particular metallurgical structure. This effect will not be considered any further here.

Moreover, *matrix effects* may introduce errors. These effects may be due to absorption and enhancement of radiation among the atoms of the constituents or may be caused by selective vaporization. Working curves (which are obtained from standards of known compositions) may still be drawn using a parametric presentation, as is exemplified for a particular constituent of a three-component system in Fig. 1. As the number of constituents increases, however, the technique very rapidly yields a problem of overwhelming complexity.

The method of relative intensities successfully eliminates the effects of correlated noise. However, it provides no countermeasure against uncorrelated noise, e.g., from lines which are not homologous or Schrot-effect noise generated in the detectors. Furthermore the conventional methods do not give a satisfactory solution to the problems generated by matrix effects. The two sets of problems thus defined have inspired the present work, which is based on the use of a digital computer in combination with the spectrometer.

• *Previous work*

The authors know of no fundamental study presenting an explorative survey of matrix effects in emission spectroscopy. In x-ray fluorescence spectroscopy Sherman[2] has made a penetrating study of these effects. A quantitative

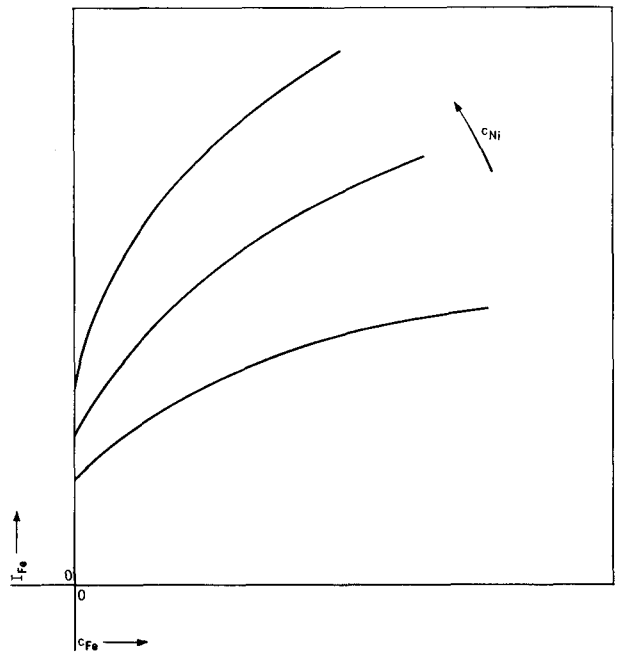


Figure 1 **Sketch of matrix effects in a three-component alloy.** *Each curve is obtained by replacing Fe with Cr, keeping the Ni-content constant.*

description leads to very complicated analytic expressions. Both in emission- and fluorescence-spectroscopy one is forced to introduce approximations when aiming at practically useful expressions. In emission spectroscopy such attempts are exemplified by Graue,[3] Majkowski,[4] and in x-ray fluorescence by Lucas-Tooth,[5] Laffolie,[6] and Marti.[7] When utilizing these and similar ideas, analogue[3,7] as well as digital techniques[5,8–10] have been employed.

Outline of the method

The present approach is characterized by the following features. A digital computer is utilized both for the calibration of the instrument and for the determination of the compositions of unknown samples (Fig. 2). The latter process will be called *inversion.*

Further, the mathematical model introduced simulates both overlapping- and matrix-effects.* Also the information from several lines representing the same constituent is simultaneously made useful. The relative significance of the different lines is considered.

The approach offers a countermeasure against uncorrelated noise of zero mean. Since recalibrations can be frequently repeated it also offers a means of reducing systematic errors due to long-term drift.

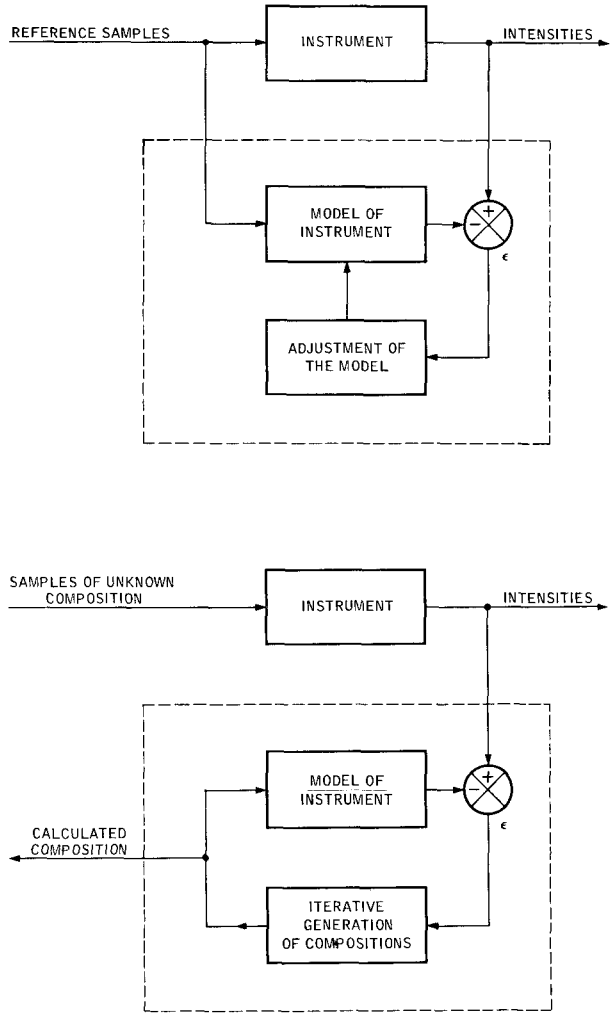
* Overlapping effects for a spectral line may be defined as interference by other spectral lines not resolved by the exit slit.

The model

Consider the case where the spectral lines involved are viewed by photomultipliers. The incident light will contribute with a current $i_k(t)$ through the k^{th} multiplier. This current will fluctuate heavily because of the instability of the light source. The current is integrated over a finite time determined by the internal standard method. In spite of the noise-suppressing effect of this method, repeated measurements of this integral will still vary from one result to the next. When a sample of composition c is repeatedly excited, the mean value of the integral of the total multiplier current will be denoted $\bar{I}_k(\mathbf{c})$ and the individual outcomes $U_k(\mathbf{c})$. Thus

$$U_k(\mathbf{c}) = \bar{I}_k(\mathbf{c}) + P_k, \tag{1}$$

Figure 2 **The two basic modes of operation of the computer: calibration and inversion.** The *dashed frames indicate the computer.*



where $\{P_k\}$ is a discrete stochastic process of zero mean. In Appendix 1 this formula is considered in some detail.

Next we discuss the term $\bar{I}_k(\mathbf{c})$ and start with the following physical reasoning. Consider a volume of gas, containing atoms of different kinds, from which light is emitted because of thermal excitation. If only the spontaneous emission is considered, the intensity of any line will be proportional to the number of atoms of the corresponding constituent, i.e., to its concentration. The same holds true for the continuous intensity spectrum of that constituent.

The primary spontaneous process thus leads to approximating the intensity $\bar{I}_k(\mathbf{c})$ with a sum of linear terms of the different concentrations. Hence the overlappings of spectral intensities are taken into account.

Suppose that the constituent l dominates the radiation of line k, i.e., the coefficient of c_l is of dominating magnitude. The radiation emitted from the atoms of constituent l may be absorbed by the atoms of the same or other constituents. Also, radiation originating from any one constituent may cause induced emission in the atoms of the l^{th} constituent. Quantitatively such processes depend on the energy levels and the transition probabilities involved.

It seems reasonable to assume that the intensity losses or gains due to these secondary processes are described by terms proportional to the two-fold products of the concentration of the constituent l with each one of the other concentrations involved, possibly including l. Letting m denote the number of constituents one is thus led to the following formula:

$$\bar{I}_k(\mathbf{c}) = \sum_{i=1}^{m} A_{ki}c_i + c_l \sum_{i=1}^{m} Q_{ki}c_i + \bar{I}_{k0}, \tag{2}$$

in which the first term describes gains and losses from the overlapping effects, and the second term, from the matrix effects. The term $\bar{I}_{k0}$ includes background radiation due to excitation of the atmosphere surrounding the light source and of vaporized electrode material.

In conclusion the model is based on the assumption that the resulting radiation is *homogeneously* generated in the emitting plasma. In the case of x-ray fluorescence spectroscopy this approach is certainly not true, since the primary emission declines exponentially with the depth. However, making some test runs with X-ray data using the present model and also using one of comparable complexity which was derived considering the nonhomogeneity[5] mentioned above we found neither method superior. Although this result is not a conclusive argument and hence deserves no further regard in this paper it indicates that the presented approximation is justifiable in the far more favourable case of emission spectroscopy.

• *The calibration*

The objective of the calibration is to determine numeri-

cally the coefficients of equations (2) from measurements of samples of known compositions. For each spectral line observed, defining a particular value of k in Eq. (2), as many equations in the unknown coefficients are obtained as there are reference samples.

In order to suppress the effects of the noise superimposed according to Eq. (1), it is advantageous to make the system of equations overdetermined, i.e. N, the number of reference samples, should if possible exceed $M = 2m + 1$, the number of coefficients in each one of the equations (2). The unknowns are determined applying the maximum likelihood method which, assuming Gaussian noise, leads to the least-squares method.

A complication arises since it is desirable to take all the constituents of the sample into account. Therefore $\sum_{i=1}^{m} c_i = 1$ and the columns of the coefficient matrix of the system of equations will be linearly dependent. This dependency could easily be removed through expressing any one of the concentrations as a function of the others. However, it is generally difficult to choose the constituent to be excluded on physical grounds only. Applying numerical arguments, it is possible to form well-defined rules concerning this elimination. The numerical procedure employed is described in Appendix 2. The normal equations are never explicitly formed. Instead, the system is solved through stepwise orthogonalization of the coefficient matrix. Thus each step will improve the solution available from the previous step. For a survey of similar methods, see Ref. 11.

Any one of the concentrations can be expressed as a linear combination of the others. Thus, there will be as many different solutions as there are constituents in the sample. Obviously these solutions are identical in the sense that each one of them could be transformed into any one of the others. This lack of uniqueness makes the physical interpretation of the individual coefficients less interesting. In fact on numerical grounds it has been found preferable not to explicitly calculate these coefficients, but rather to express Eq. (2) in terms of another set of coefficients corresponding to the use of a reference sample as described in the next section. This will not change the structure of the model but only the values of the coefficients.

• *The inversion*

The inversion implies the determination of the composition of an unknown sample using the model (1)-(2), calibrated as described in the previous section. Basically this requires the solution of a system of nonlinear equations. Since the present approach allows the use of more than one spectral line for each constituent, this system of equations may contain more equations than unknowns.

Let n be the total number of spectral lines observed. Further, let $\mathbf{U}(\mathbf{c})$ be the outcome of a specific run and $\bar{\mathbf{I}}(\mathbf{c})$ the output of the model corresponding to the composition $\mathbf{c}$,

$$\mathbf{U}(\mathbf{c}) = \begin{bmatrix} U_1(\mathbf{c}) \\ U_2(\mathbf{c}) \\ \vdots \\ U_k(\mathbf{c}) \\ \vdots \\ U_n(\mathbf{c}) \end{bmatrix}, \qquad \bar{\mathbf{I}}(\mathbf{c}) = \begin{bmatrix} \bar{I}_1(\mathbf{c}) \\ \bar{I}_2(\mathbf{c}) \\ \vdots \\ \bar{I}_k(\mathbf{c}) \\ \vdots \\ \bar{I}_n(\mathbf{c}) \end{bmatrix}.$$

Since it is desired to consider the intensities of the observed lines according to their significance, a weighting matrix Π is introduced:

$$\Pi = \begin{bmatrix} \Pi_1 & & & & 0 \\ & \Pi_2 & & & \\ & & \ddots & & \\ & & & \Pi_k & \\ & & & & \ddots \\ 0 & & & & \Pi_n \end{bmatrix},$$

where Π_k should be inversely proportional to $\sigma_k^2 = E\{P_k^2\}$. We define the optimal solution $\mathbf{c}^*$ as follows. Let

$$\boldsymbol{\varepsilon}^* = \mathbf{U}(\mathbf{c}) - \bar{\mathbf{I}}(\mathbf{c}^*).$$

Then $\mathbf{c}^*$ minimizes the quadratic form

$$f = \boldsymbol{\varepsilon}^{*T} \Pi \boldsymbol{\varepsilon}^*. \tag{3}$$

The vector $\mathbf{c}^*$ has m components. Since $\mathbf{c}^*$ defines an extremum, it holds for each one of its components

$$\left(\frac{\partial f}{\partial c_k}\right)_{\mathbf{c}^*} = 0 \qquad k = 1, 2, \cdots m. \tag{4}$$

The original, possibly overdetermined system of equations has thus been reduced to a system of m equations in m unknowns. Introducing a suitable formalism, these equations, embodying the coefficients defined in (2), may be written in a compact form. The formalism and the derivation are presented in Appendix 3.

The numerical solution of these equations may be carried through by using Newton-Raphson iterations. The favorable numerical convergence which occurs when this method is applied is due to the fact that the intensity of each specific spectral line is dominated by one particular constituent, and also that each constituent considered dominates the intensity of at least one spectral line. It has been empirically verified that a simplified version of the Newton-Raphson procedure gives quite satisfactory results. Thus, at each iteration, the equation that fits worst is identified and then only the constituent dominating this equation is changed. For a detailed presentation, see Ref. 12.

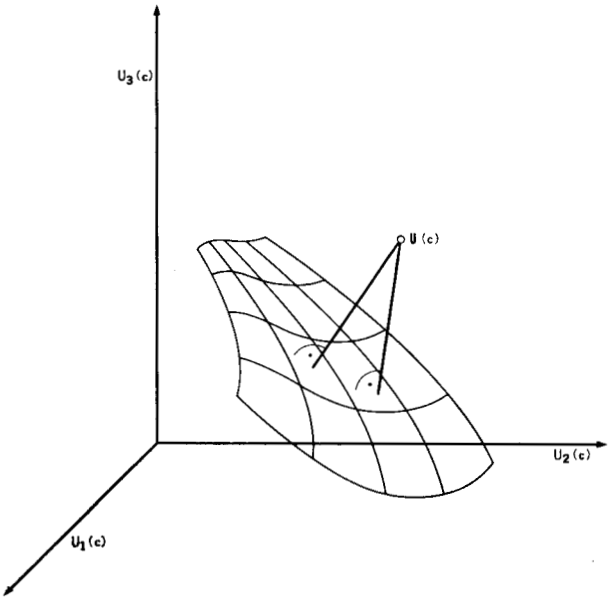


Figure 3 **Example of a case of non-uniqueness when solving the inversion problem.**

The inversion procedure does not necessarily lead to an unique answer c*. This can easily be grasped from the following geometrical picture. Let both c and $\bar{I}(c)$ be 3-dimensional. The composition of any such sample will be contained in a plane in the c-space. This plane is mapped into a surface, generally a curved one, in the intensity-space. Now suppose that the intensity outcome of a particular run is represented by a point separated from this surface. For simplicity assume that II is an identity matrix. Then an optimal solution arrived at through (4) is represented by the footpoint of a normal to the intensity surface passing through this point. One may easily visualize cases when there are several such normals (Fig. 3). However, within local regions uniqueness can be ascertained.[12] It is necessary to choose the starting point of the iterative procedure close enough to the correct solution, a requirement which has proved to be no serious obstacle in practice. One thus chooses a reference sample of composition c_0, which preferably represents an average composition in the analysis-space considered. The deviations of the concentrations from this reference composition form the working variables of the numerical procedure as described in Appendix 3.

Experimental results

The system described has been tested experimentally using a 3-meter, concave grating Hilger-Watts 30-channel polychromator, Type E-789, connected to an IBM 1620 digital computer. Altogether, more than 600 specimens have been analyzed, all representing low-alloy carbon steels and stainless chromium-nickel steels. The two types have given rise to separate calibrations of the model.

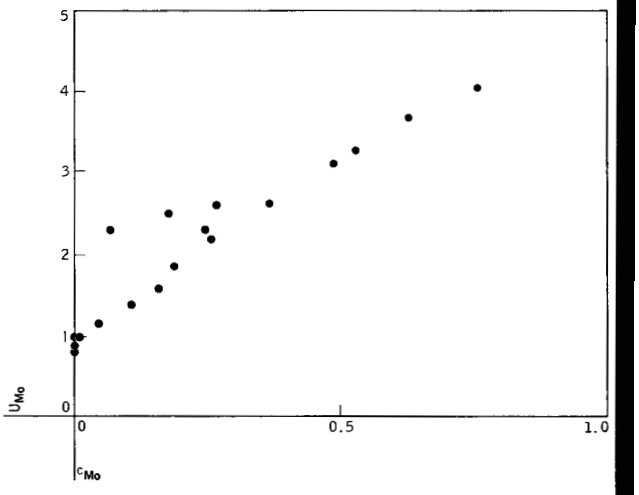
To exemplify the results of the experiments with carbon steels we choose a case exposing pronounced matrix effects. Calibration data for molybdenum are shown in Fig. 4. The matrix effects clearly prevent accurate determinations of low Mo contents if only these data are used.

Taking into account the calibration data for the remaining constituents (Fe, Si, Mn, Cr, Ni) and applying the present model, we obtained the results in Table 1 when analyzing the calibration samples. A comparison between Fig. 4 and Table 1 shows that the matrix effects have been taken care of.

Table 1 **A comparison between results obtained with the wet chemical analysis and with the computer method. The figures represent Mo-content in a carbon steel.**

Sample No.	*Wet analysis*	*Spectro-analysis*	*Sample No.*	*Wet analysis*	*Spectro-analysis*
1	0.00%	0.00%	10	0.25%	0.26%
2	0.00	0.00	11	0.26	0.27
3	0.01	0.02	12	0.27	0.26
4	0.05	0.05	13	0.37	0.36
5	0.07	0.07	14	0.49	0.49
6	0.11	0.11	15	0.53	0.52
7	0.16	0.15	16	0.63	0.63
8	0.18	0.19	17	0.76	0.76
9	0.19	0.19			

Figure 4 **Example of matrix effects which have been solved by the computer method** (*cf. Table 1*). *The data represent Mo in a carbon steel.*



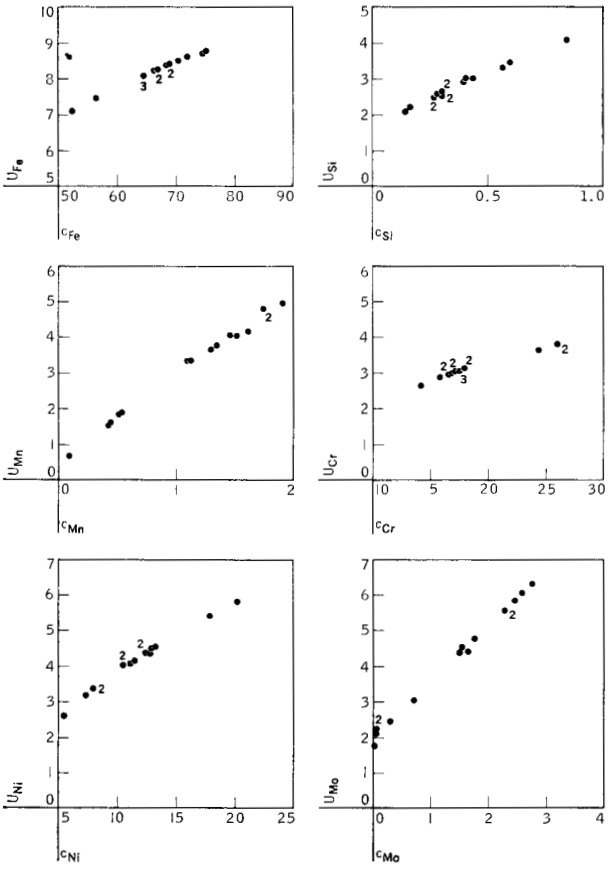


Figure 5 **Working curves representing six components of stainless steel (18/8).** *Matrix effects are not apparent. The figures in the diagram indicate the number of coinciding points.*

Simultaneous applications of the computer method and conventional methods to a large quantity of spectrochemical data representing various samples of stainless steels have not conclusively demonstrated a superior average accuracy for the former method. However, in the present investigation the lines used show very small matrix effects, as is shown in Fig. 5. Therefore the inaccuracy in the analysis of the available reference samples became an obstructive factor when aiming at a conclusion regarding the merits of the methods.

Table 2 exemplifies the uncertainty of wet analyses when determining the compositions of reference samples, in this case of one of intermediate composition. Six independent determinations were made at two different institutions. Gravimetric, photometric, titrimetric and potentiometric methods were applied. Table 2 also gives an idea of the precision of the spectrometer. Thus the same spectrum was spectroanalyzed by conventional means and with the computer method a total of 30 times each. Only one detector was used for each constituent.

Although the previous results do not justify a general statement in favor of the precision of the computer method, there are cases where the gain in accuracy is apparent. Such a case is illustrated in Fig. 6.

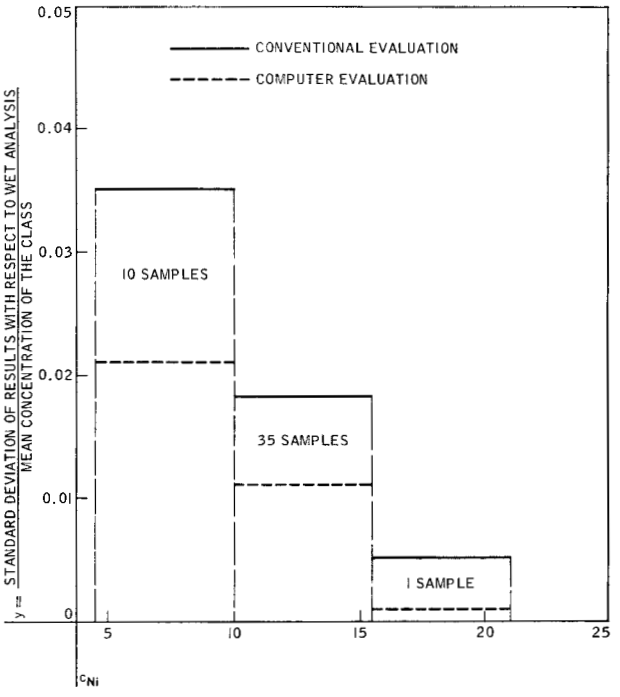
It is likely that the improvement is due to the presence of slight, scarcely noticeable matrix effects. The manually drawn working curves offer no countermeasure against such effects.

The above material also demonstrates how treacherous systematic errors may be introduced when using such curves. This is exemplified in Table 2 by the Ni-values obtained from the conventional methods; these values had to be corrected by drawing a new curve before carrying through the comparison presented in Fig. 6.

Conclusion

The experimental results presented in this paper cover a very narrow sector of the total field of possible applications of spectrum analysis. However, the methods employed to arrive at these results allow for great flexibility since they are based on the use of a digital computer. Demonstrating the usefulness of the methods in a particular application hence has a bearing also on other problems, even though it can not be stated at present that the very same model will be adequate throughout the range of applications.

Figure 6 **A comparison between the conventional and the computer method.** *The results for a particular constituent are illustrated.*



As for the problem studied, the analysis of some steels, the results have proved that it is possible to resolve certain matrix effects with the derived model. The average accuracy was limited by the inaccuracy of the reference samples and the precision of the instrument, rather than by the model. Simultaneous determinations using the conventional method and the present one indicate that systematic errors due to subjective judgments are difficult to avoid with the former one but can essentially be eliminated with the new one. Further experimental work is being done to investigate the applications of our model.

Appendix 1

Let $u(t)$ be the output of one of the photomultipliers. For simplicity we assume that the photomultipliers are of equal sensitivity. We set

$$u(t) = g(t)i + i_0 + n(t). \tag{A-1}$$

Here $i = i(\mathrm{c})$ is the time average of the current caused by the incident light from the spectral line. The function $g(t)$ is the outcome of a stochastic process $\{g(t)\}$ of mean 1, i.e., $g(t) = 1 + m(t)$, where $E\{m(t)\} = 0$, i.e. of mean zero. The approach is justified by the fact that empirically the fluctuations are roughly proportional to the amplitude of i, as exemplified in Fig. 7. Moreover i_0 denotes the mean dark current and $n(t)$ its stochastic component, i.e., $E\{n(t)\} = 0$. Eq. (A-1) is integrated over the interval* $(0, \tau)$ giving

$$U(\tau) = G(\tau)i + i_0\tau + N(\tau), \tag{A-2}$$

where the integrals are denoted with capital letters. The correction curve of the internal standard may, as stated in the main text, be obtained through averaging the output U_{ref} over many runs using the same excitation time $\tau = T$.

We make the approximation

$$i_{\mathrm{ref}}(\mathrm{c}) = i_{\mathrm{ref}}(c_{\mathrm{ref}}). \tag{A-3}$$

The correction curve is then given by the equation

$$\begin{aligned} E\{U_{\mathrm{ref}}(T)\} &= E\{G_{\mathrm{ref}}(T)\}\, i_{\mathrm{ref}}(c_{\mathrm{ref}}) + i_0 T \\ &= [i_{\mathrm{ref}}(c_{\mathrm{ref}}) + i_0]T. \end{aligned} \tag{A-4}$$

Now consider the outcomes τ and $G_{\mathrm{ref}}(\tau)$ of a particular run using the method of the internal standard. Equalizing (A-1) and (A-4) one obtains, after solving for $G_{\mathrm{ref}}(\tau)$,

$$G_{\mathrm{ref}}(\tau) = \frac{(i_{\mathrm{ref}} + i_0)T - N_{\mathrm{ref}}(\tau) - i_0\tau}{i_{\mathrm{ref}}}. \tag{A-5}$$

Assuming the lines to be homologous, we have $G(\tau) = G_{\mathrm{ref}}(\tau)$. Thus introducing (A-5) into (A-1) gives

$$U(\tau) = \left[T + i_0 \frac{T - \tau}{i_{\mathrm{ref}}} - \frac{N_{\mathrm{ref}}(\tau)}{i_{\mathrm{ref}}}\right] i + N(\tau) + i_0\tau.$$

We have $[i_0(T - \tau)/i_{\mathrm{ref}}]\, i \ll i_0\tau$. This follows from $i \ll i_{\mathrm{ref}}$ since the internal standard is the dominant constituent. In addition $\tau \approx T$. Moreover $N_{\mathrm{ref}}(\tau)\, i/i_{\mathrm{ref}} \ll N(\tau)$. We recall that the detectors are identical and thus $E\{N^2_{\mathrm{ref}}(\tau)\} \approx E\{N^2(\tau)\}$. Then we obtain

* Generally $t = 0$ is defined by the end of the preburn period.

Table 2 **Results from repeated measurements using one particular stainless steel sample (AISI 316).**

Wet chemical analysis						
Constituent	Fe	Si	Mn	Cr	Ni	Mo
Percentage, mean	64.53	.60	1.68	17.26	13.27	2.59
Standard deviation	.22	.00	.01	.22	.05	.04
Intensity values $\bar{\mathrm{I}}(\mathrm{c})$						
Mean	81.06	35.35	45.19	30.33	45.08	60.86
Standard deviation	.03	.25	.51	.14	.27	.61
Resulting analysis, computer method						
Percentage, mean	64.53	.62	1.70	17.27	13.28	2.61
Standard deviation	.14	.01	.03	.09	.11	.04
Resulting analysis, conventional method						
Percentage, mean	64.34	.61	1.71	17.24	13.49	2.62
Standard deviation	.15	.01	.02	.09	.13	.04
Corrected value (see text)					13.29	
					.14	

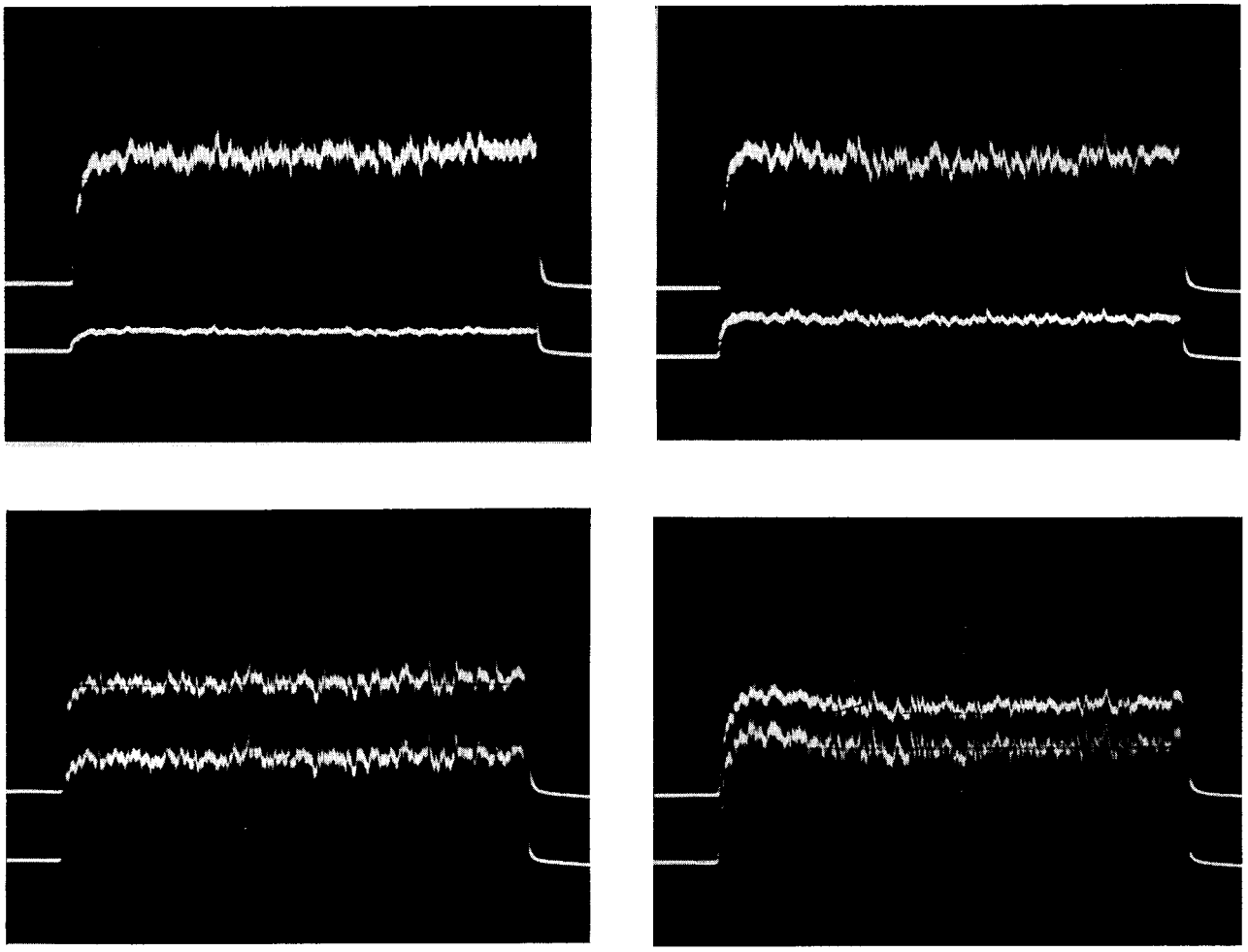


Figure 7 **Each picture shows the simultaneous variations of the intensities of an Fe-line (above) and a Cr-line with time when a sample is excited.** *The time interval shown is about one minute. The different pictures represent different samples. The lines evidently form a homologous pair.*

$$U(\tau) = Ti + N(\tau) + i_0\,\tau$$
$$= T(i + i_0) + N(\tau) + i_0(\tau - T).$$

As may be readily shown from (A-5) $E\{\tau\} = T$. Defining $T(i + i_0) = \bar{I}$ and emphasizing the dependence of the composition we finally obtain $U(\mathbf{c}) = \bar{I}(\mathbf{c}) + P$, where P is a stochastic variable of mean zero.

Appendix 2

Rewriting equations (2) using conventional notations we have

$$A\mathbf{x} \doteq \mathbf{b}, \qquad \text{(A-6)}$$

where

$$A_{(N\cdot M)} = \begin{bmatrix} {}^1c_1\ {}^1c_2 \cdots {}^1c_m & {}^1c_k\cdot{}^1c_1 \cdots {}^1c_k\cdot{}^1c_m & 1 \\ \vdots & & \\ {}^Nc_1\ {}^Nc_2 \cdots {}^Nc_m & {}^Nc_k\cdot{}^Nc_1 \cdots {}^Nc_k\cdot{}^Nc_m & 1 \end{bmatrix}$$

$$\mathbf{b}_{(N\cdot 1)} = \begin{bmatrix} {}^1U_k({}^1\mathbf{c}) \\ \vdots \\ {}^NU_k({}^N\mathbf{c}) \end{bmatrix}$$

$$\mathbf{x}_{(M\cdot 1)} = \begin{bmatrix} a_{k1} \\ \vdots \\ a_{km} \\ \hline q_{k1} \\ \vdots \\ q_{km} \\ \hline \bar{I}_{k0} \end{bmatrix}.$$

The superindex denotes the number of the sample. Neglecting the uncertainty of the analysis of the reference samples we have

$$\sum_{i=1}^{m} c_i = 1$$

for any sample. The system (A-6) is thus ill-behaved and the orthodox procedure using normal equations is not applicable. Instead an orthogonalization procedure is applied.

Basically a Schmidt orthogonalization scheme is used.[13] Out of the set of column-vectors defined by the matrix $A = [\mathbf{a}_1 \mathbf{a}_2 \cdots \mathbf{a}_M]$, an orthonormal set of base vectors is formed in a stepwise manner. In each step an additional vector from A is selected to generate a new base vector. Let S_α denote the subspace spanned by the set of base vectors at a certain step α. Let $\mathbf{b}'_\alpha$ be the orthogonal projection of $\mathbf{b}$ on S_α (Fig. 8). Expressing $\mathbf{b}'_\alpha$ as a linear combination of the columns of A selected so far, i.e. the α vectors spanning S_α, gives a solution $\mathbf{x}_\alpha$ in the least-square sense. Components of $\mathbf{x}_\alpha$ corresponding to nonselected a-vectors equal zero. The squared length of the vector

$$\boldsymbol{\varepsilon}_\alpha = \mathbf{b} - \mathbf{b}'_\alpha = \mathbf{b} - A_\alpha \mathbf{x}_\alpha \qquad \text{(A-7)}$$

equals the sum of the squared errors. That column vector among the not yet selected columns of A which forms the least angle with $\boldsymbol{\varepsilon}_\alpha$ is next chosen to increase the dimension of S_α by one giving $S_{\alpha+1}$ (Fig. 9).

If any one of the remaining vectors is found to be orthogonal to $\boldsymbol{\varepsilon}_\alpha$ within a specified tolerance, that vector is regarded as linearly dependent on the vectors spanning S_α. Such a vector is excluded from further calculations. The calculations are terminated when the length of the error vector is less than a preset value or if there are no more vectors to select.

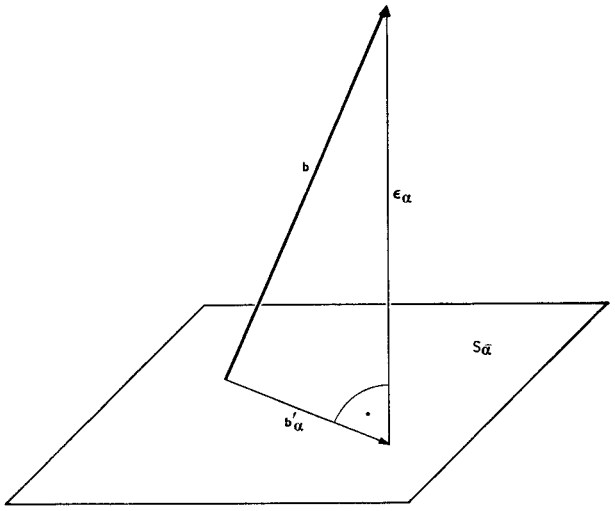
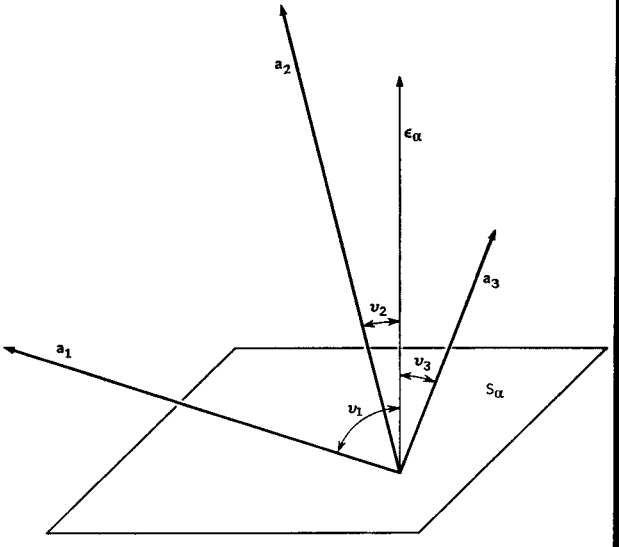


Figure 8 **Geometrical picture of the least-squares solution at step α, using the notations in the text.**

Figure 9 **Selecting a new pivot-vector for the Schmidt-orthogonalization using a least angle criterion.**



Appendix 3

Let $\mathbf{x}$ denote the deviations of the concentrations from their reference values.

$$\mathbf{x} = \mathbf{c} - \mathbf{c}_0. \qquad \text{(A-8)}$$

Introducing $\mathbf{x}$ into (2) gives an equation of identical structure. Simplifying the notations by writing $y_k = \bar{I}_k(\mathbf{c})$ this new equation may be written:

$$y_k = y_{k0} + \sum_{i=1}^{m} a_{ki} x_i + x_l \sum_{i=1}^{m} q_{ki} x_i. \qquad \text{(A-9)}$$

There will be n such equations. They can be written in a condensed form, as will now be demonstrated.

Indices may be assigned to constituents and lines in an arbitrary way. Table 3 exemplifies a possible choice.

Let the second line of Table 3 define a column vector $\mathbf{x}_D$. This n-vector is obtained from the m-vector $\mathbf{x}$ through a linear transformation: $\mathbf{x}_D = D\mathbf{x}$. The matrix D thus defined is of order $(n \cdot m)$ and contains only ONES and ZEROS.

Table 3 **Assignment of indices to the constituents and lines.**

Dominating constituent	1	2	$\cdots$	m	1	2	3	1	2	1
Concentration	x_1	x_2	$\cdots$	x_m	x_1	x_2	x_3	x_1	x_2	x_1
Spectral line	1	2	$\cdots$	m	$m+1$	$\cdots$				n
Output	y_1	y_2	$\cdots$	y_m	y_{m+1}	$\cdots$				y_n

Its columns will be denoted $\mathbf{d}_i$, that is, $D = [\mathbf{d}_1\mathbf{d}_2 \cdots \mathbf{d}_m]$. Once indices have been assigned to the constituents and to the lines, the matrix D is uniquely determined.

We will also let the components of $\mathbf{x}$ define a matrix, obtained as follows: Let the elements of the vector $\mathbf{x}_D = D\mathbf{x}$ be placed along the diagonal of a matrix, the off-diagonal elements of which equal zero. The $(n \cdot n)$ matrix thus obtained will be denoted X. Then (A-9) becomes $\mathbf{y} = \mathbf{y}_0 + A\mathbf{x} + XQ\mathbf{x}$, where A and Q are $(n \cdot m)$ matrices, $\mathbf{y}$ and $\mathbf{y}_0$ are $(n \cdot 1)$ matrices.

We will now substitute this expression into the equations (4). The transformation (A-8) leads to the following equivalent set of equations:

$$\frac{\partial f}{\partial x_k} = 2\frac{\partial \boldsymbol{\varepsilon}^T}{\partial x_k}\Pi\boldsymbol{\varepsilon} = 0.$$

From:

$$\frac{\partial \boldsymbol{\varepsilon}^T}{\partial x_k} = -\frac{\partial \mathbf{y}^T}{\partial x_k},$$

it follows that

$$\frac{\partial \mathbf{y}^T}{\partial x_k}\Pi(\mathbf{U} - \mathbf{y}) = 0.$$

We have:

$$\frac{\partial \mathbf{y}}{\partial x_k} = A\mathbf{e}_k + \frac{\partial X}{\partial x_k}Q\mathbf{x} + XQ\mathbf{e}_k,$$

where $\mathbf{e}_k$ is a unit vector of dimension m
Writing

$$Q = \begin{bmatrix} \mathbf{q}_1^T \\ \mathbf{q}_2^T \\ \vdots \\ \mathbf{q}_n^T \end{bmatrix}$$

we also have:

$$\frac{\partial X}{\partial x_k}Q\mathbf{x} = \begin{bmatrix} \mathbf{q}_1^T\mathbf{x} & & & 0 \\ & \mathbf{q}_2^T\mathbf{x} & & \\ & & \ddots & \\ 0 & & & \mathbf{q}_n^T\mathbf{x} \end{bmatrix}\mathbf{d}_k$$

Introducing the notation

$$\begin{bmatrix} \mathbf{q}_1^T\mathbf{x} & & & 0 \\ & \mathbf{q}_2^T\mathbf{x} & & \\ & & \ddots & \\ 0 & & & \mathbf{q}_n^T\mathbf{x} \end{bmatrix} = \operatorname{diag}[Q\mathbf{x}]$$

we have:

$$\frac{\partial \mathbf{y}}{\partial x_k} = A\mathbf{e}_k + XQ\mathbf{e}_k + \operatorname{diag}[Q\mathbf{x}]\,\mathbf{d}_k.$$

Writing $R(\mathbf{x}) = A + XQ + \operatorname{diag}[Q\mathbf{x}]D$ and denoting the column vectors of this matrix by $\mathbf{r}_k(\mathbf{x})$ the equations (4) may finally be written

$$\mathbf{r}_k^T\Pi(\mathbf{U} - \mathbf{y}) = 0 \qquad k = 1, 2 \cdots m.$$

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