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A NEW APPROACH TO X-RAY SPECTROCHEMICAL ANALYSIS

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ABSTRACT

A simple fundamental relation between relative X-ray intensities and mass concentrations of the elements in any multi-component chemical system has been recognized. This relation permits quantitative analyses to be made, either by X-ray emission spectrography or by electron probe microanalysis, more simply and with equal or better accuracy than by any previously known correction method. Computations involve only the solution of simultaneous linear equations.

A NEW APPROACH TO X-RAY SPECTROCHEMICAL ANALYSIS

Introduction

X-ray spectrochemical analysis is based on the phenomenon that chemical elements emit X-radiation of characteristic wavelengths when excited by higher energy electrons (electron probe microanalysis) or X-rays (X-ray emission spectrography). Qualitative analysis is accomplished by diffracting the X-ray spectrum from a specimen into characteristic wavelengths according to the Bragg equation, $n\lambda = 2d \sin\theta$, and relating these wavelengths to the chemical elements by the Moseley relation $1/\lambda \propto Z^2$. Quantitative analysis, which depends on the relation between the measured intensity of a characteristic line of an element and the weight fraction of that element in the specimen, is complicated because of the many factors that influence the intensity of characteristic radiation. These factors are of two general types, namely, experimental factors related to the X-ray apparatus and measurement conditions, and compositional factors which are functions of the specimen itself. In general, the accuracy of an X-ray spectrochemical analysis depends on the constancy with which the experimental factors are maintained during the measurements and how accurately the measured intensities can be related to the composition of the specimen.

The experimental factors that affect the intensities of characteristic lines in the X-ray spectrum from a specimen, e.g., excitation voltage, X-ray optics, detector statistics, etc., are well known and have been discussed in detail by Birks (1959)[1] and Liebhafsky et al. (1960) for X-ray emission spectrography and by Castaing (1951, 1960) and Birks (1963) for electron probe micro-analysis. Castaing introduced the concept of relative intensity, i.e. the ratio of the intensity of characteristic radiation from an element in a specimen to the intensity of the same characteristic radiation emitted by the pure element under identical conditions of excitation, and showed that use of this ratio yields intensity measurements that are not affected by the properties of the X-ray apparatus. This most useful way of representing the measured intensity of a characteristic wavelength of X-radiation is common in electron probe microanalysis and should be adopted in X-ray emission spectrography wherever convenient.

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[1] Dates and/or names in parentheses refer to publications listed in the References.

The compositional factors inherent in the specimen itself present the major problem in X-ray spectrochemical analysis and are in fact the limiting factors in practical quantitative analysis. X-rays generated beneath the surface of a specimen are subject to absorption along the path they travel within the specimen and the magnitude of the absorption of an emitted characteristic line will depend on the mass absorption coefficient of the matrix material. Enhancement, or increase in intensity of a characteristic line, occurs when X-radiation emitted by another element in the matrix excites the characteristic spectrum of the element measured. Absorption and enhancement together constitute the matrix effect in X-ray emission spectrography and to these may be added the dependence of electron excitation and back-scatter on the atomic number of the matrix, in the case of electron probe microanalysis. Duncumb and Shields (1963) have attempted to correlate some of the methods proposed for evaluating matrix effects, particularly atomic number and absorption corrections for which divergencies in the literature are most marked. They conclude that no universal method for calculating matrix corrections exists and pin their hopes for the future on increased use of the digital computer for theoretical calculations.

It is the purpose of this paper to point out a simple fundamental relation that exists between the relative X-ray intensities and mass concentrations of the elements in multi-element chemical systems, regardless of the matrix effects. The relation permits quantitative analyses of multi-component systems by X-ray emission spectrography or electron probe microanalysis to be made more simply and with equal or better accuracy than ever before.

The Intensity - Concentration Relation

In a recent publication, one of us (Lachance, 1964) proposed a simple method for converting measured X-ray intensities into mass compositions. The method is based on the relation that the relative intensity of a characteristic line of a given element in a binary system is directly proportional to the weight fraction of that element and inversely proportional to one plus the product of a constant and the weight fraction of the other element. That is

$$R_A = \frac{C_A}{1 + C_B \propto_{AB}} \quad - - - - - - - - - - \quad (1)$$

and $\qquad R_B = \dfrac{C_B}{1 + C_A \propto_{BA}}$ - - - - - - - - - - -(2)

where C_A and C_B are the mass concentrations of elements A and B expressed as weight fractions; R_A and R_B are the relative intensities of characteristic lines of elements A and B expressed as ratios of the net intensities of the lines in the binary mixture to the net intensities of the pure elements, i.e. $R_A = I_A/I(A)$, $R_B = I_B/I(B)$; and $\propto_{AB}$ and $\propto_{BA}$ are constants for the system AB for a given set of experimental conditions. Similarly for a multi-component system consisting of elements A, B, C, - - - - n, the relative intensity of element A is given by

$$ R_A = \dfrac{C_A}{1 + C_B \propto_{AB} + C_C \propto_{AC} +++ C_n \propto_{An}} \; - - - -(3) $$

The simple intensity - mass concentration relation noted above has been tested by the writers on experimental data from many chemical systems including several ternary and one five-component system and has been found to be valid in every case. Some examples are given in Appendix I. Data taken from the literature were used where possible to assure a variety of operating conditions and instruments, including several types of X-ray spectrographs and electron probes. Since the systems involved chemical elements differing in atomic number by as little as 1 and as much as 86, and the intensities had been measured on K spectra, L spectra, and combinations of both, it is obvious that the relation holds regardless of atomic number or matrix effects.

The relation given in Equation 3 leads to the new concept in quantitative X-ray spectrochemical analysis that any multi-component system may be regarded as a series of binary systems for which $\propto$ constants may be determined and used to eliminate all compositional effects of the complex system. While the form of Equation 3 shows the basic relation that exists between the relative intensity and mass concentration of a given element, it is only when the system as a whole is considered that the value of the relation becomes apparent. Thus for any system of n components, a series of n simultaneous linear equations may be written and solved to determine $\propto$ constants, mass concentrations, or measured intensities, depending on the available data.

Binary System

If specimens of the pure components A and B of a binary system AB and at least one intermediate member of known composition are available, the two $\propto$ constants for the system may be determined empirically. The experimental values required are I_A and I_B, the measured net intensities of the characteristic radiation emitted by elements A and B in the binary compound, and I(A) and I(B) the measured net intensities of the characteristic radiation emitted by pure elements A and B. From these data are obtained the relative intensities $R_A = I_A/I(A)$ and $R_B = I_B/I(B)$. Since C_A and C_B, the mass concentrations of A and B, are known, Equations 1 and 2 may be solved for $\propto_{AB}$ and $\propto_{BA}$, viz.

$$\propto_{AB} = \frac{C_A - R_A}{R_A C_B} \quad\text{------------------(4)}$$

$$\propto_{BA} = \frac{C_B - R_B}{R_B C_A} \quad\text{------------------(5)}$$

In the case where the pure end members of the binary system are not available, the two $\propto$ constants may still be determined provided a minimum of two specimens of known composition are available for analysis. The known compositions C_A', C_A'', C_B', C_B'' and experimental data I_A', I_A'', I_B', I_B'' for the two standard samples may be substituted to yield the following two sets of simultaneous equations which may then be solved for $\propto_{AB}$ and I(A) and $\propto_{BA}$ and I(B).

$$\left.\begin{array}{l} C_A' I(A) = I_A' + I_A' C_B' \propto_{AB} \\[6pt] C_A'' I(A) = I_A'' + I_A'' C_B'' \propto_{AB} \end{array}\right\} \text{-------------(6)}$$

$$\left.\begin{array}{l} C_B' I(B) = I_B' + I_B' C_A' \propto_{BA} \\[6pt] C_B'' I(B) = I_B'' + I_B'' C_A'' \propto_{BA} \end{array}\right\} \text{-------------(7)}$$

The accuracy with which the $\propto$ constants can be determined is entirely dependent upon the accuracy with which the compositions of the standards are known and the precision with which the intensity data can be measured. In practice it is desirable to make use of

as many standards as possible and average the results to obtain values for the $\propto$ constants.

Having determined the values of the $\propto$ constants for the binary system AB, these values may now be used with measured intensities to determine the mass concentrations of A and B in any member of the binary system. The most practical forms of the equations for this purpose are obtained by substituting $1 - C_A$ for C_B and $1 - C_B$ for C_A in the denominators of the right-hand sides of Equations 1 and 2 and rearranging terms as follows:

$$C_A = \frac{1 + \propto AB}{1/R_A + \propto_{AB}} \quad ------------- \quad (8)$$

$$C_B = \frac{1 + \propto BA}{1/R_B + \propto_{BA}} \quad -------------- \quad (9)$$

Since the relation $C_A + C_B = 1$ holds for a binary system, it can be applied to the right-hand sides of Equations 8 and 9 to yield the further useful relation

$$\propto_{AB} + \propto_{BA} + \propto_{AB} \propto_{BA} = \frac{1 - R_A - R_B}{R_A R_B} \quad -- \quad (10)$$

Equation 10 provides an internal check of the reliability of the constants or intensity data or both, for any given binary system.

Multi-component Systems

Following the new concept of quantitative X-ray spectro-chemical analysis given by Equation 3, the relative intensity-mass concentration relation in any multi-component system may be regarded as the sum of the relations that exist in each of the binary systems that make up the total system. Thus in the ternary system ABC, three binary systems AB, BC, CA are involved and in each binary system two $\propto$ constants account for the relation between relative intensity and mass concentration. The complete set of relations for the system ABC is therefore:

$$C_A = R_A(1 + C_B \propto_{AB} + C_C \propto_{AC}) \quad ------ \quad (11)$$

$$C_B = R_B(1 + C_A \propto_{BA} + C_C \propto_{BC}) \text{ - - - - - - -(12)}$$

$$C_C = R_C(1 + C_A \propto_{CA} + C_B \propto_{CB}) \text{ - - - - - - -(13)}$$

It is obvious that once the $\propto$ constants applicable to the system are known, the mass concentrations may be calculated from the measured relative intensities by inserting these data in Equations 11, 12 and 13 and solving simultaneously for the three unknowns C_A, C_B and C_C.

If the system is such that the six $\propto$ constants have not previously been determined from the binary systems, they can be determined directly from Equations 11, 12 and 13 provided that specimens of pure A, B, and C are available and complete intensity data are obtained from these and from at least two standards of known composition in the ternary system. If the pure components of the ternary system are not available for analysis, the six $\propto$ constants and three net intensities of the pure components may be calculated provided net intensity data are obtained from three standards of known composition $C_A^{'} \ C_B^{'} \ C_C^{'}$, $C_A^{''} \ C_B^{''} \ C_C^{''}$, $C_A^{'''} \ C_B^{'''} \ C_C^{'''}$. This is accomplished by solving the following three simultaneous equations for $\propto_{AB}$, $\propto_{AC}$ and $I(A)$:

$$
\left.
\begin{aligned}
C_A^{'} I(A) &= I_A^{'}(1 + C_B^{'} \propto_{AB} + C_C^{'} \propto_{AC}) \\
C_A^{''} I(A) &= I_A^{''}(1 + C_B^{''} \propto_{AB} + C_C^{''} \propto_{AC}) \\
C_A^{'''} I(A) &= I_A^{'''}(1 + C_B^{'''} \propto_{AB} + C_C^{'''} \propto_{AC})
\end{aligned}
\right\} \text{ - - - - (14)}
$$

Similar equations for C_B and C_C may be written and solved for $\propto_{BA}$, $\propto_{BC}$ and $I(B)$ and $\propto_{CA}$, $\propto_{CB}$ and $I(C)$, respectively.

Discussion

The fact that Equation 3 applies to X-ray spectrochemical analysis in general, regardless of whether the measured X-rays are excited by X-ray quanta or high-energy electrons indicates that a common approach to the calculation of $\propto$ constants may be feasible. The semi-quantitative agreement between the values of $\propto$ constants determined from published data for a limited number of similar systems suggests that it may be possible to record fundamental constants for all binary systems, and compute corrections that may

be applied to these constants to make allowance for experimental factors, such as excitation voltage, incident and take-off angles, etc.

Claisse (1956) derived the following equation relating measured intensity to mass concentration for a binary mixture AB:

$$I_A = \frac{K\,C_A}{C_A(\mu_1 + \mu_2)_A + C_B(\mu_1 + \mu_2)_B} \quad \text{------(15)}$$

where

I_A = measured intensity of the characteristic radiation of A,

C_A, C_B = mass concentrations of A and B expressed as weight fractions ($C_A + C_B = 1$),

$(\mu_1)_A$, $(\mu_1)_B$ = mass absorption coefficient of elements A and B for the incident radiation,

$(\mu_2)_A$, $(\mu_2)_B$ = mass absorption coefficients of elements A and B at the wavelength of the characteristic radiation of A,

K = a proportionality constant.

For pure element A, $C_A = 1$, $C_B = 0$, and Equation 15 becomes

$$I(A) = \frac{K}{(\mu_1 + \mu_2)_A} \quad \text{------------------(16)}$$

By substituting $1 - C_B$ for C_A in the denominator of Equation 15 and dividing by Equation 16 we find the following expression for the relative intensity of A:

$$\frac{I_A}{I(A)} = R_A = \frac{C_A}{1 + C_B\left[\dfrac{(\mu_1 + \mu_2)_B - (\mu_1 + \mu_2)_A}{(\mu_1 + \mu_2)_A}\right]} \quad \text{------- (17)}$$

The form of Equation 17 is identical to that of Equation 1, therefore

$$\propto_{AB} = \frac{(\mu_1 + \mu_2)_B - (\mu_1 + \mu_2)_A}{(\mu_1 + \mu_2)_A} \text{---------} (18)$$

It must be noted, however, that the Claisse derivation was based on the special geometry that both the incident exciting radiation and emergent fluorescence radiation are at an angle of 45° to the specimen surface. For the general case of radiation striking the specimen at an angle of incidence ϕ_1 and emerging at an angle ϕ_2, the expression for $\propto_{AB}$ becomes:

$$\propto_{AB} = \frac{(\mu_1 \cosec \phi_1 + \mu_2 \cosec \phi_2)_B - (\mu_1 \cosec \phi_1 + \mu_2 \cosec \phi_2)_A}{(\mu_1 \cosec \phi_1 + \mu_2 \cosec \phi_2)_A} \text{--} (19)$$

In developing Equation 15, Claisse made the simplifying assumption that the incident radiation could be regarded as being of one effective wavelength for excitation of the characteristic radiation of the element in question. The term μ_1 is therefore semi-quantitative and is assumed to be the mass absorption coefficient of the element at a wavelength slightly below the absorption edge of the characteristic radiation being measured. If we assume values of 2.00, 1.73 and 1.47A for the effective excitation wavelengths for CrK_α, FeK_α and NiK_α radiation, respectively, we may calculate $\propto$ constants for the three binary systems, Cr-Fe, Cr-Ni and Fe-Ni. In order to compare with the constants determined empirically from the data of Noakes (1954) (see Appendix) we assume an incident angle $\phi_1 = 60°$ and emergent angle $\phi_2 = 30°$ (General Electric X-ray Spectrometer). Thus for calculation of $\propto_{FeNi}$, the following values of the mass absorption coefficient were taken from the tabulation of Birks (1963):

$$(\mu_1)_A = \mu/\rho \text{ for Fe at } \lambda \ 1.73 \quad = 400$$

$$(\mu_2)_A = \mu/\rho \text{ for Fe at } \lambda \ 1.937 \quad = \ 76$$

$$(\mu_1)_B = \mu/\rho \text{ for Ni at } \lambda \ 1.73 \quad = \ 66$$

$$(\mu_2)_B = \mu/\rho \text{ for Ni at } \lambda \ 1.937 \quad = \ 94$$

A comparison of $\propto$ constants for Cr, Fe and Ni systems, calculated by Relation 19 and determined from the data of Noakes is given in the table below. The good semi-quantitative agreement suggests that Relation 19 may be used to predict rough values of the $\propto$ constants for unknown systems, and that a more rigid treatment of the theory of excitation might lead to more precise results.

Constant	From Relation 19	From Empirical Data of Noakes (1954)
α FeNi	- 0.57	- 0.45
α NiFe	+ 1.47	+ 1.20
α FeCr	+ 1.13	+ 1.42
α CrFe	- 0.53	- 0.37
α CrNi	- 0.46	- 0.31
α NiCr	+ 0.76	+ 0.85

There would be little value here in discussing the many corrections that have been proposed to convert measured X-ray intensities into primary intensities and mass concentrations, in electron probe microanalysis. Excellent summaries of progress in this field are given by Duncumb and Shields (1963) and Wittry (1964). These writers conclude that there is as yet no method available of applying all of the required corrections on a routine basis. Since the corrections for inter-element effects are applied to the measured intensities, i.e.

$$C_A = R_A \begin{pmatrix} \text{Absorption} \\ \text{correction} \end{pmatrix} \begin{pmatrix} \text{Fluorescence} \\ \text{correction} \end{pmatrix} \begin{pmatrix} \text{Atomic} \\ \text{Number} \\ \text{correction} \end{pmatrix}$$

These corrections may be taken as equivalent to the terms $(1 + C_B \, \alpha_{AB} + C_C \, \alpha_{AC} \, ++)$ in Equation 3 and used to compute α values for any system, e.g. for the binary AB,

$$\alpha_{AB} = \frac{\begin{pmatrix} \text{Absorption} \\ \text{correction} \end{pmatrix} \begin{pmatrix} \text{Fluorescence} \\ \text{correction} \end{pmatrix} \begin{pmatrix} \text{Atomic No.} \\ \text{correction} \end{pmatrix}_{AB} - 1}{C_B}$$

It is apparent, however, that values computed for α by this method will be semi-quantitative at best due to the lack of precise methods of calculating the absorption, fluorescence and atomic number corrections. At present, experimentally determined values for α constants are generally more reliable for quantitative analyses and computed values are of considerable value for qualitative and semi-quantitative analyses.

Conclusions

The simple linear relation given in Equation 3 has been found to be valid for all chemical systems for which the writers have obtained reliable data, either by experiment or from the literature. The fact that the relation holds under such widely varying conditions of both electron and primary X-ray excitation and X-ray intensity measurement, suggests that Equation 3 describes a fundamental relation in X-ray spectrochemical analysis. This concept leads to the following useful applications.

1. For a given binary chemical system, under fixed operating conditions, two $\propto$ constants may be determined and used to convert relative intensity measurements directly into mass concentrations of the two elements, at any concentrations in the binary.

2. For a given multi-component system of n chemical elements, n (n-1) binary $\propto$ constants may be used to convert relative intensity measurements directly into mass concentrations of every element present. The $\propto$ constants may be determined from binary systems or from standards in the multi-component system.

3. Alpha constants may be computed semi-quantitatively from a knowledge of absorption coefficients (X-ray emission spectrography) or absorption, fluorescence and atomic number corrections (electron probe microanalysis), and used to predict inter-element effects in multi-component systems.

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Appendix

The following are examples of the general application of equation 3 to data published on X-ray emission spectrography and electron probe spectrochemical analysis.

A.   X-ray Emission Spectrography (Binary Systems)

Table 1

System: Cu-Sn and Cu-Zn (Alloys)

% Cu*	Int. Cu (cps)*	% Sn*	C_{Cu}	R_{Cu}	C_{Cu} Computed (see below)
100.00	24,724	0.0	1.0	1.0	1.0
96.62	23,323	3.34	.9662	.9433	.9678
94.54	22,426	5.42	.9454	.9070	.9453
92.62	21,667	7.35	.9262	.8763	.9267
90.61	20,870	9.36	.9061	.8441	.9057

$$C_{Cu} \text{ computed from } R_{Cu} \left[1 + C_{Sn} \,(.78) \right]$$

% Cu*	Int. Cu (cps)*	% Zn*	C_{Cu}	R_{Cu}	C_{Cu} Computed (see below)
65.27	17,740	34.73	.6527	.7175	.6527
62.95	17,247	37.05	.6295	.6976	.6304
67.61	18,244	32.39	.6761	.7379	.6758
69.98	18,750	30.02	.6998	.7584	.6992

$$C_{Cu} \text{ computed from } R_{Cu} \left[1 + C_{Zn} \,(-.26) \right]$$

* Data from Lucas-Tooth and Price (1961).

Table 2

System: Cu-Fe, Mo-Cu and Fe-Zn (as Oxides)

% Cu* (as oxide)	% Fe* (as oxide)	Observed Q*, Corrected for Dead Time	R_{Cu}	C_{Cu} (as oxide) Computed (see below)
66.7	33.3	2.30	.435	.669
50.0	50.0	3.66	.273	.496
33.3	66.7	6.30	.159	.332

% Mo* (as oxide)	% Cu* (as oxide)	Observed Q*, Corrected for Dead Time	R_{Mo}	C_{Mo} (as oxide) Computed (see below)
66.7	33.3	1.78	.562	.672
50.0	50.0	2.59	.386	.500
33.3	66.7	4.24	.236	.329

% Fe* (as oxide)	% Zn* (as oxide)	Observed Q*, Corrected for Dead Time	R_{Fe}	C_{Fe} (as oxide) Computed (see below)
66.7	33.3	1.42	.705	.659
50.0	50.0	1.81	.552	.497
33.3	66.7	2.52	.397	.344

Q = the ratio of the intensity of the fluorescent beam of an element in a mixture of known composition to that of the free element, as measured in terms of time for a fixed count. R_{Cu}, R_{Mo}, and R_{Fe} are the reciprocal of Q.

$$C_{Cu} \text{ computed from } R_{Cu} \left[1 + C_{Fe} (1.63) \right]$$
$$C_{Mo} \text{ computed from } R_{Mo} \left[1 + C_{Cu} (.59) \right]$$
$$C_{Fe} \text{ computed from } R_{Fe} \left[1 + C_{Zn} (-.197) \right]$$

* Data from Sherman (1954).

B. X-ray Emission Spectrography (Ternary and Multi-component Systems)

Table 3

System: $ZnO - Al_2O_3 - Fe_2O_3$ (Prepared for Pure Oxides)

C_{ZnO}	$C_{Al_2O_3}$	$C_{Fe_2O_3}$	R_{ZnO}	C_{ZnO} Computed (see below)
.0100	.990	.00	.0100	-
.0100	.695	.295	.00514	.00994
.0100	.495	.495	.00378	.00972
.0100	.295	.695	.00315	.01008
.0100	.00	.990	.00254	.01041

$$C_{ZnO} \text{ computed from } R_{ZnO} \left[1 + C_{Fe_2O_3} \ (3.13) \right]$$

Data: Geological Survey of Canada X-ray laboratory.

Table 4

System: Fe, Ni, Cr (Stainless Steels)

Sample No.	C_{Fe*}	C_{Ni*}	C_{Cr*}	R_{Fe*}	R_{Ni*}	R_{Cr*}	C_{Fe} comp. see (a)	C_{Ni} comp. see (b)	C_{Cr} comp. see (c)
Invar I	.6413	.3587	-	.7576	.2037	-	.6360	.3590	-
Invar II	.6383	.3551	-	.7651	.2010	-	.6420	.3560	-
X101	.6177	.1060	.2478	.4699	.0549	.3391	.6207	.1077	.2506
X102	.5486	.1757	.2513	.4288	.0933	.3371	.5475	.1814	.2483
X103	.5875	.1307	.2539	.4561	.0691	.3388	.5911	.1335	.2506
X104	.5251	.2064	.2446	.4218	.1138	.3174	.5232	.2089	.2355
X107	.5308	.2510	.1860	.4633	.1438	.2593	.5325	.2595	.1873
X108	.4401	.3663	.1640	.4144	.2168	.2488	.4509	.3681	.1788
X109	.4117	.3960	.1575	.4203	.2362	.2129	.4372	.3916	.1525
X112	.4396	.3766	.1525	.4130	.2276	.2306	.4394	.3807	.1657
X115	.2430	.5848	.1350	.2705	.4122	.2084	.2541	.5922	.1492
X119	.0910	.7670	.1295	.0914	.6188	.2253	.0809	.7660	.1649
X120	.0789	.7711	.1445	.0869	.6422	.2022	.0743	.7774	.1476
X121	.0157	.7577	.1975	.0088	.6443	.2609	.0085	.7533	.1986
Fe	1.0000			1.0000					
Ni		1.0000			1.0000				
Cr			1.0000			1.0000			

*Data from Noakes (1954).

Note: The chemically determined values for iron (C_{Fe*}) were not obtained directly but represent balances.

(a), (b), (c): C_{Fe}, C_{Ni}, C_{Cr} computed by solving the three equations

$$C_{Fe} - R_{Fe} \propto_{FeNi} C_{Ni} - R_{Fe} \propto_{FeCr} C_{Cr} = R_{Fe}$$

$$- R_{Ni} \propto_{NiFe} C_{Fe} + \qquad C_{Ni} - R_{Ni} \propto_{NiCr} C_{Cr} = R_{Ni}$$

$$- R_{Cr} \propto_{CrFe} C_{Fe} - R_{Cr} \propto_{CrNi} C_{Ni} + \qquad C_{Cr} = R_{Cr}$$

$$\propto_{FeNi} = -0.45 \qquad \propto_{FeCr} = 1.42 \qquad \propto_{NiCr} = 0.85$$

$$\propto_{NiFe} = 1.20 \qquad \propto_{CrFe} = -0.37 \qquad \propto_{CrNi} = -0.31$$

Table 5

System: Cu-Sn-Zn (Alloys)

C_{Cu*}	C_{Sn*}	C_{Zn*}	R_{Cu*}	C_{Cu} Computed (see below)
.8788	.0711	.0501	.8401	.8757
.8793	.0911	.0296	.8241	.8763
.8793	.1124	.0083	.8102	.8795
.8985	.0709	.0306	.8583	.8989
.8673	.1128	.0199	.7983	.8644
.8400	.1101	.0499	.7790	.8358

$$C_{Cu} \text{ computed from } R_{Cu} \left[1 + C_{Sn} (.78) + C_{Zn} (-.26) \right]$$

*Data from Lucas-Tooth and Price (1961).

Note: The parameters used in the above are identical to those used for the binary systems Cu-Sn and Cu-Zn (see Table 1).

Table 6

System: Fe-Ni-Cr-W-Mo (Stainless Steels)

Sample No.	C_{Fe}*	C_{Ni}*	C_{Cr}*	C_W*	C_{Mo}*	R_{Fe}	C_{Fe} Computed (see below)
Fe	.9920	.0027	.0000	.0000	.0005	.992	–
25118	.8006	.0034	.0386	.1400	.0037	.6522	.7996
25583	.7475	.0029	.0422	.1853	.0028	.5910	.7553
6297	.8593	.0107	.1042	.0000	.0052	.7163	.8640
6298	.8530	.0080	.1208	.0000	.0037	.6958	.8589
6299	.8506	.0059	.1298	.0000	.0020	.6759	.8433
6300	.8493	.0021	.1404	.0000	.0006	.6681	.8452
6318	.6454	.1548	.1656	.0032	.0011	.4968	.6443
6319	.6422	.1436	.1788	.0026	.0006	.4833	.6387
6320	.6449	.1337	.1868	.0008	.0001	.4810	.6421
BM 1	.6953	.0902	.1680	.0000	.0352	.5099	.7052
BM 13	.7194	.0808	.1717	.0000	.0225	.5212	.7102
BM 14	.7060	.0837	.1785	.0000	.0237	.5060	.6972

$$C_{Fe} \text{ computed from } R_{Fe} \left[1 + C_{Ni} (-.13 + C_{Cr} (1.88) + C_W (1.04) + C_{Mo} (2.24) \right]$$

*Data from Gillieson, Milliken and Young (1962).

C. Electron Probe (Binary Systems)

Table 7

System: Ru-W (Alloys)

C_{Ru*}	C_{W*}	R_{Ru*}	R_{W*}	C_{Ru} Computed (see below)	C_W Computed (see below)
.832	.168	.570	.180	.823	.168
.562	.438	.267	.444	.576	.424
.355	.645	.130	.655	.352	.637
.191	.809	.061	.826	.191	.796
.058	.942	.012	.965	.042	.960

$$C_{Ru} = R_{Ru} \left[1 + C_W (2.64) \right]$$
$$C_W = R_W \left[1 + C_{Ru} (-.08) \right]$$

System: Rh-W (Alloys)

C_{Rh*}	C_{W*}	R_{Rh*}	R_{W*}	C_{Rh} Computed (see below)	C_W Computed (see below)
.911	.089	.776	.088	.916	.092
.688	.312	.425	.306	.694	.316
.564	.436	.293	.423	.552	.435
.410	.590	.185	.555	.425	.566
.153	.847	.069	.814	.188	.820
.024	.976	.008	.970	.024	.971

$$C_{Rh} \text{ computed from } R_{Rh} \left[1 + C_W (2.03) \right]$$
$$C_W \text{ computed from } R_W \left[1 + C_{Rh} (.05) \right]$$

System: Cu-Au (Alloys)

C_{Cu*}	C_{Au*}	R_{Cu*}	R_{Au*}	C_{Cu} Computed (see below)	C_{Au} Computed (see below)
.794	.206	.789	.159	.796	.212
.598	.402	.585	.324	.596	.409
.399	.601	.386	.505	.397	.594
.201	.799	.194	.730	.202	.794

$$C_{Cu} \text{ computed from } R_{Cu} \left[1 + C_{Au} (.047) \right]$$
$$C_{Au} \text{ computed from } R_{Au} \left[1 + C_{Cu} (.44) \right]$$

Similar results are obtained on the systems Ni-Pt, Fe-Ni, Ag-Au, Ta-Ru, Ta-Os, and W-Ir.

*Data from Ziebold and Ogilvie (1963).

Table 8

System: Various Uranium Compounds and Alloys

Alloy or Intermetallic Compound*	C_{U*}	R_{U*}	C_U Computed (see below)	
UC	.952	.92	.948	
UC_2	.908	.866	.912	(a)
UAl_3	.746	.644	.745	
UAl_4	.688	.578	.688	(b)
UTi (20% at)	.952	.937	.954	
UTi (50% at)	.833	.779	.829	
UTi (80% at)	.555	.474	.555	(c)
UNi_2	.670	.580	.672	
UNi_5	.448	.353	.446	(d)
UZr (20% at)	.912	.911	.912	
UZr (50% at)	.721	.719	.721	
UZr (80% at)	.391	.390	.392	(e)

(a) C_U computed from $R_U [1 + C_C (.63)]$

(b) C_U computed from $R_U [1 + C_{Al} (.61)]$

(c) C_U computed from $R_U [1 + C_{Ti} (.38)]$

(d) C_U computed from $R_U [1 + C_{Ni} (.48)]$

(e) C_U computed from $R_U [1 + C_{Zr} (.01)]$

*Data from Kirianenko, Maurice, Calais and Adda (1963).

Table 9

System: Cu-Au and Zr-Si (Alloys)

C_{Au*}	C_{Cu*}	R_{Au*}	C_{Au} Computed (see below)
.238	.762	.174	.236
.527	.473	.433	.528

C_{Au} computed from $R_{Au} [1 + C_{Cu} (.47)]$

C_{Zr*}	C_{Si*}	R_{Zr*}	C_{Zr} Computed (see below)
.620	.380	.544	.614
.796	.204	.748	.800

C_{Zr} computed from $R_{Zr} [1 + C_{Si} (.34)]$

*Data from Poole and Thomas (1961).

Table 10

System: Fe-Ni (Alloys)

C_{Ni*}	$R_{Ni(1)*}$	$C_{Fe(2)}$	C_{Ni} Computed (see below)
.0515	.040	.9485	.053
.103	.0775	.897	.100
.449	.3805	.551	.451

C_{Ni} computed from $R_{Ni} [1 + C_{Fe} (.33)]$

(1) from % Ni before correction.
(2) obtained by difference.

*Data from Philibert (1963).

D.   Electron Probe (Ternary Systems)

Table 11

System: Au-Ag-Cu (Alloys)

C_{Au}*	C_{Ag}*	C_{Cu}*	R_{Au}*	C_{Au} Computed (see below)
.8000	.1493	.0506	.787	.794
.7997	.0997	.1001	.783	.810
.5996	.2997	.1002	.573	.598
.5996	.2002	.1997	.573	.612
.4004	.4488	.1502	.377	.401

C_{Au} computed from R_{Au} $[1 + C_{Ag} (.049) + C_{Cu} (.29)]$

*Data from Ziebold and Ogilvie (1964).

Table 12

System: Fe-Ni-Cr (Stainless Steels)

C_{Fe}*	C_{Ni}*	C_{Cr}*	R_{Fe}*	C_{Fe} Computed (see below)
.704	.10	.16	.652	.705
.679	.09	.185	.616	.675
.627	.10	.205	.556	.616
.840	.003	.133	.759	.820
.700	.091	.184	.627	.687
.620	.133	.237	.555	.623
.864	.005	.091	.835	.879
.715	.248	.030	.745	.730
.523	.205	.247	.453	.506

C_{Fe} computed from R_{Fe} $[1 + C_{Ni} (-.15) + C_{Cr} (.6)]$

*Data from Ziebold and Ogilvie (1964).