Procedures for quantitative surface chemical analysis
-Internal standard and external standard-
In the situation of instrumental analysis of "solid samples"

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It can be said that quantitative surface chemical analysis is an instrumental analysis of solid samples. Because,it is usually performed without dissolving of samples in the aqueous state like common chemical analysis. Probes for the sample taken and surface information signals to be detected are electron, ion and/or electro-magnetic waves. Of course, these signals change according to the measuring conditions, and are influenced by enviromental elements and their chemical states during the escape from surfaces.

It may be interesting to compare the quantitative surface analytical method like XPS or AES with other instrumental analytical methods for solid samples.

Instrumental analysis in which theory does not fit to
the experimental results.

The typical instrumental analysis in which theory does not fit to the experimental results is emission spectral analysis.
In emission spectral analysis, usually the theoretical spectral intensity is given by Boltzmann's equation supposing the homogeneous and thermal equilibrium plasma as shown in the equation.

$I_{qp}=Cnh\nu_{qp}g_qA_{qp}/Z(n)\cdot exp(-E_q/kT)$

Where, I is spectral emission intensity, C is instrumental function, n is number of atom, h is Planck's constant, ν is oscillation number, g_q is statistic gravity at level q, A_{qp} is transition probability from level q to that of p, Z is patition function which is the function of temperature, E_q is excitation energy of atomic line at level q, k is Boltzmann's constant and T is temperature.
An optimum spectral line of an element in the sample to be analyzed is selected as an internal standard. The intensity ratios of the spectral line of the analyte element to that of internal standard are plotted against the composition ratios of those elements to make calibration

curve with calibration reference samples. This calibration curve is used
for the quantification. In this case, there are required conditions for
the internal standard. However,those conditions are not satisfied in
practically used plasmas for the excitation of elements in the samples ;
spark, glow and others. These plasmas are non-thermal equilibrium and
not homogeneous, and the partition of excited atoms in the plasma and
the light emission intensity change according to the change of plasma
temperature.

Therefore,Boltzmann's equation (and Saha's equation) can only be
employed for the qualitaive or semi-qualitative consideration of
emission intensities. In spite of these facts, emission spectral
analysis has been performed as a powerfull analytical technique for
solid samples getting straight calibration curves after a lot of
experiments and experiences.

Instrumental analysis in which theory fits to the experimental
results.

Contrary to the emission spectral analysis, theory(T.Shiraiwa and N.
Fujino:Japanese J. Appl. Phys.,5(1966)886 et.al.) cleanly fits the
experimental results in X-ray fluorescence analysis. Calibration curves
for Cr-Fe alloys obtained using external standard are shown in figures.
Various correction methods for the quantitative X-ray fluorescence
analysis have been proposed based on this theory; dj-method, α factor
-method and fundamental parameter method. However,these theoritical
equations and correction methods cannot be strictly applied to non
-homogeneous samples like ores because of effects of grain size and so
on. In this case samples are dissolved in solution or fused to make
briquettes with internal standard elements, and the quantification is
performed with the internal standard method correcting the matrix
effects.

The situation of EPMA is intermediate of the privious instrumental
analytical methods. The correction method; ZAF method by external method
and others, are employing.

The sample taken depth of these previous methos are μm level.

Now, how is the surface chemical analysis; XPS or AES,the sample
taken depth of this analytical method is below a sub-hunded nm.
Practically, following analytical conditions are required even if in the

case of surface analysis: 1)The sample is not always a simple binary alloy. 2)Each sample has each surface. 3)The history of sample is often unknown. 4)Suitable references cannot be found for all elements. 5)Each instrument has each characteristics.

What should we do practical quantification by XPS or by AES -internal standard or external standard- or.......?
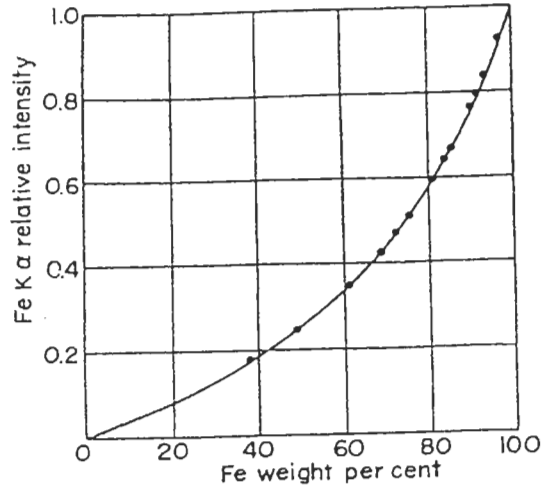
Relative intensity of the primary fluorescent Fe $K\alpha$ x-rays from iron-chromium binary alloys. Solid curve is theoretical and filled circles are experimental.
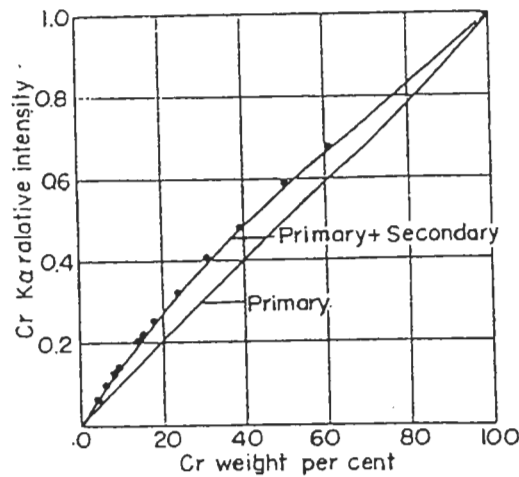
Relative intensities of the primary and the secondary fluorescent Cr $K\alpha$ x-rays from iron-chromium binary alloys.
Lower curve is the theoretical primary fluorescent x-ray intensity ratio and upper curve is the sum of the primary and the secondary, and filled circles are experimental.