PREFACE

Converting intensities to concentrations in XRF—the need for diversity

The X-ray fluorescence technique for the compositional analysis of materials is a victim of its success. The continuing efforts to increase the number of elements amenable to the technique by improving the stability and sensitivity of instrumentation and the linking of these instruments to ever more powerful computers has gradually extended the field of application. Inherent to this extension is the need to deal effectively with the dreaded matrix effects, i.e., the fact that emitted intensities are always the resultant of an absorption process and quite often, of an additional enhancement process. Thus the need for either correcting or compensating for matrix effects in ever increasing types of materials. Not only must this need be met but it must also satisfy the demands of academia where the theoretical aspects will have a high priority, and also the demands of industry where the practical aspects of day-to-day laboratory operation must definitely be taken into consideration.

At this stage, the reader may very well ponder: but we have diversity aplenty, it being claimed as far back as ten years ago that there were some fifty-plus models available for the correction for matrix effects. But, as also pointed out on a number of occasions in the literature, this multiplicity of models is often only apparent. The diversity being advocated here is not a call for more of the same but refers to the need for approaches where the correction process is inherently different. The dilemma stems from the fact that collectively, authors have often given the same name to different things, and, at the same time have not escaped from using different names for the same thing. All this in the guise of seeking that elusive goal—the universal method. One possible framework for categorizing XRF methods for converting intensities to concentrations is to examine the premises and concepts that led to various mathematical expressions. The various combinations can then be examined as to their implications and likely field of application.

The premises relate directly to the analytical context under consideration. Can it be assumed that the specimens meet the prerequisite for a strict theoretical treatment, i.e., flat, homogeneous and infinitely thick. Can it be assumed that the specimens will fall in the category of type materials or will a qualitative analysis be required as a first step. Another factor of no less importance is whether turn around time, cost, availability of standards, and existing laboratory resources have to be taken into account. A case could almost be made that each laboratory’s analytical context is unique.

Independently of premises, analysts can categorize the various concepts that underlie the various approaches proposed for dealing with matrix effects. All correction procedures are to some degree based on some form of theory, although this may range from being based explicitly on the time-honoured physical bases of X-ray fluorescence emission to simply being based on accepted multi-regression processing of experimental data. Conversely, methods can be categorized as to whether the magnitude of the matrix effect is evaluated globally (internal standard, double dilution, Compton scatter), or whether the method falls in what is generally termed 'mathematical', i.e., the total correction is synthesized into a sum of individual corrections for each component in the specimen. As the theoretical aspects of matrix effects were elucidated over the years, a number of authors have proposed that analysts need not be locked-in or prisoner of anyone school of thought and recommend a combination of approaches in order to retain the advantages of each.
Some implications are straightforward: the fundamental parameters approach, whether expressed in its original form or expressed in anyone of the influence coefficient forms that were subsequently developed, implies the need for few standards, whereas a purely statistical approach implies the need for many more standards. This relates to the fact that in the former, the onus for correcting the matrix effect rests on having reliable values for the fundamental parameters, whereas in the latter, the onus rests on carrying out series of least squares fitting. Other implications are less apparent. Consider for example methods based on the use of influence coefficients. When can they be labelled fundamental, theoretical, empirical, modified, etc.? It certainly does not relate to the symbol or model used. The alpha model is a case in point. The alphas can be tagged with any of the above labels depending on what conceptual approach was used in defining them. It is the failure to make this distinction that has resulted in a number of conflicting statements regarding influence coefficient methods.

The application of numerical methods brings together the sequential steps: adequate specimen preparation, precise intensity measurements, valid calibration and effective correction for matrix effects. Ideally, methods should generate 'true' compositional data. In practice analysts can only aspire to produce accurate results, namely, concentrations that can be confirmed by independent techniques as being within the plus-minus range deemed acceptable in the premises. The essential purpose of the calibration step is to establish the instrument's sensitivity for each analyte under fixed operating conditions. One can build confidence in this step by observing how well intensity data that are theoretically corrected for matrix effects are linearized in concentration versus intensity plots. Confidence in having an effective correction can only be gained by processing a number of standards that did not serve for calibration, as unknowns. Being aware of the implications of a numerical correction method should prevent analysts from hopelessly attempting to apply it beyond its capability.

Very few, if any, analysts are given carte blanche in developing analytical methods. There are bound to be limitations imposed by the specific context under consideration. This implies that choices will have to be made, experienced analysts being well aware that developing analytical methods is the art of compromise. The watchword is to be on guard-familiarity is soporific; there will remain the tendency to breed consent and lean towards whatever methods one is used to. This should not be carried to the extent of closing the door to genuine diversification.

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