ADAPTIVE OBSERVATION AND ESTIMATION OF TRACE ELEMENTS IN AN INDUCTIVELY COUPLED PLASMA

G. M. Bashin, A. N. Dmitrienko, and A. T. Savichev

Rules are proposed for observing and estimating element traces that are invariant with respect to background in an atomic emission spectrometer. The concentration dependence of the analytical parameter is used to determine samarium in aqueous solution with an atomic emission spectrometer fitted with an inductively coupled plasma source. The determination error is estimated.

Data-acquisition systems and chemometry methods are widely used in monitoring spectrometric data, and have given rise to optimal methods of observing weak signals corresponding to element traces. Signal observation (qualitative analysis) precedes parameter estimation (determination of element traces).

One can provide quasi-optimal observation and estimation of weak signals from element traces in atomic emission spectrometry with inductively coupled plasmas. An observation rule was derived invariant with respect to background and quasi-optimal on a maximin criterion, and estimates were made of the relative error of measurement in determining traces of lanthanum.

Here we propose adaptive algorithms invariant with respect to background for observing and estimating signals from an atomic emission spectrometer under conditions of a priori uncertainty over the energy parameters.

Let there be $R$ independent observations at the spectrometer output, each of which consists of $N$ independent realizations $X_i = \{x_{ij}\}$ of a spectral line, whose intensity is governed by the contents of the elements in the object ($i = 1, 2, ..., R; j = 1, 2, ..., N$). Similarly, to each observation there correspond $M$ independent realizations $Y_i = \{y_{ij}\}$ of the spectral line from a blank specimen, where $x_{ij}, y_{ij} \geq 0$. We assume that the probability density for the line intensities $x_{ij}$ and $y_{ij}$ can be represented by right-sided families of the form $p(x_{ij}) = [(1 + \gamma_i) \nu_i]^{-1} f(x_{ij}/[(1 + \gamma_i)\nu_i])$ and $p(y_{ij}) = \nu_i^{-1} f(y_{ij}/\nu_i)$ having unknown scale parameters $(1 + \gamma_i)\nu_i$ and $\nu_i$, in which $\gamma_i = \varepsilon_i/\nu_i$ is the ratio of the scale parameters for the lines of the test element in the absence of background $\varepsilon_i$ and from the blank specimen $\nu_i$ (signal-background ratio), while the differentiable function $f(t) \geq 0$ satisfies the normalization condition

$$\int_0^\infty f(t)dt = 1,$$

where it is assumed that $f(t)$ is known completely.

We note that the ratio $\sigma^2$ of the variance to the square of the mathematical expectation is a constant governed only by the form of the distribution for the sample values of this family of spectrometry distributions.

This model for the line distributions for the test and blank specimens assumes an additive relationship between the signal and the background when one has information on the test element present in the scale parameters, together with the time dependence of the signal—background ratio and the background intensity, i.e., nonstationarity in the signal due, for example, to spectrometer drift.

The task of observing traces of elements amount to testing hypothesis $H_0: \gamma_i = 0$ against the alternative $H_1: \gamma_i > 0$.

The decision on signal observation is taken for the following [4-6] for this observation model with known scale parameters for the background and signal distributions:

in which $\zeta_i = 1/N \sum_{j=1}^{N} \zeta_{ij}$ are the minimal sufficient statistics for the mixture of signal and background,

$$\zeta_{ij} = \ln \frac{f(x_j / (1 + \gamma_i) \nu_j)}{f(x_j / \nu_j)};$$

(2)

where $c$ is the threshold parameter, which is determined by the optimization criterion, and in particular for the Neumann-Pearson criterion it is the probability $\alpha$ of spurious decisions on observing element traces.

If the signal is weak ($\gamma_i << 1$), a linear approximation applies for a minimal sufficient statistic in (1):

$$\zeta_i = -\gamma_i \sum_{j=1}^{N} (x_j / \nu_j) [\ln f(x_j / \nu_j)]',$n

in which the prime denotes the derivative of $\ln f(t)$ with respect to the argument $t$.

In particular, if the sample sets have $\Gamma$ distributions ($\mathcal{F}(t) = t^{-1} e^{-t}$), we have $\zeta_i = -n \ln(1 + \gamma_i) + \nu_i^{-1} [\gamma_i / (1 + \gamma_i)] (x_j)$ for any values of $\gamma_i$, and when we exclude the term independent of the sample values, we have:

$$\zeta_i = \nu_i^{-1} \sum_{j=1}^{N} (x_j / \nu_j) [\ln f(x_j / \nu_j)],$$

where $\langle x_j \rangle = \frac{1}{N} \sum_{j=1}^{N} x_j$.

When there are stationary test sets ($\nu_i = \nu$, $\gamma_i = \gamma$) for the mixture of signal with background and for the background, the minimal sufficient statistic is defined by the left-hand side of (1).

If $\nu_i$ and $\gamma_i$ are known a priori, the optimal signal processing amounts to nonlinear transformation, minimal sufficient statistic generation, and weighted accumulation.

We see from (1) and (2) that the decision statistic $\Psi$ (statistic to be compared with the threshold) is dependent on the scale parameters $\mu_i = \nu_i + \gamma_i$ (or $\gamma_i$) and $\nu_i$, which are not known a priori. We consider the following cases for $\gamma_i$: 1) The $\gamma_i$ are known a priori; 2) the minimal value $\gamma_{0i}$ is known a priori; and 3) the $\gamma_i$ are not known a priori.

In the first case, we use maximum-likelihood estimators ($\nu_i$) for the parameters $\nu_i$ that are the solutions to the following equations [4] in the decision rule (1):

$$\sum_{j=1}^{M} x_j [\ln f(x_j / \nu_i)]' + M < \nu_i > = 0.$$ 

(3)

In the second case, we substitute the minimal value $\gamma_{0i}$ for $\gamma_i$ in (1), i.e., we use a minimax approach [5], while instead of the $\nu_i$ we use the maximum-likelihood estimators derived from (3).

In the third case, we use the maximum-likelihood estimator for $\nu_i$ and $\mu_i$ in (1):

$$\sum_{j=1}^{M} x_j [\ln f(x_j / \mu_i)]' + N < \mu_i > = 0.$$ 

(4)

Then the solutions to (4) correspond to the two-sided alternative $\gamma_i \neq 0$, while with the alternative $\gamma_i > 0$ it occurs with the estimator $\langle \mu_i \rangle$ assigned the value $\langle \nu_i \rangle$ if the inequality $\langle \mu_i \rangle < \nu_i$ is obeyed.

For realizations having $\Gamma$ distributions, $\langle \nu_i \rangle = n^{-1} (\nu_i)$, $\langle \mu_i \rangle = n^{-1} (x_i)$ for the alternative $\gamma_i \neq 0$ and

$$< \mu_i >= \begin{cases} n^{-1} < x_i >, & \text{if } n^{-1} < x_i > < \nu_i >, \\ < \nu_i >, & \text{if } n^{-1} < x_i > \leq < \nu_i >. \end{cases}$$