

The Sherman equations as a nonlinear Perron eigenvalue problem

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Abstract When a chemical sample composed of N elements is analyzed using sequential selective excitation by a tunable polyenergetic X-ray beam and selective measurement of the characteristic X-rays, the production of secondary fluorescence does not interfere with the measurements. This experimental situation leads to a particular case of the Sherman equations which can be written as a set of non-linear equations. The same kind of equations are also obtained when we excite a chemical sample with a polyenergetic X-ray beam and neglect the production of secondary fluorescence. This set of equations can be regarded as a non-linear eigenvalue problem. A non-linear extension of the Perron Frobenius theorem ensures that there is one and only one physically acceptable solution, and also leads to a method to obtaining it. The propagation off measurements errors of sample fluorescence to errors in the calculated sample concentrations, has been simulated, and the results show that the solution is well conditioned. The case of production of secondary fluorescence can not be treated, in general, as a nonlinear Perron eigenvalue problem, but it has been shown that it is rather plausible that Sherman equations corresponding to the actual chemical elements and that include the production of secondary fluorescence have one and only one physically acceptable solution. An exhaustive search could elucidate the existence and unicity of solutions for the equations corresponding to the actual chemical elements.

Keywords X-ray fluorescence analysis · Sherman equations · Non linear Perron eigenvalue problem

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1 Introduction

In a previous work [1] it was shown that the Sherman equations brought about by an experimental situation in which the excitation with monoenergetic X-ray beams and the measurement are both selective, can be interpreted as a linear Perron eigenvalue problem and the existence and unicity of the solution is guaranteed. Moreover, the iterative method of Von Misses provides the solution, and it was shown that it is stable with respect to the uncertainties in the measurement data. In the present work we solve the nonlinear case corresponding to selective excitation with polyenergetic X-rays and selective measurement. We also make some considerations about the equations corresponding to polyenergetic non selective excitation and selective measurement, where the secondary fluorescence is present and measured.

2 Selective excitation and selective measurement

Let us consider the following experimental situation of selective excitation and selective measurement: We have a thick sample composed of N chemical elements which is excited at an incident angle Ψ_1 by a tunable polyenergetic photon source of known spectral distribution (i.e. an X-ray tube where the end point of the spectrum can be varied by modifying the kVp). The fluorescence produced is measured at a takeoff angle Ψ_2 with a detector of efficiency $\varepsilon(h\nu)$ as a function of the energy $h\nu$, $\varepsilon(h\nu) = \varepsilon \varepsilon_r(h\nu)$ and whose relative efficiency $\varepsilon_r(h\nu)$ is known and the absolute efficiency ε is unknown. When the sample is excited sequentially with N different X-ray beams, each one produced by a kVp such that the end point energy of the beam is above the K edge of each element but just below the K edge of the next element, and we measure the K alpha fluorescence of the i th element produced by the i th X-ray beam, there is no contribution of the secondary fluorescence to the measurements, and the Sherman equations [2] can thus be written as:

$$M_i = \varepsilon \frac{S \Omega}{4\pi \sin \Psi_1} c_i \int_{E_{K_i}}^{h\nu \text{Max}_i} \frac{\varepsilon_r(E_{K\alpha i}) \phi_i(h\nu) \sigma_i(h\nu)}{\frac{\sum_{j=1}^n \mu_j(h\nu) c_j}{\sin \Psi_1} + \frac{\sum_{j=1}^{j=n} \mu_j(E_{K\alpha i}) c_j}{\sin \Psi_2}} dh\nu \quad (1)$$

$$\begin{aligned} \sum_{j=1}^{j=n} c_j &= 1, \\ c_i &> 0 \quad \forall i \\ \varepsilon &> 0, \end{aligned} \quad (2)$$

where M_i is the measured K-fluorescence of element i , ε is the absolute efficiency of the detector, S is the irradiated surface area of the specimen; Ω is the solid angle subtended by the detector; c_i is the concentration of element i ; E_{K_i} is the energy of the K-edge of the i th element; $h\nu \text{Max}_i$ is the energy at the end point of the spectral distribution of the i th exciting X-ray beam and it is just under $E_{K_{i+1}}$; $E_{K\alpha i}$ is the energy of the $K\alpha$ characteristic radiation of the element i ; and $\varepsilon_r(E_{K\alpha i})$ is the relative efficiency at energy $E_{K\alpha i}$. The function $\phi_i(h\nu)$ is the spectral distribution of the i th exciting beam as a function of the photon energy $h\nu$; $\sigma_i(h\nu)$ is the $K\alpha$

fluorescence production cross section of element i as a function of the photon energy $h\nu$; $n = N$ is the number of elements (sorted by increasing atomic number); $\mu_j(h\nu)$ is the attenuation coefficient of element j as a function of the photon energy $h\nu$, and $\mu_j(E_{K\alpha i})$ is the attenuation coefficient of element j at the energy of the characteristic radiation of element i , i.e. $E_{K\alpha i}$. Equation 2 is the condition of normalization for the concentrations: $\|c\|_1 = 1$. The measured K-fluorescence, the absolute efficiency, the area, the solid angle, the sines of the incidence and takeoff angles, the attenuation coefficients, the spectral distribution and the fluorescence cross sections are positive and the concentrations, c_i and the absolute efficiency, ε have to be positive too.

The above experimental situation can be achieved by using X-ray beams produced by an X-ray tube excited with a kV source of variable kilovoltage, as proposed by Figueroa [3], but using selective counting instead of integral counting as Figueroa did.

These equations can be written as a nonlinear eigenvalue problem in the following way:

The Eq. 1 can be written as:

$$M_i = \varepsilon \frac{S \Omega}{4\pi \sin \Psi_1} c_i \int_{E_{K_i}}^{h\nu Max_i} \frac{f_i(h\nu)}{\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j}, \tag{3}$$

where $f_i(h\nu) = \varepsilon_r(E_{K\alpha i}) \phi_i(h\nu) \sigma_i(h\nu)$, and $\mu_{i,j}(h\nu) = \frac{\mu_j(h\nu)}{\sin \Psi_1} + \frac{\mu_j(E_{K\alpha i})}{\sin \Psi_2}$. It should be noted that $f_i(h\nu) > 0$ and $\mu_{i,j}(h\nu) > 0$.

By defining $\lambda = \varepsilon \frac{S \Omega}{4\pi \sin \Psi_1}$, $\mu_{i,j}(h\nu) = \frac{1}{\sin \Psi_1} \mu_j(h\nu) + \frac{1}{\sin \Psi_2} \mu_j(E_{K\alpha i})$, and $F_i(c_j) = \int_{E_{K_i}}^{h\nu Max_i} \frac{f_i(h\nu)}{\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j}$, Eq. 3 can be written as follows:

$$M_i = \lambda c_i F_i(c_j),$$

and defining $H_i(c_j) = \frac{M_i}{F_i(c_j)}$, it can be expressed as a non linear eigenvalue problem.

$$\begin{aligned} H_i(c_j) &= \lambda c_i & (4) \\ \sum_{j=1}^{j=n} c_j &= 1, \\ c_i &> 0 \quad \forall i, \\ \lambda &> 0. \end{aligned}$$

In the case of a polyenergetic excitation of a multi elemental sample with a single X-ray beam, and neglecting the secondary fluorescence, the Sherman equations are written in the same fashion as 4, but in this case $F_i(c_j)$ are defined as $F_i(c_j) = \int_{E_{K_i}}^{h\nu Max} \frac{f_i(h\nu)}{\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j}$, with $f_i(h\nu)$ being now $f_i(h\nu) = \varepsilon_r(E_{K\alpha i}) \phi(h\nu) \sigma_i(h\nu)$. Now $\phi(h\nu)$ is the spectral distribution of the only X-ray beam used for excitation and $h\nu Max$, $h\nu Max > E_{K_n}$, is the energy at the end point of $\phi(h\nu)$.

3 Solution of the equations

3.1 A theorem due to Morishima and Fujimoto [4]

An application $H(\mathbf{x}) : R^n \rightarrow R^n$, $\mathbf{x} = (x_1 \dots x_n)$ is called a non-negative non-decreasing homogeneous transformation of degree one if it satisfies the following four conditions.

- (1) Nonnegativeness: $H(\mathbf{x})$ is a continuous map from $[0, \infty) \times \dots \times [0, \infty)$ into itself.
- (2) Monotonicity: $H(\mathbf{x}) \leq H(\mathbf{y})$ for all $\mathbf{x} \leq \mathbf{y}$. Here, $\mathbf{x} \leq \mathbf{y}$ denotes the product ordering on R^n : $\mathbf{x} \leq \mathbf{y}$ if, and only if, $x_i \leq y_i \forall i$ such that $1 \leq i \leq n$.
- (3) Homogeneity: $H(\alpha \mathbf{x}) = \alpha H(\mathbf{x})$.
- (4) Irreducibility: For any nonempty subset $\Omega \subset \{1, \dots, n\}$, the relations $x_i = y_i \forall i \in \Omega$ and $x_i < y_j \forall j \notin \Omega \Rightarrow \exists i \in \Omega$ such that $H_i(\mathbf{x}) \neq H_i(\mathbf{y})$

When the above conditions are fulfilled, the following conclusions are obtained.

- (1) There are $\lambda > 0$ and $\mathbf{z} > 0$ such that $H(\mathbf{z}) = \lambda \mathbf{z}$.
- (2) \mathbf{z} is unique up to multiplication by a scalar.
- (3) \mathbf{z} is the only nonnegative eigenvector of H .
- (4) $|\lambda_i| \leq \lambda$ for all eigenvalue λ_i of H .

3.2 Fulfillment of the hypothesis of the Morishima's theorem

Let us now check out that the conditions of the above theorem are fulfilled by the transformation H brought about by the Sherman equations:

- (1) Nonnegativeness: Since $c_j > 0 \forall j$, $f_i(h\nu) > 0 \forall i, h\nu$ and $\mu_{i,j}(h\nu) > 0 \forall i, j, h\nu$ it can be seen that $F_i(c_j) = \int_{E_{K_i}}^{h\nu \text{Max}_i} \frac{f_i(h\nu)}{\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j} > 0 \forall c_j > 0, \forall i \forall i$ and so happens with each $H_i(c_j) = \frac{M_i}{F_i(c_j)}$.
- (2) Monotonicity: Since $\mu_{i,j}(h\nu) > 0 \forall i, j, h\nu$, the linear combination $\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j$ is $> 0 \forall c_j > 0, \forall i$ and monotonically increasing with c_j , so that, $F_i(c_j) = \int_{E_{K_i}}^{h\nu \text{Max}_i} \frac{f_i(h\nu)}{\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j}$ is > 0 and it is monotonically decreasing with c_j , so that, the $H_i(c_j) = \frac{M_i}{F_i(c_j)}$ are monotonically increasing with $c_j, \forall i, j$ and H is monotonic
- (3) Homogeneity: The linear combination $\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j$ is homogeneous, then, $F_i(\alpha c_j) = F_i(\alpha c_j)/\alpha$ and $H_i(\alpha c_j) = \alpha H_i(c_j)$, and H is homogeneous too.
- (4) Irreducibility: The linear combination $\sum_{j=1}^{j=n} \mu_{i,j}(h\nu) c_j$ is irreducible because the values of $\mu_{i,j}(h\nu)$ are all different $\forall h\nu$ (except, perhaps, at the most, in a discrete set of values of $h\nu$, since $\mu_j(h\nu) \simeq Z^3 h\nu^{-3}$, Z being the atomic number of the element j), so that, the inverses of the linear combination, the integral of such inverses, and the inverse of the integral are also irreducible.

The foregoing reasoning assures that conclusions 1–4 hold and then the Sherman equations considered have one and only one physically acceptable solution.

3.3 Calculation of the physically acceptable solution of the Sherman equation corresponding to selective excitation and selective measurement

The physically acceptable solution can be calculated by an iterative procedure similar to the Von Misses method.

Step 1: Let us take a positive unnormalized vector $c_{un}0$ (for example $c_{un}0_i = M_i$) and normalize it. Call the result $c0$, and take $\lambda 0 = \sum_{j=1}^{j=n} c_{un}0_j$:

$$c0_i = \frac{c_{un}0_i}{\lambda 0}.$$

Step 2: Substitute $c0$ for c in the left-hand side of Eq. 4 to get $c_{un}1$. Normalize the result and obtain $\lambda 1$ and $c1$:

$$c_{un}1_i = H_i(c0_j), \quad \lambda 1 = \sum_{j=1}^{j=n} c_{un}1_j \quad c1_i = \frac{c_{un}1_i}{\lambda 1}.$$

Step 3: Substitute $c1$ for c and $K1$ for K again in the left-hand side of Eq. 4, to get $c_{un}2$. Normalize the result and obtain $\lambda 2$ and $c2$:

$$c_{un}2_i = H_i(c0_j) \quad \lambda 1 = \sum_{j=1}^{j=n} c_{un}1_j \quad c1_i = \frac{c_{un}1_i}{\lambda 1}.$$

Repeat m times:

The Von Misses method defines a continuous map from $(0, 1]^N \rightarrow (0, 1]^N$ if we define $H(0) = 0$, the map is upper hemi-continuous and the Kakutani’s fixed point theorem [5] tells us that there is at least a fixed point. Since the nonlinear Perron’s Theorem assures that the solution is unique, then, $c = \lim_{m \rightarrow \infty} cm$ is the Perron eigenvector, and $\lambda = \lim_{m \rightarrow \infty} \sum_{j=1}^{j=n} c_{un}m_j$ is the Perron eigenvalue of the transformation H . The convergence is fast, and cm , when m is large enough, is a good approximation to the Perron eigenvector, while λm is also a good approximation to the Perron eigenvalue λ . In the linear case, at iteration m , the relative error in the estimate of the dominant eigenvalue λ is of the order of $\left\| \frac{\lambda_2}{\lambda} \right\|^m$, where λ_2 is the eigenvector of greater norm among the non-dominant eigenvectors.

The normalized eigenvector c is the only physically acceptable solution and λ is the global efficiency of the experimental setup.

The need to take a vector with all its components positive as the first term of the iteration should be pointed out. Let us explain why: Since transformation H is positive, each intermediate result, cm_i , is positive too, and the iterative multiplication method converges to the unique physically acceptable solution. If there were negative elements in the seed, the iterative method could diverge, so that, mathematically speaking, we have to impose on M_i ,—the production of fluorescence for each element present in the sample—the condition that it should be greater than zero, which is a natural physical

feature of the results of fluorescence measurements. The iteration can also be performed without normalizing the $c_{un}m_i$ at each step, but computational problems of underflow or overflow are likely to appear.

4 Error simulation

In a previous work [1] we have studied the Sherman equations that appear when the selective excitation is monoenergetic (or when the excitation is monoenergetic and the secondary fluorescence is neglected) and the authors arrived to a linear Perron eigenvalue problem and the error propagation was studied analytically and numerically therefore obtaining a priori bounds on the errors, and showing that the propagation of errors is stable. In the present work we have only simulated the error propagation in a ternary sample composed of I, Ag and Br. The errors assumed in the measurements of each element are $\pm 1\%$ for I, $\pm 5\%$ for Ag, and $\pm 5\%$ for Br. The results of the simulation appear in Fig. 1.

5 More general case: the presence of secondary fluorescence

The usual experimental situation, exciting with a unique polyenergetic X-ray beam, is such that secondary radiation is produced and measured. When the production of secondary radiation is included in the equations, Sherman equations for an experimental situation in which a unique polyenergetic X-ray beam is employed for the excitation of a sample composed of n elements are:

$$M_k = \varepsilon \frac{S \Omega}{4\pi \sin \Psi_1} c_k \left\{ \int_{E_{K_k}}^{hvMax} \frac{\varepsilon_r(E_{K\alpha k}) \phi(h\nu) \sigma_k(h\nu)}{\frac{\sum_{j=1}^{j=n} \mu_j(h\nu) c_j}{\sin \Psi_1} + \frac{\sum_{j=1}^{j=n} \mu_j(E_{K\alpha k}) c_j}{\sin \Psi_2}} dh\nu \right. \\ \left. + \frac{1}{2} \sum_{i=k+1}^n \left(c_i \int_{E_{K_i}}^{hvMax} \frac{\varepsilon_r(E_{K\alpha k}) \sigma_i(h\nu) \sigma_k(E_{K\alpha i})}{\frac{\sum_{j=1}^{j=n} \mu_j(h\nu) c_j}{\sin \Psi_1} + \frac{\sum_{j=1}^{j=n} \mu_j(E_{K\alpha k}) c_j}{\sin \Psi_2}} \right. \right. \\ \left. \left. \bullet \left[\frac{\sin \Psi_1}{\sum_{j=1}^{j=n} \mu_j(h\nu) c_j} \ln \left(1 + \frac{\sum_{j=1}^{j=n} \mu_j(h\nu) c_j}{\sin \Psi_1 \sum_{j=1}^{j=n} \mu_j(E_{K\alpha i}) c_j} \right) \right. \right. \right. \\ \left. \left. \left. + \frac{\sin \Psi_2}{\sum_{j=1}^{j=n} \mu_j(E_{K\alpha k}) c_j} \ln \left(1 + \frac{\sum_{j=1}^{j=n} \mu_j(E_{K\alpha k}) c_j}{\sin \Psi_2 \sum_{j=1}^{j=n} \mu_j(E_{K\alpha i}) c_j} \right) \right] dh\nu \right) \right\}$$

The equations can be written in shorthand as:

$$M_k = \lambda c_k \left(P_k(c_j) + \sum_{i=k+1}^n c_i S_{k,i}(c_j) \right),$$

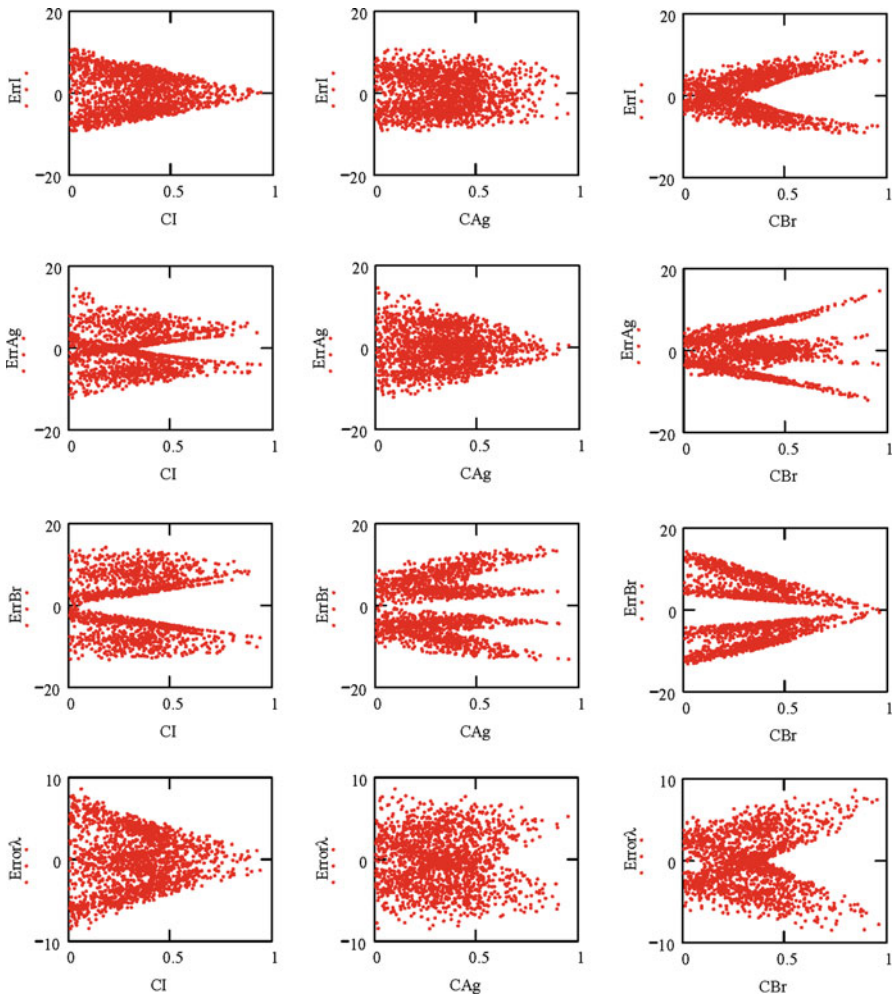


Fig. 1 Monte Carlo simulated errors in the concentrations of I, Ag and Br and in the eigenvalue l in function of the concentrations of I, Ag and Br. The simulated errors have been obtained by assuming errors of $\pm 1\%$ in the measurement of I, of $\pm 5\%$ in the measurement of Ag and of $\pm 9\%$ in the measurement of Br. The errors are measured in %

and as a nonlinear eigenvalue problem:

$$H_k(c_j) = \frac{M_k}{P_k(c_j) + \sum_{i=k+1}^n c_i S_{k,i}(c_j)} = \lambda c_k$$

The hypothesis 1, 3 and 4 of the Morishima’s Theorem are fulfilled, but the monotonicity is no longer guaranteed a priori, even in the case of a bicomponent sample. We can see in the equation for $H_k(c_j)$ that for small values of $c_j, \forall j > k$, the production of primary fluorescence decreases with c_j and the production of secondary fluorescence, $\sum_{i=k+1}^n c_i S_{k,i}(c_j)$, increases with c_j , so that, the monotonicity with respect

to c_j is not guaranteed and it depends on the actual values of $\sigma_k(E_{K\alpha j})$, nevertheless $H_k(c_j)$ is monotonic with respect to $c_j \forall j \leq k$. The author has tested the monotonicity of the equations corresponding to several pairs of actual chemical elements, and the functions are monotonic. It is necessary to increase by a factor greater than 2 the actual value of $\sigma_k(E_{K\alpha j})$ in order to lose the monotonicity.

On the other hand the equations corresponding to several samples composed of two elements, but modified by increasing $\sigma_k(E_{K\alpha i})$ in such a way that the monotonicity is lost, have been iterated by the Von Misses method and the iterations converge to a solution.

There seems to be two ways to figure out the question about the unicity of the solutions of the Sherman equations that include secondary radiation:

The first one is ad hoc for the actual values of cross sections and attenuation coefficients of the elements of the periodic table, and it consists of making an exhaustive test of the monotonicity of the Sherman equations that include the production of secondary fluorescence. It will require about 2^N checks corresponding to all possible ways of exciting secondary fluorescence when the sample is composed of N chemical elements, and each check requires to perform m^N evaluations of H in the range $[0, 1]^N$ m being the number of nodes that are taken in the interval $[0, 1]$. The author has performed several tens of tests of bi and tricomponent samples, and the monotonicity condition is fulfilled, being necessary to increase by a factor greater than 2 the actual value of $\sigma_k(E_{K\alpha i})$ in order to lose the monotonicity. Therefore, it seems rather plausible that the Sherman equations brought about by the analysis of actual chemical elements are a non linear Perron eigenvalue problem with one and only one solution.

The second way is a general one and calls for a generalization of the Perron's Theorem to functions $H_k(c_j)$ such that are monotone only $\forall j = k$, relaxing the condition that $H_k(c_j)$ have to be monotone $\forall j, \forall k$, as it is required by the existing nonlinear generalizations of the Perron's Theorem.

6 Conclusions

In a particular experimental situation characterized by polyenergetic selective excitation and selective measurements, Sherman equations turn into a nonlinear Perron eigenvalue problem and the existence of one and only one physically acceptable solution whose concentration values are positive and normalized is guaranteed. The existence and uniqueness of that physically acceptable solution strongly bounded to the positivity of the fluorescence production cross sections and of the attenuation coefficients, and to the positivity of the fluorescence measurements.

An iterative convergent method has been proposed for calculating such a solution.

In a simple simulated situation the propagation of errors is stable.

It has been shown that it is rather plausible that the Sherman equations corresponding to actual chemical elements and that include the production of secondary fluorescence have one and only one physically acceptable solution.

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