

An stable approach to a kind of problems involving the inversion of a Volterra integral equation of the first kind: application to x-ray fluorescence analysis

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Abstract In some physical problems it is necessary to obtain a function coming from the inversion of an unstable problem, and use it to calculate some global quantities by integrating it weighted by the appropriate weighting functions. When the desired function comes from a first kind Volterra integral equation, the explicit inversion can be avoided by integrating by parts in the integrals in which the above mentioned function appears. That is the case of the fundamental parameters method of x-ray fluorescence analysis. To obtain the concentrations of chemical elements in the sample which is analyzed it is necessary to calculate some integrals of the spectral distribution of the fluorescence exciting x-ray beam multiplied by a weighting function which depends on the concrete analysis to be done. The spectral distribution of the fluorescence exciting beam is related to the experimental measurements of the fluorescence excited on a set of targets made up of pure elements by a Volterra integral equation of the first kind, and it can be obtained by inverting the Volterra equation. By integrating by parts in the integrals in which the spectral distribution appears we avoid the unstable reconstruction of the spectrum of the fluorescence exciting x-ray beam and the concentrations can be calculated in a stable fashion.

Keywords Volterra integral equation of the first kind · Global quantities · Stable

1 Introduction

In a wide class of physical problems it is necessary to obtain, in an unstable way, from a set of measurements, M , a function, V , but such a function is only needed to calculate global quantities Q , defined as integrals of that function V multiplied by some

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weighting function W . These global quantities, Q , may be considered as generalized moments of V (see the Sect. 7.4 Finding Generalized Moments of Solutions of the book of G. Milton Wing) [1].

In an symbolic and informal way we can write:

$$M = A V \quad (1.1)$$

where A represents the action of the experimental apparatus or procedure.

The global quantities Q are defined as:

$$Q = \int V W \quad (1.2)$$

with

$$V = A^{-1} M \quad (1.3)$$

A^{-1} habitually represents the unstable inversion of an ill posed problem, so, we must rely on the regularizing properties of the integration process in order to have a reliable value for Q .

But the global quantities Q can informally be also written as:

$$Q = \int (A^{-1} M) W = \int M (A^{-1+} W) \quad (1.4)$$

whatever A^{-1+} means.

The unstable application of A^{-1} to experimental data is avoided and A^{-1+} is applied to W which usually is (or can be represented) as a known elementary function and we can have $A^{-1+} W$ represented also by an elementary function and the integral can be calculated in a stable fashion.

This methodology has been formalized by the author for two physical problems.

In the first one [2], M is the narrow beam attenuation curve of an x-ray beam, V is the spectral distribution of the above mentioned beam, A is directly related with the Laplace transform and Q are dosimetric and radiometric quantities. W and $A^{-1+} W$ are represented by a pair of analytical Laplace transforms [3–6].

In the second one [7], M is the number of K_{α} photons produced on a set of fluorescence thin targets made of pure chemical elements, V is the spectral distribution of the fluorescence exciting beam, A is a Volterra integral equation of the first kind with separable kernel and Q are concentrations of chemical elements. A is reduced to a derivative, and, when integrating by parts, $A^{-1+} W$ is the derivative of W .

Here we present a general approach for physical problems where A is a Volterra equation of the first kind without restricting the kernel to be separable.

2 The case of volterra equations of the first kind

When the desired function comes from a first kind Volterra integral equation, the explicit inversion can be avoided by integrating by parts in the integrals in which the above mentioned function appears.

We will follow in this section the notation of the classical book on integral equations of Tricomi [9].

A Volterra integral equation of the first kind

$$\int_0^x K(x, y) \phi(y) dy = f(x) \quad (0 \leq x \leq h) \tag{2.1}$$

with a nonvanishing ‘diagonal’ $K(x, x)$ in the basic interval $(0, h)$, and if the derivatives

$$\frac{df(x)}{dx} \equiv f'(x), \quad \frac{\partial K}{\partial x} \equiv K'_x(x, y), \quad \frac{\partial K}{\partial y} \equiv K'_y(x, y) \tag{2.2}$$

exist and are continuous, can be reduced to one of the second kind in the following way:

If we set

$$\int_0^x \phi(y) dy = \Phi(x), \tag{2.3}$$

we obtain the second kind Volterra equation

$$\Phi(x) - \int_0^x \frac{K'_y(x, y)}{K(x, x)} \Phi(y) dy = \frac{f(x)}{K(x, x)}, \tag{2.4}$$

which can be stably solved in a standard stable way using iterative methods or the resolvent kernel.

The calculation of global quantities

$$Q = \int_0^h \phi(x) W(x) dx \tag{2.5}$$

can be accomplished in the following way: By integrating by parts we get

$$Q = [\Phi(x) W(x)]_0^h - \int_0^h \Phi(x) W'(x) dx \tag{2.6}$$

3 Stability analysis

Sometimes, the weighting function $W(x)$ is obtained in a numerical way, and the numerical derivative, $W'(x)$, is unstable. Let us analyze what happens if $W(x)$ is fitted by a derivable elementary function $W_{fitted}(x)$.

By integrating by parts $Q_{fitted} = \int_0^h \phi(x) W_{fitted}(x) dx$, the following identity appears:

$$Q_{fitted} = \int_0^h \phi(x) W_{fitted}(x) dx \equiv [\Phi(x) W_{fitted}(x)]_0^h - \int_0^h \Phi(x) W'_{fitted}(x) dx \quad (3.1)$$

Comparing

$$Q_{fitted} = \int_0^h \phi(x) W_{fitted}(x) dx \quad (3.2)$$

with

$$Q = \int_0^h \phi(x) W(x) dx \quad (3.3)$$

we get

$$Q - Q_{fitted} = \int_0^h \phi(x) (W(x) - W_{fitted}(x)) dx \quad (3.4)$$

and using the Schwartz inequality

$$(Q - Q_{fitted})^2 \leq \left(\int_0^h \phi(x) (W(x) - W_{fitted}(x)) dx \right)^2 \leq \int_0^h \phi(x)^2 dx \int_0^h (W(x) - W_{fitted}(x))^2 dx, \quad (3.5)$$

so, if $W_{fitted}(x)$ is near $W(x)$ in the L_2 sense, the difference between Q and Q_{fitted} is small and Q can be approximated by Q_{fitted} calculated as

$$Q_{fitted} = [\Phi(x) W_{fitted}(x)]_0^h - \int_0^h \Phi(x) W'_{fitted}(x) dx \tag{3.6}$$

A similar argument can be used when instead of $\Phi(x)$ we have a function $\Phi_{approximate}(x)$ coming from an experimentally measured $f(x)$, $f_{experimental}(x)$, and also when the kernel $K(x, y)$ is known numerically and a fit $K_{fitted}(x, y)$ to a derivable function has to be used in order to calculate the derivative $K'_y(x, y)$.

4 An example: x-ray fluorescence analysis by the fundamental parameters method

In the case of the fundamental parameters method of x-ray fluorescence analysis [7], the knowledge of the spectral distribution of the fluorescence exciting x-ray beam is needed in order to calculate the concentrations of chemical elements in the sample analyzed.

To obtain the concentrations it is necessary to calculate some integrals of the spectral distribution of the fluorescence exciting beam multiplied by a weighting function which depends on the concrete analysis to be done. The spectral distribution of the fluorescence exciting beam is related to the experimental measurements of the fluorescence excited on a set of targets made of pure elements by a Volterra integral equation of the first kind, and it can be obtained by inverting the Volterra equation. The unstable explicit inversion of the first kind Volterra integral equation can be avoided by integrating by parts in the integrals in which the spectral distribution appears.

When considering a sample excited by an x-ray beam, the fluorescence intensity I_i as emitted by one of the elements in the sample is generically written as:

$$I_i = \int_{E_z}^{E_{max}} \phi(h\nu) f(h\nu) d h\nu \tag{4.1}$$

where E_{max} is the maximum x-ray beam energy, and $f(h\nu)$ is a function depending upon the actual excitation conditions. For the real case of a homogeneous multicomponent thick sample, function $f(h\nu)$ is:

$$f(h\nu) = \varepsilon(K\alpha_i) \frac{C_i}{\sqrt{2}} \frac{\sigma_i(h\nu)}{\mu_s(K\alpha_i) + \mu_s(h\nu)} \tag{4.2}$$

where $K\alpha_i$ is the energy corresponding to line $K\alpha$ of the the i -th element, $\varepsilon(K\alpha_i)$ is the detection efficiency for the $K\alpha_i$ x-rays, C_i is the concentration of the said element, $\sigma_i(h\nu)$ is the fluorescence production cross-section of the i -th element $\mu_s(K\alpha_i)$ is the mass attenuation coefficient of the sample at the energy of the $K\alpha$ x-rays of the i -th

element, and $\mu_s(h\nu)$ is the mass attenuation coefficient of the sample at energy $h\nu$. Incidence and exit angles are 45° .

The spectral distribution of the fluorescence exciting beam can be related to the experimental measurements of the fluorescence excited on a set of targets made of pure elements by a Volterra integral equation of the first kind, and it can be obtained by inverting the integral equation. When the targets are thin, the kernel is separable, but by experimental considerations [8] it is convenient to use a set of thick targets, and, in that case the kernel is not separable, and the general formalism presented for first kind Volterra equations has to be used.

Let us consider an infinite-thickness sample of atomic number Z which is excited by an x-ray beam. The fluorescence emission intensity $N(E_Z)$ of such sample can be expressed as:

$$N_{Z,\infty} = \varepsilon(K\alpha_Z) \frac{1}{\sqrt{2}} \int_{E_Z}^{E_{max}} \frac{\phi(h\nu)\sigma_Z(h\nu)}{\mu_Z(K\alpha_Z) + \mu_Z(h\nu)} dh\nu \quad (4.3)$$

where E_Z is the binding energy of the samples K shell, E_{max} is the energy of the end point of the excitation x-ray beam, $\varepsilon(K\alpha)$ is the detection efficiency for the $K\alpha$ x-rays of the element Z , $\phi(h\nu)$ is the differential spectral distribution of the excitation beam photon flux, $\sigma_Z(h\nu)$ is the fluorescence cross section for the $K\alpha$ x-rays, $\mu_Z(h\nu)$ is the mass attenuation coefficient of the sample Z at energy $h\nu$, and $\mu_Z(K\alpha)$ is the attenuation energy for the $K\alpha$ x-rays emitted by the sample Z .

Let us assume that variable E_Z is a continuous variable E , then a first kind Volterra integral equation can be written

$$N(E) = \varepsilon(K\alpha(E)) \frac{1}{\sqrt{2}} \int_E^{E_{max}} \frac{\phi(h\nu)\sigma(E, h\nu)}{\mu(K\alpha(E)) + \mu(E, h\nu)} dh\nu \quad (4.4)$$

or

$$N(E) = \int_E^{E_{max}} \phi(h\nu) K(E, h\nu) dh\nu \quad (4.5)$$

with

$$K(E, h\nu) = \varepsilon(K\alpha(E)) \frac{1}{\sqrt{2}} \frac{\phi(h\nu)\sigma(E, h\nu)}{\mu(K\alpha(E)) + \mu(E, h\nu)} \quad (4.6)$$

The explicit unstable inversion of the first kind Volterra integral equation needed to obtain explicitly the spectral distribution can be avoided by integrating by parts in the integrals in which the spectral distribution appears. Defining

$$-\int_{h\nu}^{E_{max}} \phi(y) dy = \Phi(h\nu) \quad (4.7)$$

the first kind Eq. (4.5) becomes a second kind Volterra equation which can be solved in a standard stable way using iterative methods or the resolvent kernel.

$$N(E) = [\Phi(h\nu) K(E, h\nu)]_E^{E_{max}} - \int_E^{E_{max}} K'_{h\nu}(E, h\nu) \Phi(h\nu) dh\nu \quad (4.8)$$

$$\Phi(E) = -\frac{N(E)}{K(E, E)} - \int_E^{E_{max}} \frac{K'_{h\nu}(E, h\nu)}{K(E, E)} \Phi(h\nu) dh\nu \quad (4.9)$$

By using the value of $\Phi(h\nu)$ from (4.7) and that of $f(h\nu)$ from (4.2) in (4.1) and integrating by parts, we have the following expression for the measured fluorescence intensity of the i -th element, I_i :

$$I_i = [\Phi(h\nu) f(h\nu)]_{E_Z}^{E_{max}} - \int_{E_Z}^{E_{max}} \Phi(h\nu) f'_{h\nu}(h\nu) dh\nu \quad (4.10)$$

The values of the concentrations C_i are obtained by solving the equation system made up from the theoretical expressions (4.10) where $\Phi(h\nu)$ is obtained in a stable way from the experimental values of fluorescence $N_i(E_i)$.

5 Conclusions

It has been shown that the unstable explicit inversion of a first kind Volterra integral equation can be avoided when the searched function is used only to calculate global quantities by integrating it weighted by weighting functions. The first kind Volterra integral equation is converted, by integrating by parts, in a second kind Volterra integral equation, which can be solved in a stable way. The integrals defining the global quantities are modified by integrating by parts and can be calculated using the stable solution of the second kind Volterra integral equation.

It has been presented a concrete example dealing with the fundamental parameters method of x-ray fluorescence analysis.

References

1. G.M. Wing, A Primer on Integral Equations of the First Kind: the Problem of Deconvolution and Unfolding, Assisted by John D. Zahrt. (Cambridge University Press, Cambridge, 1991). Section 7.4 finding generalized moments of solutions
2. V. Delgado, P. Ortiz, The narrow beam attenuation curve as a functional description of a low energy x-ray beam. x-ray Spectrom. **20**, 343–344 (1991)

3. V. Delgado, P. Ortiz, Calculation of integral quantities from the narrow beam attenuation curve of a low energy x-ray beam. *Rad. Prot. Dosim.* **48**(3), 273–277 (1993)
4. P. Ortiz, V. Delgado, The narrow beam attenuation curve as a mean of assessing the energy imparted to a phantom by a low energy x-ray beam. *Rad. Prot. Dosim.* **49**(1–3), 349–351 (1993)
5. V. Delgado, P. Ortiz, Energy imparted to a phantom by a low energy x-ray beam: calculation from its narrow beam attenuation curve and comparison with experiments. *Appl. Rad. Isot.* **46**, 437–438 (1995)
6. V. Delgado, P. Ortiz, Determination of the energy fluence of diagnostic x-ray beams from field measurements of attenuation curves. *Med. Phys.* **24**, 1089–1906 (1997)
7. V. Delgado, C. Martínez, The number of K_{α} photons produced on a set of thin targets as a functional description of the fluorescence exciting x-ray beam. *X-Ray Spectrom.* **22**, 312–316 (1993)
8. V. Delgado, C. Martínez, Description of a fluorescence exciting x-ray beam using the fluorescence produced on a set of thick targets. *X-Ray Spectrom.* **24**, 255–259 (1995)
9. F.G. Tricomi, *Integral Equations*. Pure Appl. Math. vol. 5 (Interscience, New York, 1957)