Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Ultramicroscopy 102 (2005) 327–337
ultramicroscopy
www.elsevier.com/locate/ultramic

Independent component analysis: A new possibility for analysing series of electron energy loss spectra

Noël Bonnet[a,b,*], Danielle Nuzillard[c]

[a]INSERM, UMRS 514 (IFR53), Hôpital Maison Blanche, 45, rue Cognacq Jay, 51092 Reims Cedex, France
[b]Centre de Recherches en STIC (CReSTIC-LERI), Rue des Crayères, BP 1035, 51687 Reims Cedex 2, France
[c]Centre de Recherches en STIC (CReSTIC-LAM), UFR Sciences Exactes et Naturelles, BP 1039, 51687 Reims Cedex 2, France

Received 11 February 2004; received in revised form 12 November 2004; accepted 22 November 2004

Abstract

A complementary approach is proposed for analysing series of electron energy-loss spectra that can be recorded with the spectrum-line technique, across an interface for instance. This approach, called blind source separation (BSS) or independent component analysis (ICA), complements two existing methods: the spatial difference approach and multivariate statistical analysis. The principle of the technique is presented and illustrations are given through one simulated example and one real example.

PACS: 02.50.Sk; 02.70.−c; 68.35.DV; 82.80.P

Keywords: Electron energy loss spectroscopy; Independent component analysis; Blind separation of sources; Interface; Multivariate statistical analysis

1. Introduction

Improvements in electron energy loss spectroscopy (EELS) techniques have made possible the development of many experimental studies in the field of core-loss spectroscopy, including the study and use of near-edge structures. Among these techniques, the spectrum-image technique (or its spectrum-line variant) plays an important role for performing spatially resolved EELS.

Besides experimental advances, such as the increase of spatial and spectral resolutions, data analysis techniques also play their role in the improvement of the technique. The spatial-difference technique can be cited as one of the data analysis techniques that helped to get useful information from series of spectra recorded across interfaces [1,2]. Another set of methods, dedicated

*Corresponding author. INSERM, UMRS 514 (IFR53), Hôpital Maison Blanche, 45, rue Cognacq Jay, 51092 Reims Cedex, France. Tel.: +33326787771; fax: +33326065861.
E-mail address: noel.bonnet@univ-reims.fr (N. Bonnet).

0304-3991/$ - see front matter
doi:10.1016/j.ultramic.2004.11.003

to larger sets of spectra, comes from multivariate statistical analysis (MSA). [3–5]. The last developments in this category concern the oblique analysis method [6]. These two groups of methods proved already useful but they are also prone to several drawbacks that suggest that more sophisticated methods for analysing series of spectra would be welcome.

In the work described in this paper, we explore a new approach called blind source separation (BSS), or independent component analysis (ICA). This technique has been used to solve many problems in data analysis, signal and image processing. We expect that it could be useful in electron energy-loss spectroscopy, especially when mixtures are involved.

The rest of the paper is organized as follows. In the next section, we briefly summarize the two groups of methods already in use for analysing series of spectra: the spatial difference method and MSA, including oblique analysis. In the following section, we present the general principles of ICA/BSS. Then, we illustrate the application of one of its variants in the field of EELS. Finally, we draw some conclusions and offer some directions for future work.

2. Summary of data analysis methods in use

Here, we concentrate on data analysis methods aiming at discovering unknown spectra within series of recorded spectra. This problem arises for specimens where the EEL spectrum is dominated by the matrix component and an unknown component is present locally at low concentration. The problem may also be to quantify the variation of composition of (known and unknown) components across an interface. Two groups of methods are already in use for trying to cope with these problems.

2.1. *The spatial difference approach*

This approach deals with two spectra, one of them being recorded in the matrix region and the other being recorded where a variation of the chemical composition is expected. Two variants of the method can be used:

- the difference between the two spectra is computed, after some sort of normalization has been performed on one of the spectra [1]. The resultant difference provides information on the difference between the *new* spectrum and the reference spectrum.
- the spectrum in the region of unknown composition is modelled as a linear combination of the matrix spectrum and the new (unknown) spectrum [2]:

$$S_I = \alpha S_M + (1 - \alpha) S_U, \tag{1}$$

where S_I stands for the recorded spectrum, S_M for the matrix spectrum and S_U for the unknown spectrum.

The difficulty is to estimate the coefficient α. This is often done through a trial-and-error approach.

The drawbacks of the spatial difference approach have been identified for a long time: with the first variant, care must be taken to avoid confusing the new spectrum with artefacts due to any energy drift, for instance [7]. With the second variant, the approach remains subjective with respect to the scaling factor, even if general guidelines have been devised for choosing it properly [2,8,9].

A variant of the spatial difference method, called the normalized spatial difference method (NSD) was also suggested by Imhoff et al. [10].

2.2. *Multivariate statistical analysis*

With the development of the spectrum-line approach [11], or even more with the spectrum-image approach, it becomes worth processing a series of spectra at once rather than pairs of spectra. Multivariate techniques are able to do so and to extract the different sources of information contained in such complete series [3–5]. More specifically, a series of spectra can be decomposed into an average spectrum $\bar{S}$ and a set of orthogonal components Ψ_k common to all the spectra of the series. Any spectrum of the series (S_i) can thus be