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Review

The role of chemometrics in single and sequential extraction assays: A review Part I. Extraction procedures, uni- and bivariate techniques and multivariate variable reduction techniques for pattern recognition

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ABSTRACT

Element mobility and availability in natural solid matrices can be studied with single and sequential extraction procedures; such procedures provide reliable and useful information only if the experiments are correctly planned and executed and the results are properly interpreted. Chemometrics can be a valuable tool for these aims, especially taking into account the large amounts of data generated with extraction essays and the complexity of the processes under investigation. This review deals with the application of chemometrics in research studies involving single and sequential extractions on soils or sediments, for several purposes: the development and optimization of the extraction conditions, the calculation of element fractionation, the visual illustration of the experimental results, the acquisition of different areas of information, including relationships among variables, similarities and differences among samples, causes of the observed behaviour (e.g. source identification), risk assessment, models and predictions of future events. In Part I of the review, following an overview on extraction procedures, the applications of univariate and bivariate chemometric methods are reported; then the principles of multivariate techniques for pattern recognition based on variable reduction, their applications and the main findings obtained are addressed.

Ornella Abollino received her PhD in Chemical Sciences in 1991 from the University of Torino. She is presently Associate Professor of Analytical Chemistry at the Faculty of Pharmacy, University of Torino. Her research activities are mainly focused on the following topics: development of voltammetric and spectroscopic procedures for the determination and speciation of trace metals; study of element fractionation in sediment and soils from remote and anthropized areas; characterization of metal content in pharmaceutical formulations; interaction between trace metals and plants; application of chemometric techniques for the processing of experimental results related to the above mentioned matrices.

Mery Malandrino received her PhD in Chemical Sciences in 2001 at the University of Torino. She is presently Researcher of Analytical Chemistry at the Faculty of Sciences of the University of Torino. She is mainly involved in the development of sensitive analytical procedures capable of characterising complex environmental matrices, such as soils, sediments and atmospheric particulate matter. She uses chemometrics to interpret experimental results. The purpose of her studies is to gain insight into the behaviour of elements in uncontaminated ecosystems and their influence on climate changes. Furthermore, she studies the development of eco-compatible decontamination procedures for polluted soils.

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Agnese Giacomino graduated in Chemistry in 2003 at the University of Torino. She received her PhD in Chemical Sciences in 2007 at the University of Torino. Now she is holder of a research grant at the Department of Analytical Chemistry of the University of Torino. Her research activities are finalized to study the behaviour of metals in different natural matrices (soils, sediments, vegetables, seawater), using chemometrics for data processing, to characterize the composition of pharmaceutical formulations, to develop new procedures of remediation of contaminated soils, to study analytical methods for the determination of trace metals.


Edoardo Mentasti has been full professor of Analytical Chemistry at the Faculty of Sciences of the University of Torino from 1980 to 2007 and is now retired. He has been Editor-in-chief of the Journal Annali di Chimica from 1996 to 2006. His main research interests are the development of preconcentration and speciation procedures for trace metal ions coupled to determination by atomic spectroscopy, the development of voltammetric methods of analysis, the characterization of environmental compartments (seawaters, lacustrine ecosystems, sediments, soils) with the aid of chemometric techniques, the interaction between trace metals and clays, the remediation of contaminated soils.

1. Introduction

Single and sequential extraction procedures are widely used for the investigation of solid matrices, such as soil, sediment, sludge, fly ash and atmospheric particulate matter [1–4]. They provide information on the mobility and availability of metals and other elements, meanwhile identifying their potential negative impact through their release into other environmental compartments and entry into the food chain.

Mobility and availability depend on the reactivity and on the binding behaviour of elements with the components of the matrix, and cannot be assessed only from the values of the total concentrations. Single extractions may be used for estimating the most potentially mobile element fraction and/or, in the case of soils, the proportion amenable for plant uptake. A single extracting reagent (normally a ligand, diluted acid or salt) is used to treat the sample and measurement is made on the amount of elements released from the matrix of interest [2,3]. A more detailed overview on the properties and behaviour of the elements under investigation may be achieved through the utilization of sequential extractions. Reagents with different chemical properties are applied, usually in order of increasing strength, so that elements are leached according to different mechanisms, e.g. acidification or complexation. This results in a process that is more time consuming than single extractions, but one that provides the partitioning of the total element contents into fractions of different availability [1–4].

Extraction assays allow us to obtain reliable and useful information only if the experiments are correctly planned and executed and if the results are properly interpreted. Extraction treatments give rise to large amounts of data, especially when coupled to rapid multielement analytical techniques, and many research studies also report the main properties of the considered matrices (such as pH, content of organic matter, soil texture) which are important in order to understand their behaviour. The combination of the complexity of the matrices and phenomena under study with the generation of large data sets renders interpretation difficult. Chemometric techniques can be a valuable tool in connection with single and sequential extraction procedures for several purposes: the development and optimization of the extraction conditions; the calculation of element fractionation; the visual illustration of the experimental results; the acquisition of different areas of information, including relationships among variables, similarities and differences among samples, causes of the observed behaviour (e.g. source identification), models, risk assessment and predictions of future events [5–7]. Chemometrics is deemed to be particularly advantageous when dealing with complex systems, such as soils and sediments, due to the possibility of using multivariate techniques, which take into account the behaviour of multiple variables simultaneously; nevertheless, it should be emphasized that also univariate and bivariate chemometric methods are important, since they remain indispensable for a correct and complete data processing and interpretation, even when sophisticated multivariate techniques are subsequent applied.

This review describes the application of chemometric techniques in research studies involving single and sequential extraction treatments on soils or sediments. Following an overview on extraction procedures, in which both advantages and disadvantages are ascertained, the applications of univariate and bivariate chemometric methods are reported; then the principles of the multivariate chemometric techniques most frequently adopted, the aims of the research studies in which they were used and the main findings obtained with their application will be addressed. In particular, Part I of the review will be focused on variable reduction methods for pattern recognition, one of which, namely principal component analysis (PCA), is the multivariate technique most extensively used in conjunction with extraction assays.

To our knowledge, two reviews on element extraction from soils and sediments to date have included a chapter devoted to the application of chemometrics to the experimental results [1,2], but no extensive treatment of this subject currently exists. We are confident that the present work will be of use to researchers interested in adopting the powerful tools of chemometrics in order to exploit the potentialities of single and sequential extractions of elements from solid matrices.

2. Overview on single and sequential extraction procedures

2.1. Single extractions

The main extracting reagents used in single extraction procedures can be classified, according to their chemical properties, as:

- ligands, mainly diethylene triamine pentaacetic acid (DTPA) and ethylene diamine tetraacetic acid (EDTA); despite concerns of being over-aggressive for this purpose (see next paragraph), they are employed for the purpose of estimating plant-available fraction of elements [9–11]. The Standards, Measurements and Testing (SMT) Program (formerly BCR) developed and validated a single extraction protocol (0.05 M ammonium EDTA, 1 h, room temperature) [12];
- unbuffered salts, called ‘soft’ or ‘mild’ extractants, such as CH_3COONH_4, $CaCl_2$, $NaNO_3$ and $BaCl_2$. A SMT protocol exists (0.01 M $CaCl_2$, 3 h) [4]. They are regarded as more suitable than more aggressive extractants, such as chelating agents and acids, to predict the plant-available fraction of elements: therefore the