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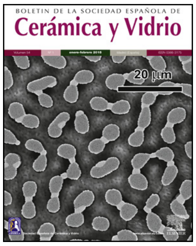

Determination of minor and trace elements in geological materials used as raw ceramic materials

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ABSTRACT

A study has been undertaken to develop a methodology to determine minor and trace elements in geological ceramic raw materials by wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometry. The set up of the methodology has been done either by optimising not only the sample preparation process but also optimising the measurement with the aid of the software Pro-Trace, and also by making an exhaustive compilation of reference materials for calibration and validation.

The developed method is precise and accurate and allows the analysis of Ba, Ce, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Rb, S, Sr, Ta, Th, U, V, Y, Zn and Zr present in the sample as minor or trace elements in geological materials used as raw ceramic material in a relatively short period of time. Besides, the method is more environmentally friendly than other methodologies as it does not require the use of solvents or reagents.

Determinación de elementos minoritarios y traza en materiales geológicos utilizados como materias primas cerámicas

Palabras clave:
Elementos minoritarios
Elementos traza
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RESUMEN

Se ha llevado a cabo un estudio para el desarrollo de una metodología para la determinación de elementos minoritarios y traza en materias primas geológicas cerámicas mediante espectrometría de fluorescencia de rayos X por dispersión de longitudes de onda (WD-FRX). La puesta en marcha se ha llevado a cabo no solo mediante la optimización del proceso de preparación de muestra sino mediante la optimización de la medida con la ayuda del software Pro-Trace y mediante una exhaustiva recopilación de materiales de referencia para calibración y validación.

El método desarrollado es preciso y exacto, y permite el análisis de Ba, Ce, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Rb, S, Sr, Ta, Th, U, V, Y, Zn y Zr presentes en la muestra como elementos minoritarios y traza en materiales geológicos utilizados como materias primas cerámicas en un tiempo relativamente corto. Además, el método es más respetuoso con el medio ambiente que otras metodologías ya que no requiere el uso de disolventes o reactivos.

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Introduction

The development of new analysis methods capable of determining minor and trace elements in ceramic raw materials has been demanded because of the emergence of new ceramic products with technical characteristics and novel functionalities demands, as some elements present in very low concentrations can generate defects in the final product.

The presence of compounds such as pyrites and other sulfur compounds that can decompose at elevated temperatures during the firing process of ceramic materials originates defects in the final product; other elements such as Ti and Fe compounds generate colouring problems, and the presence of U and Th in materials such as zirconium silicates can cause high levels of radioactivity.

Trace elements in rocks have often been determined using atomic absorption spectrometry (GFAAS or FIAS-AAS), inductively coupled plasma atomic emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), which are extremely sensitive but require a tedious pretreatment, including decomposition with acid, due which implies the conduction of digestions, entailing the ensuing increase of the uncertainty and long analysis times, for that reason, analyses of numerous samples are difficult by these methods [1]. Bennett, in his book "XRF analysis of ceramics, minerals, and allied materials" [2], gives a general idea of how to characterise ceramics, minerals, and allied materials by WD-XRF, but does not refer to the analysis of trace elements.

The use of XRF in the analysis of geological samples is increasing, mainly because of the precision and accuracy with which the major elements and a wide range of trace elements may be determined. Although it is an old and well-established technique, it continues to find widespread use in the analysis of soils and other environmental samples. One reason for the continuing popularity of the technique is the simple sample preparation [3]. Its contribution to a substantial extent to the complete elemental characterisation allows the elucidation of its geological origin or the study of the evolution of mineral deposition with time. Furthermore, XRF is frequently used for the verification of the quality and the physical characteristics of industrial mineral processes. Across the years, many authors have pointed out the new applications of XRF in the field of geological minerals [4,5]. In the field of nanotechnology and the development of catalysts and new ceramic materials, the XRF technique continues to be one of the favourable analytical tools routinely applied in the characterisation process of these materials [6,7]. Another advantage of XRF against classical techniques is the analysis of U and Th, present in geological samples in very low concentrations. Techniques such as spectrophotometry, spectrofluorimetry, flame and graphite furnace AAS, ICP-OES, or neutron activation analysis (NAA) present different interferences and/or low sensitive which increase their detection limit of U and Th, which entail the necessity of a tedious sample preparation to concentrate these analytes [8].

This study has been undertaken to obtain such a methodology for the determination of minor and trace elements in materials such as sands, clays, kaolins, feldspars and feldspathoids, calcites, dolomites, etc., by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF), and making an exhaustive compilation of reference materials to calibrate and validate the methodology. The following elements were analysed: Ba, Ce, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Rb, S, Sr, Ta, Th, U, V, Y, Zn y Zr.

The developed method is precise and accurate and allows the analysis of minor and trace elements in geological materials used as raw ceramic material in a relatively short period of time. The use of a great number of standards has yield a huge concentration range for all the analysed elements. Besides, the method is more environmentally friendly than other methodologies as it does not require the use of solvents or reagents due to the lack of any sample digestion process; reducing in this way the adverse environmental impact of analytical methodologies [9].

Experimental

Materials and equipment

The importance of "reliable" analyses of rocks reference materials in the calibration of modern instrumental techniques has already been stressed. In this respect, compilations of data for all available silicate samples are very valuable. However, these lists of data do have one drawback: they give little indication of the error limits in quoted values apart from a crude classification into "usable", "proposed", or "recommended" values as opposed to "for information" or "order of magnitudes values" depending on the favoured terminology of the compiler. The calculation of statistically meaningful uncertainty limits from such data is not simple since interlaboratory bias cannot readily be quantified on a statistical basis [10].

The results of many geological reference materials indicate that there are few major elements whose values are known with a confidence better than 1% (one sigma). Furthermore, for several elements, coefficients of variation exceed 5%, sometimes substantially so, even though the concentration of the element is significantly above the expected detection limit of modern analytical techniques. And so we have the contradiction that many modern instrumental methods are capable of achieving instrument precisions often exceeding 0.1% relative. Uncertainties in analyses of individual reference materials used for calibrating instruments can be overcome by incorporating a large number of such samples (often over 20) in the calibration data set do that discrepancies will cancel out. However, the only way in which the accuracy of a calibration can be satisfactory tested is by the analysis of individual reference and comparing analysed results with data [10].

In the case of trace elements, with a few notable exceptions, error in the analyses of reference materials usually exceeds 5% relative (one sigma). The problems mentioned for setting up and assessing the accuracy of major element calibrations are even more serious for trace element data. An associated difficulty is that is often necessary to determine these elements down to detection limit levels. Such data cannot be achieved unless the calibration line passes through the origin, and in instruments that are calibrated directly from reference materials, this is not always easy to achieve without a highly critical evaluation of the reliability of individual datum points [10].

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