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# Occurrence of soluble organic compounds in thermal waters by ion trap mass detection

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ABSTRACT

Thermal waters can be regarded as worth developing because of their human health implications and, if thermal tourism is promoted, their importance to the local economy. Galicia, in the North-West of Spain, has numerous sources of thermal waters spread all over the region. They have been used for therapeutic purposes since Roman times. Ourense, with 82 sources (9 spas), is becoming one of the richest Spanish provinces in hydromineral and thermal resources. In this work, the most representative springs of thermal waters from the city of Ourense – Outariz, Chavasqueira, Tinteiro and As Burgas – were analysed in order to identify the presence of several chemical classes of soluble organic compounds responsible for their biological activity. The waters studied are hyperthermal, with temperatures ranged between 45 and 66 °C. Different extraction techniques, liquid–liquid extraction (LLE), solid phase extraction (SPE) and solid phase micro-extraction (SPME), combined with gas chromatography–electron impact ion trap mass spectrometry (GC–(EI)ITMS) were used to cover a wide variety of compounds. The most characteristic chemical families of extractable organic compounds detected are thoroughly discussed. Most of the substances belonging to phenol, aldehyde, esther, ketone, and elemental sulphur groups occur in all samples. Large amounts of elemental sulphur were found in Tinteiro spring, providing to this water of numerous beneficial clinical effects.

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## 1. Introduction

Galicia, a region located in the North-West part of Spain, has vast mineral–medicinal resources in its soils, as there are more than three hundred sources registered, of which 20 are used by spas (Dirección Xeral de Industria, Enerxía e Minas, 2003). These are mainly found inland, where they have been carrying out important work in stimulating the economy of the region. The use of thermal waters for bath and health resort purposes in Galicia dates back to Roman times. Over the last few years, after a long period of decline, there has been an increasing resurgence in Galician spas; becoming the city of Ourense in a reference for prestige in the area of health tourism. Recently, Ourense was designated by the Galician Regional Parliament as Thermal Capital of Galicia, title that will guarantee public and private inversions in this growing sector.

The chemistry of thermal waters has attracted the attention of numerous and varied studies. Major, minor and trace inorganic components, as well as isotope composition are the usual chemical measurements evaluated basically to investigate the water origin, to study the water–rock interaction mechanisms, to discriminate among hydrochemical facies and isotopic groups and to identify the major geochemical processes that affect water composition (Levet et al., 2002; Nathenson et al., 2003; Gemici and Tarcan, 2004; Kralj, 2004a,b; Ramírez-Guzmán et al., 2004; Lambrakis and Kallergis, 2005; Virgilio-Cruz and França, 2006; Marques et al., 2006; Yalcin, 2007; Lambrakis and Stamatis, 2008; Olivier et al., 2008). However, much less attention has been paid to the characterization of trace organic compounds in thermal waters. Up to now, only Kárpáti et al. (1999) and Di Giogia et al. (2006) tackled this topic. The first ones analysed formation waters produced from wells tapping the aquifers of the clastic Pannonian Basin and Mesozoic carbonates for the content of hexane soluble organic compounds, whereas the second ones studied the occurrence of organic compounds in the sulphurous thermal waters of Calabria (Italy). In spite of having a different origin that thermal water, hydrothermal vent water and produced water have been more studied in this respect (Brault et al., 1988; Simoneit et al., 1990; Marchand et al., 1994; Bayona et al., 2002; Sirivedhin et al., 2004).

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Dissolved organic matter consists of numerous compounds with a wide range of chemical properties, such as alcohols, acids, esters, ketones and hydrocarbons (Deroux et al., 1996). It would be of great interest to try to identify the *sensu lato* organic compounds content responsible for the biological activity of the thermal waters, because the four representative waters from Ourense selected in this study are used principally both in spas and for drinking water. The work reported in this paper represents the first attempt to characterize the organic components in the thermal waters from the city of Ourense. Analytical procedures were developed for such purpose. Different extraction techniques (LLE, SPE, and SPME) combined with GC–(EI)ITMS were used to identify several chemical classes of soluble organic compounds.

## 2. Experimental

### 2.1. Geological setting

The city of Ourense (Fig. 1) is located in the bottom of a hollow generated by the erosion produced by the Miño River and their main tributary rivers known as Barbaña and Lonia. This hollow is connected through steep slopes with a flat elevated plateau. Lithologically the city is situated on granite crystalline rocks covered by alluvial soils. Two groups of granite rocks are contacted by intrusion along both sides (North and South) of the Miño River. In the North side, there are peraluminous granite rocks with two micas and muscovites. This is the side where the thermal springs Chavasqueira, Tinteiro and Outariz are situated. In the South side, the granite material can be classified as calco-alkaline and subalkaline. In this area As Burgas spring is located.

The crystalline nature of these rocks with almost zero porosity determines that the hydrological circulation has place along their fractures, which make possible a deep circuit of percolation, storing and emergence of these spring waters. The fracturation has played an important role in the morphological development of the city valley, but not all fractures play the same role in thermal waters dynamics. A detailed analysis has made possible to associate thermal springs to N 120° E fractures, with compressive directions from NW to SE, which contribute to water circulation in such a direction.

### 2.2. Selected thermal water springs and sampling procedure

The city of Ourense (NW Spain) presents many points where springs and mineral–medicinal waters exist at present. The concentration of these points allows establishing three main areas of emission, as far as it can be seen in the map showed in Fig. 1. The chemistry of the four spring waters selected is summarized

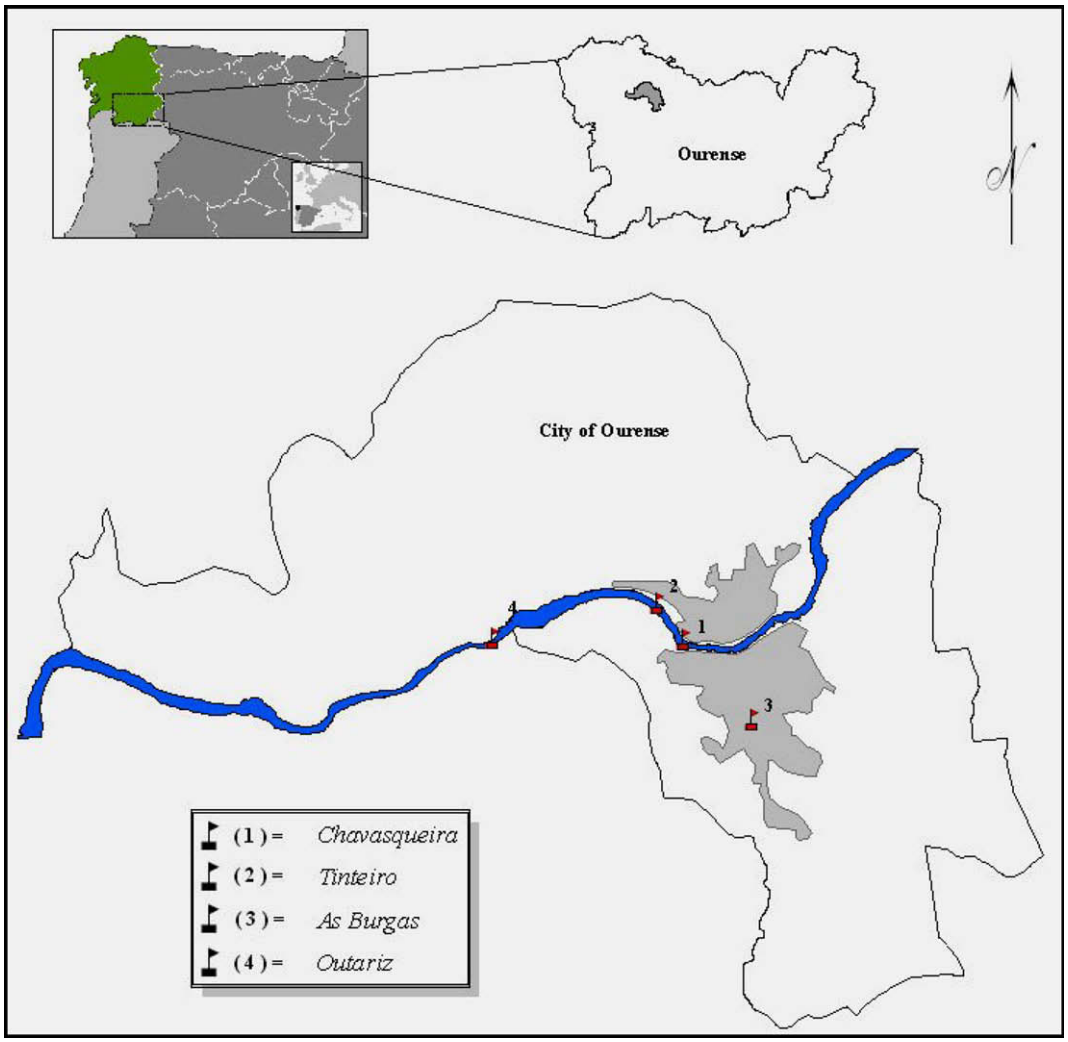


**Fig. 1.** Map of Ourense showing the location of the thermal springs.

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