



High-Temperature Liquid Chromatography Inductively Coupled Plasma Atomic Emission Spectrometry hyphenation for the combined organic and inorganic analysis of foodstuffs

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ABSTRACT

The coupling of a High-Temperature Liquid Chromatography system (HTLC) with an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) is reported for the first time. This hyphenation combines the separation efficiency of HTLC with the detection power of a simultaneous ICP-AES system and allows the combined determination of organic compound and metals. The effluents of the column were introduced into the spectrometer and the chromatograms for organic compounds were obtained by plotting the carbon emission signal at a characteristic wavelength versus time. As regards metals, they were determined by injecting a small sample volume between the exit of the column and the spectrometer and taking the emission intensity for each one of the elements simultaneously. Provided that in HTLC the effluents emerged at high temperatures, an aerosol was easily generated at the exit of the column. Therefore, the use of a pneumatic nebulizer as a component of a liquid sample introduction system in the ICP-AES could be avoided, thus reducing the peak dispersion and limits of detection by a factor of two. The fact that a hot liquid stream was nebulized made it necessary to use a thermostated spray chamber so as to avoid the plasma cooling as a cause of the excessive mass of solvent delivered to it. Due to the similarity in sample introduction, an Evaporative Light Scattering Detector (ELSD) was taken as a reference. Comparatively speaking, limits of detection were of the same order for both HTLC-ICP-AES and HTLC-ELSD, although the latter provided better results for some compounds (from 10 to 20 mg L⁻¹ and 5–10 mg L⁻¹, respectively). In contrast, the dynamic range for the new hyphenation was about two orders of magnitude wider. More importantly, HTLC-ICP-AES provided information about the content of both organic (glucose, sucrose, maltose and lactose at concentrations from roughly 10 to 400 mg L⁻¹) as well as inorganic (magnesium, calcium, sodium, zinc, potassium and boron at levels included within the 6–3000 mg L⁻¹) species. The new development was applied to the analysis of several food samples such as milk, cream, candy, isotonic beverage and beer. Good correlation was found between the data obtained for the two detectors used (*i.e.*, ICP-AES and ELSD).

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1. Introduction

High-Temperature Liquid Chromatography (HTLC) has emerged as a good alternative to High Performance Liquid Chromatography (HPLC) for the separation and determination of organic compounds [1–3]. A common HTLC system requires from a pre-heating conduction in which the temperature of the mobile phase is accommodated to that of the column in order to avoid temperature gradients during the separation step [4,5]. An additional component is the column heating unit. On this subject there are several

approaches such as the use of a Gas Chromatography (GC) oven [6], a heating tape [7] or a heating metallic body [8]. An obvious constraint of this technique is the stability of the stationary phase. Separation degradation caused by a deterioration of the column has been a subject of great concern. The development of new columns containing graphite [9], zirconia [10,11] or polymeric [12,13] stationary phases has renewed the interest on HTLC. As the mobile phase leaves the column at high temperature, a cooling system must be used in order to avoid both positive and negative effects on sensitivity [14].

One of the advantages of working in reversed phase at high temperatures is that pure water can be employed as mobile phase. Thus, from an environmental point of view, HTLC emerges as a “green” separation methodology. Moreover, the preparation is sim-

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plified and the cost of the mobile phase is severely depressed as compared with conventional reversed phase liquid chromatography (RPLC). From an analytical point of view, HTLC shows several important advantages over HPLC [15]: (i) shorter analysis times thus leading to narrower peaks and higher sensitivities in terms of peak height; (ii) improved efficiency and hence, resolution; and, (iii) possibility of using longer columns because of the decrease in the back-pressure. It could be stated that HTLC is especially efficient and suitable in those cases in which a few analytes must be separated.

An additional advantage of HTLC is that the number of detectors that can be adapted becomes larger than in HPLC. On this subject, HTLC has been adapted to detection techniques such as visible-UV spectrophotometry [16,9], fluorimetry [17], refractometry [19], Evaporative Light Scattering Detection (ELSD) [18,19], Flame Ionization Detection [20], Mass Spectrometer [21] and Nuclear Magnetic Resonance [22].

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is an elemental analysis technique that has enormously evolved in the last twenty years. This technique is currently used in routine analysis laboratories for the determination of trace metals in samples of different nature. In order to carry out the analysis, the liquid sample should be transformed into an aerosol. Then, a spray chamber is used to introduce only the finest aerosol droplets into the plasma where the different elements are atomized/ionized and further excited. The emission signal obtained at characteristic wavelengths is directly proportional to the analyte concentration in the sample [23]. In ICP-AES the sample introduction system plays a critical role, because it precludes the obtained analytical signal. In general terms, it can be stated that the finer the aerosol generated by the nebulizer the higher the mass of analyte delivered to the plasma and hence the higher the sensitivity. There are some studies that demonstrate the suitability of an ICP-AES as a HPLC detector for the determination of organic compounds [24]. This application implies the measurement of the signal at a carbon characteristic wavelength. The HPLC-ICP-AES hyphenation has been applied to the determination of aminoacids [25–27], saccharides [28,29], carboxylic acids and alcohols [30,31]. Advantages over conventional chromatographic detectors include: (i) better limits of detection for some organic compounds; (ii) wider dynamic ranges; (iii) universality for non-volatile compounds, since the carbon signal only depends on the carbon concentration and is independent of the carbon chemical form; and (iv) cleaner backgrounds. A drawback observed is that retention times are sometimes too long and, hence, the cost of the determination increases severely since the total argon flow under typical ICP-AES operating conditions is about 20 L/min. Therefore, the development of rapid separation methods is crucial to make this detector competitive in terms of analytical cost.

The determination of organic compounds by ICP-AES requires the use of mobile phases free of organic solvents. This later point fits perfectly with some applications and work done in HTLC. So far ICP-AES has not been used in conjunction with HTLC to determine organic compounds. Besides this, none of the detectors mentioned previously provides elemental information for inorganic species. The main goal of the present work was thus to develop a new HTLC-ICP-AES coupling for the simultaneous determination of carbohydrates and metals in food samples. Both groups of species are very important to control the quality and safety of foodstuffs [32]. In order to accomplish the proposed aim the interface between both techniques was studied and optimized so as to obtain the best separation efficiencies and analytical figures of merit. The results were compared against those provided by a conventional ELSD that, as in the case of ICP-AES, requires the sample to be transformed into an aerosol. The developed coupling was applied to the analysis of several food samples.

2. Experimental

2.1. Apparatus

Fig. 1 shows a schematic layout of the HTLC-ICP-AES system employed in the present work. A HPLC pump Model PU-2085 (Jasco Inc., Tokyo, Japan) was used throughout. Two valves (Mod. 7725(i), Rheodyne, USA) with 20 μ L loops were adapted. Valve 1 in Fig. 1 was used to inject the sample (or standards) for separating the organic compounds in the column. Valve 2 in turn was used to inject the sample (or standards) after the column for the determination of metals. In this way, the peaks obtained for the metals present in the sample were registered before the first organic compound left the column. The heating system consisted of a CG oven (GC-2014 Shimadzu, Kyoto, Japan). In the present work temperatures ranged from 70 to 175 °C. A 2 m length 1/16" id stainless steel capillary inserted into the oven was employed for mobile phase preheating. A 100 mm length 4 mm id column with 5 μ m graphitic carbon porous spherical particles was employed for the first time for the separation of carbohydrates (Hypercarb, Thermo electron corporation, UK) [33]. This column has been previously used for the determination of monosaccharides at temperatures below 60 °C using water as mobile phase [34].

An Optima 4300 DV Perkin-Elmer (Überlingen, Germany) ICP-AES system was used to simultaneously obtain the intensity at the wavelengths studied. Signals were axially taken, because of the increased sensitivity. This system was equipped with a 40.68 MHz free-running generator and a polychromator with an échelle grating. Two Segmented-array Charge-coupled Device (SCD) detectors allowed the simultaneous measurement of several lines in the UV and visible electromagnetic spectrum zones. The sampling time was set at 1.2 s so as a point was acquired every 1.75 s. This sampling time allowed to obtain from 15 to 20 points per peak. Under these conditions peak area RSDs were always lower than 5%. Table 1 summarizes the ICP-AES experimental conditions used. Carbon emission signal was registered for the determination of organic compounds. Additionally six metals were simultaneously determined (Table 1).

A glass pneumatic concentric nebulizer (Type TR-30-1A, Meinhard Glass Products, Santa Ana, CA) was employed to introduce the mobile phase into the ICP-AES system (Fig. 1). In a different approach, the aerosol was generated by thermostating the capillary at the exit of the column at a temperature close to that used for the separation (*i.e.*, from 150 to 220 °C). To achieve this, a heating tape and a temperature controller (JP Selecta, Barcelona, Spain) fitted to a thermocouple were used (Fig. 1B). These nebulizers were coupled to three different spray chambers. Two of them were of Cyclonic type [35] and the third one was a single pass device [36]. Their inner volumes were 44, 42 and 20 cm³, respectively. Cyclonic #1 and single pass spray chambers were home-made whereas Cyclonic #2 was purchased from Glass Expansion (Australia). The main difference among designs was related with the aerosol path inside the chambers and the dead volume. All three chambers were refrigerated with water at room temperature in order to lower the mass of vapor solvent reaching the plasma thus preventing the plasma cooling.

Table 1
Instrumental conditions for the ICP-AES spectrometer used.

RF power (kW)	1.35
Argon outer gas flow rate (L/min)	15
Argon intermediate gas flow rate (L/min)	0.2
Element/wavelength (nm)	C/193.090; Na/589.592; Ca/317.933; Zn/206.200; Mg/280.271; K/766.490; B/249.677

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