Innovative coupling of supercritical fluid extraction with ion mobility spectrometry

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ABSTRACT

This paper describes a pioneer on-line hyphenation between a supercritical fluid extraction (SFE) and an ion mobility spectrometry (IMS) detector through a Tenax TA sorbent trap as retention interface. By means of a simple design, taking advantage of both techniques, this new coupling allows us to extract and preconcentrate analytes and in a second step to determine them. As result, an increase in the accuracy of the analytical process was achieved by elimination of sample transfer from one device to another. In addition, this new coupling reduces the time needed for the optimization of a new SFE method, since the detector can monitor on-line the efficiency of the extraction.

The parameters affecting the coupling and its success have been studied in detail via the extraction of benzene and toluene from soil samples. Finally, the suitability of IMS as on-line detector to monitor compounds of industrial interest extracted by SFE was evaluated taking as a model, the extraction and detection of 1,8-cineole (eucalyptol) in rosemary aromatic plants, which could be extrapolated on an industrial scale.

1. Introduction

The supercritical fluid extraction (SFE) technique offers advantages as a separation technique due to the non-toxic nature of the most used fluid CO_2. Moreover, SFE is a versatile technique that allows the extraction of non-polar compounds due to the solvent properties of CO_2, which can be modified by the addition of a polar solvent such as methanol, ethanol and others. When a new SFE method is developed, the obtained extracts are usually recovered in a liquid solvent or in a solid trap. A solid-liquid phase collection or empty vessel trap collection may also be used [1]. Later, the extracts are usually analysed off-line with gas chromatography (GC), liquid chromatography (LC) or spectroscopic methods for quantification of the leaching yield. However, the analyte collection following SFE remains an important area for improvement due to problems related to collection temperature, fluid flow rate, extraction time, analyte volatility and so on, which hamper -and slow down the optimization of a good extraction method of SFE. In this situation, the direct monitoring of the extracts in real time by coupling the supercritical fluid extractor with the analytical detector provide

advantages such as: improvement of the recovery or extraction yield, reduction of sample manipulation avoiding errors related to this step [1], automatization and integration of sample pre-treatment step, reduction of risk of loss of thermolabile analytes which is beneficial for trace analysis, decrease of optimization and analysis times, costs and human participation. For all these benefits, the SFE device has already been on-line coupled to different analytical instrumentation [2–4]. Considering liquid phase separations, the SFE has been mainly coupled to LC [5–8]. In addition, the efficiency of on-line coupling with other techniques, such as capillary electrophoresis [9,10], or supercritical fluid chromatography [11–13], has also been successfully tested. In most cases, the coupling of SFE to the different instruments have been accomplished using laboratory-made programmable arm [9], continuous flow system [10], valves [13] or sorbent traps [11,12]. Furthermore, GC have also been on-line coupled to SFE [14] being the most common to connect the restrictor from the SFE directly with the inlet liner of the GC [14–17]. Additionally, the hyphenation of SFE-GC has been carried out using a sorbent trap and valve systems [18].

As a gas detector, ion mobility spectrometry (IMS) is emerging in

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the analytical chemistry field due to its potential to detect and monitor trace levels of volatile and semivolatile chemical compounds. This inexpensive tool is also characterized by its portability, ease of use and operation at atmospheric pressure, among other advantages [19]. One of the known bottlenecks of this technique is how to introduce volatile compounds. Until now, multiple strategies have been designed to overcome this problem, such as the use of permeation tubes, thermal desorption units or headspace samplers [20]. But their main disadvantage is that most of them must be handled manually, and this may imply a loss of robustness of the proposed analytical method.

In this article the advantages of SFE as a sample introduction system and the advantages of IMS as a powerful detector to monitor some target analytes extracted by SFE has been combined and studied for the first time. A successful environmentally-friendly hyphenation between both instruments, SFE and IMS, was carried out using a column filled with Tenax TA material as a sorbent trap to couple both devices. The proper and reliable functioning of the present new coupling was successfully demonstrated by analyzing toluene and benzene from soil sample, characterizing the methodology in terms of precision and sensitivity. Additionally, the utility of this new hyphenation to solve a real problem on an industrial scale was studied. The extraction of eucalyptol as a model bioactive compound [21] was chosen to demonstrate the usefulness of the coupling due to its beneficial properties [22,23]. Eucalyptol has also been previously extracted by SFE in plants or essential oils such as lavender, eucalyptus, tansy and coriander [24–26]. However, eucalyptol has been rarely determined by IMS, and its determination has been focused on breath [27]. In this work, rosemary plant was selected as an interesting sample due to its high content of eucalyptol [28,29].

2. Material and methods

2.1. Reagents, chemicals and samples

Benzene, toluene, ethylbenzene, (m-, p- and o-) xylenes (BTEX), eucalyptol (synonym: 1,8-cineole) and methanol used for standard preparations were obtained from Sigma Aldrich (St Louis, MO, USA). The Tenax TA porous polymer sorbent (2,6-diphenylene oxide) was purchased from Scientific Instrument Services (Ringoes, New Jersey, USA). Diatomaceous earth was obtained from Sigma Aldrich (St Louis, MO, USA). Purified nitrogen (N_2, 5.0) was provided by Abelló Linde (Barcelona, Spain). Ultrapure CO_2 (99.9%) in cylinder with a dip tube was supplied by Carburos Metálicos (Barcelona, Spain).

Soil samples were collected from the street. They were sieved in order to homogenize the sample, which means removing pebbles and rocks, and breaking up large soil aggregates.

Fresh rosemary (*Rosmarinus officinalis* L.) was purchased in a local market of the city of Córdoba, Spain. The plant was triturated using a stainless-steel grinder.

2.2. Instrumentation

2.2.1. Supercritical fluid extractor

All supercritical fluid extractions were performed using a modular Jasco SFE system (Tokyo, Japan) consisting of one pump model PU-2080 Plus used to supply the CO_2, a backpressure regulator (BPR) model BP-2080 Plus, and a CO-2060 Plus oven as extraction chamber to place a stainless-steel extraction cell of 5 mL (Análisis Vínicos, Tomelloso, Spain). Depending on the final purpose, a configuration for solid or liquid samples could be used.

The standard configuration of the device was modified using two Rheodyne 7000 L valves (Cotati, CA), V1 and V2, allowing to isolate the extraction cell between analyses, and the use of the static and dynamic extraction mode, respectively. The whole scheme is shown in Fig. 1. As a supercritical fluid, CO_2 pure was used. The SFE was controlled by ChromNav software (version 1.19.03).

2.2.2. Interface description

A direct SFE-IMS coupling was not possible for the following reasons: if the IMS device had been hyphenated before the BPR of the SFE, the high pressure originated in the SFE system could damage the drift tube of the IMS device. Moreover, if IMS detector had been coupled after BPR, instability of baseline would have been observed in the spectra. For these reasons, it was necessary to use a solid trap in order to adsorb and desorb the analytes before introducing them into the IMS device. Fig. 1 shows the interface (sorbent trap) designed for SFE-IMS, meeting this requirement.

1-g of solid Tenax TA, as sorbent trap, was placed into a stainless-steel tube of 250 mm length and 6 mm i.d. that was used as column, in order to adsorb and desorb the analytes. Glass wool was used in the extremes of the column to avoid the loss of the material. Before being used, the Tenax TA sorbent was activated in an oven at 250 °C by passing N_2 gas at a flow rate of 100 mL/min for 4 h [30].

In the experimental set-up, this column was placed in a chromatographic oven model 5890 supplied by HP Hewlett Packard (Minnesota, USA). The inlet part of the column was connected to the restrictor of the SFE device and the outlet part to the IMS detector (see Fig. 1), through a Rheodyne 6-port switching valve (V3) from Valco (Houston, Texas). All connections were made using 1/16″ o.d. x 0.010-in. i.d. stainless steel tubes (Sigma Aldrich). The temperature of the restrictor was controlled using a heat transfer jacket (Ramem, Madrid, Spain) in order to avoid condensation.

2.2.3. Ion mobility spectrometer

The IMS instrument with an ultraviolet lamp as a photoionization source was supplied by G.A.S. Gesellschaft für Analytische Sensorsysteme mbH (Dortmund, Germany). The instrument uses a 230 V/50–60 Hz power supply and a constant electrostatic field of 333 V/cm. In addition, the drift tube has a length of 12 cm and operates at room temperature and pressure. Purified nitrogen was used as sample and drift gas. Data obtained was processed with GASpector software (version 3.9.9.DSP from G.A.S.). The IMS method to detect a mixture of BTEX was previously described [30] and all spectra were recorded in the positive ion mode. The IMS operational parameters are summarized in Table 1. This same method was employed to detect eucalyptol.

2.3. Overall manifold and working procedure

The procedure to extract and determine analytes using SFE-IMS (Fig. 1) was divided into two steps: first the analytes were selectively extracted using SFE and adsorbed onto the sorbent trap, and as a second step. Thermal desorption and measurement by the IMS were carried out consecutively.

The sample was homogenised and placed in a 5 mL stainless steel extraction cell. Once the operational conditions of pressure and temperature were reached, CO_2 was passed through the system with a constant flow rate.

Under these conditions, the extraction of the analytes and the adsorption on the sorbent column was started (Fig. 1). At this point, the sample was extracted in the static mode during a certain time. Then valve V2 was switched to extract the analytes in the dynamic extraction mode until the extraction was completed. During this step, valve V3 allowed the analytes to reach the column placed in the oven set to a specific temperature, while N_2 was passing through the IMS device. The heat transfer jacket that covers the restrictor was also set at a certain temperature.

After the adsorption step, valve V3 was switched to desorption position to thermally desorb the analytes from the column enabling their simultaneous detection on the IMS. At the same time the extraction cell of SFE device was depressurized. The direction of the desorption of the analytes was the same as the direction in which they were adsorbed on the sorbent trap.