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Mass spectrometry/gas chromatography–mass spectrometry approach for rapid screening/quantitative determination of perchloroethylene in air

Pablo Richter[a,*], Carolina Zúñiga[a,b], Katia Calderón[b], Rodrigo Carrasco[b]

[a] Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, P.O. Box 233, Santiago, Chile
[b] Centro Nacional del Medio Ambiente (CENMA), Universidad de Chile, Av. Larraín 9975, La Reina, Santiago, Chile

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Abstract

A new mass spectrometry/gas chromatography–mass spectrometry (MS/GC–MS) approach has been developed for the screening and quantitative determination of perchloroethylene (PERC) in workplace and outdoor air samples, which could be extended to the screening and analysis of other analytes and samples. This approach may be rapidly modified in order to be used directly as an MS detector for screening purposes or alternatively as a common GC–MS, for confirmation. The screening alternative by MS is approximately 20 times faster than the quantitative-confirmatory determination by GC–MS. Detection limits of both alternatives are sufficiently low to screen and determine PERC in the above-mentioned matrixes. The advantage of this approach over others previously described is that, in the present case, the sample passes through the chromatographic column only when the confirmatory GC–MS is used. For the MS screening method, the chromatographic column is bypassed by using an appropriate selection valve. In this way, the column lifetime is extended and screening time is considerably shortened.

Keywords: Screening system; Mass spectrometry; GC–MS; Perchloroethylene; Air samples

1. Introduction

Perchloroethylene (PERC), also known as tetrachloroethylene, is a solvent commonly used in dry-cleaning operations. PERC enters the body when breathed in with contaminated air or when consumed with contaminated food or water. Once in the body, PERC can remain stored in fat tissue. This volatile compound is regulated as a hazardous air pollutant due to its toxicity. The OSHA method for determination of PERC in the workplace involves the use of adsorbent tubes for sample collection and GC-FID for sample analysis [1]. In the case of outdoor atmospheric samples, PERC as well as other VOCs are determined by the TO-14 United States Environmental Protection Agency (US-EPA) method [2], which involves sampling in canisters and GC–MS analysis.

The development of rapid screening methods is currently becoming significantly important in analytical chemistry. Conventional methods used in analytical laboratories are usually not compatible with the highly desirable routine and extensive monitoring. When timely decisions are made, the delivery of rapid analytical information, not necessarily possessing a high level of accuracy and precision, is highly appreciated. It must be stressed that screening approaches are not a substitute for but rather a complement to the reference conventional techniques [3,4].

In recent years, there has been an increasing demand for analysis of samples considering their volatile constituents. Mass spectrometry coupled to gas chromatography (GC–MS) has been the most widely used technique to study this type of pollution [5–8] but, as stated above, the development of nonseparative methods for the resolution and determination of different analytes is of great interest owing to their speed. Consequently, the direct coupling of mass spectrometry with methods such as solid-phase microextraction (SPME-MS) [9], or headspace (HS-MS) [10–15], has been developed for the analysis of raw materials and foods in the agrofood industry. These techniques provide “fingerprints” of the products under analysis, and the information, suitably processed by applying chemometric data treatment (such as hierarchical cluster analysis (HCA), linear discriminant analysis (LDA) and soft independent modeling class analogy (SIMCA)), can be used to differentiate such products.

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[*] Corresponding author. Fax: +56 2 678 2809.
E-mail address: prichter@ciq.uchile.cl (P. Richter).

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In the same context, a mass spectrometer coupled to a gas chromatograph can also be directly used as a screening system by keeping the column temperature at a level high enough to avoid chromatographic resolution of the target analytes [4]. Under these conditions, the MS provides a global signal, which can be differentiated on the basis of chemometric data treatment. This system provides the additional advantage that samples containing the analyte near an imposed threshold, or samples in which the presence of the analyte is doubtful, can be subjected in the same system to conventional gas chromatographic mass spectrometry detection for confirmatory purposes.

The aim of this study was to assess a new mass spectrometry/gas chromatography–mass spectrometry (MS/GC–MS) approach for the screening and quantitative determination of PERC and eventually other VOCs in air samples. In the present case, the sample passes through the chromatographic column only when the confirmatory GC–MS is used. For the MS screening method, the chromatographic column is bypassed by using an appropriate selection valve.

2. Experimental

2.1. Reagents

Perchloroethylene 99.9% (Supelco, Bellefonte, PA, USA, 48571) was used for calibration purposes in the determination of PERC in workplace samples. Working standards in the interval 1–100 ppm_v were prepared by dilution of this standard with helium in Tedlar bags (Supelco, Bellefonte, PA, USA, 24633).

A TO-14 standard (Supelco Bellefonte, PA, USA, 4-1902) was used directly as a quality control standard of workplace determinations. The same standard was used for calibration in the determination of VOCs in outdoor samples. Working standards in the interval 0.1–320 ppb_v were prepared by dilution of the TO-14 standard with helium in canisters.

Helium 5.0 UHP (AGA, Chile) was used as a diluting gas, as a carrier gas and also for the canister cleaning process.

Liquid nitrogen (AGA, Chile) was used for cold-trap preconcentration in outdoor sample analysis.

2.2. Instruments and apparatus

An autosampler (model 7016, Entech Instruments Inc., CA, USA) and a gastight syringe (Hamilton, Reno, NV, USA, 80600) were, respectively, used to inject the outdoor and workplace samples.

An air preconcentrator (model 7000, Entech Instruments Inc., CA, USA) was used in the analysis of outdoor samples.

Three-liter stainless steel canisters (Entech Instruments Inc., CA, USA) were used for sample collection and preparation of working standards starting form a TO-14 standard. The vacuum or pressure inside the canister during sampling was measured with a high-quality gauge on the canister (CS-1100, Entech Instruments Inc., CA, USA).

Analyses were conducted using a gas chromatograph Hewlett-Packard model 6890 HRGC coupled to a 5973 MSD, equipped with a 60 m DB-1 column (1 μm film thickness, 250 μm I.D., J&W Scientific Inc., CA, USA).

A 6-port selecting valve (Valco, Houston, TX, USA) was assembled in the upper part of the chromatograph (Fig. 1) in order to select subjecting the sample directly to MS (position 1) or to GC–MS (position 2). The transfer line connected to the 6-position valve was a 5 m fused silica capillary (250 μm I.D.).

2.3. Sampling

Workplace samples were taken inside 19 dry-cleaning shops located in the following sectors in eastern Santiago city: Lo Barnechea, Las Condes, Vitacura, Providencia, La Reina, Peñalolén, Ñuñoa, Macul, La Florida and Puente Alto. Two kinds of integrated samples were taken inside the 19 dry-cleaning shops:

(a) full period single sample measurement (one 8-h sample), and

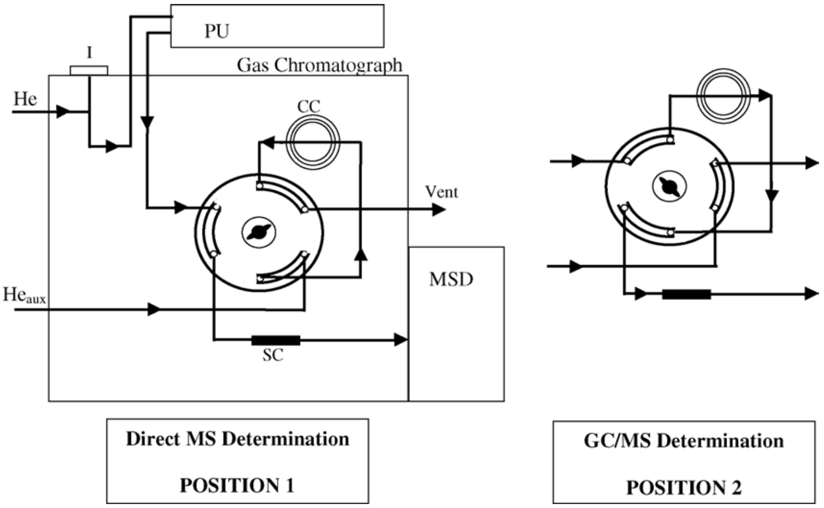

Fig. 1. Manifold for implementation of the method. PU, preconcentration unit; I, injector; CC, chromatographic column; He_{aux}, auxiliary helium gas; SC, silica capillary; MSD, mass selective detector.