Direct chromatographic methods in the context of green analytical chemistry

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We review analytical protocols based on gas and liquid chromatography (GC and LC), but involving no sample preparation. Green analytical chemistry seeks to minimize negative impacts of analytical chemistry. Direct analytical methods ideally fulfill this requirement, as they preclude sample preparation – the most polluting step of the analytical procedure.

We describe examples of GC methodologies for environmental and food analysis using on-column, programmed temperature vaporizers and injectors with sorbent-packed liners.

Although LC methods are less amenable to eliminating sample pretreatment, we also present some successful applications of direct LC methods in environmental and food analysis, and bioanalysis.

Keywords: Analytical protocol; Direct chromatographic method; Direct injection; Environmental analysis; Food analysis; Gas chromatography; Green analytical chemistry; Liquid chromatography; Vaporizer; Waste minimization

Abbreviations: APCI, Atmospheric pressure chemical ionization; BTEX, Benzene, toluene, ethylbenzene, xylenes; DAD, Diode-array detector; DAI, Direct aqueous injection; ECD, Electron-capture detector; EPA, Environmental Protection Agency; ETBE, Ethyl tert-butyl ether; FID, Flame-ionization detector; GAC, Green analytical chemistry; GC, Gas chromatography; LC, Liquid chromatography; LOD, Limit of detection; LVI, Large-volume injection; MS, Mass spectrometry; MTBE, Methyl tert-butyl ether; PTV, Programmed temperature vaporization; RSD, Relative standard deviation; SPME, Solid-phase microextraction; THMs, Trihalomethanes; VOX, Volatile organohalogen compounds; WHO, World Health Organization

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1. Introduction

Green analytical chemistry (GAC) is an aspect of green chemistry and of the concept of sustainable development. GAC focuses on reducing the environmental impact of analytical methodologies. There are several approaches to achieve this goal {e.g., green sample pretreatment [1], application of environmentally benign solvents and reagents [2], reducing the impact of chromatographic analysis by shortening chromatographic separation times [3], miniaturization of analytical devices [4], and management of analytical wastes [5]}. The idea of GAC is spreading in analytical laboratories and the need to make analytical chemistry greener is becoming more widely accepted.

Direct analytical techniques (i.e. without sample preparation) are particularly desirable from the GAC point of view. Such techniques include ion-selective electrodes, immunoassays, and some coulometric and spectroscopic methods. However, chromatography with various detection systems is frequently applied to environmental, industrial, biomedical and food analysis of organic compounds. Generally, chromatographic analysis requires sample pretreatment for the preconcentration of analytes and the removal of interferents. The great number of chromatographic analyses carried out and the potential to generate wastes during sample preparation make it desirable to introduce direct chromatographic methods.

We review direct chromatographic methodologies. We show that the sample-preparation step can be successfully omitted when performing gas or liquid chromatographic (GC or LC) analysis, making this greener. We compare the results obtained with direct chromatographic methodologies with those of some methodologies involving sample preparation.

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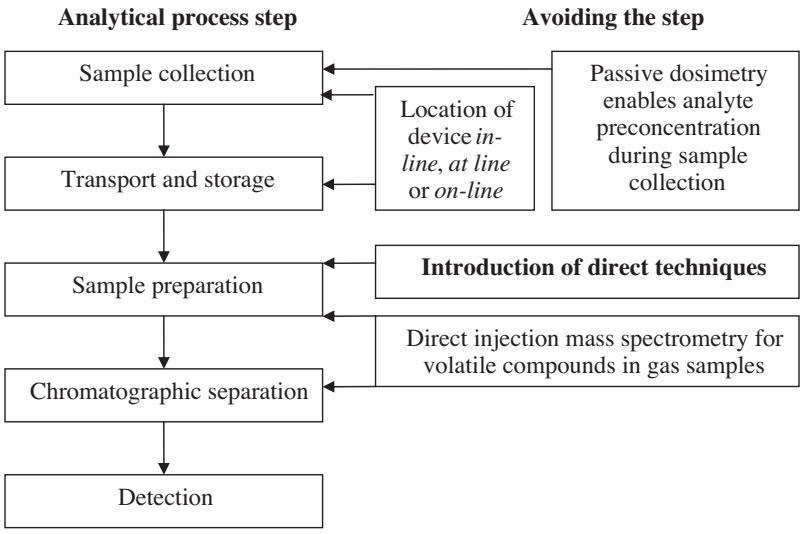

Figure 1. Steps in the determination of organic compounds and ways of avoiding particular steps of analysis.

2. The analytical process in the light of green chemistry

The analytical process usually comprises sample collection, transportation and storage, and then sample preparation and final analysis (see Fig. 1). Its role is to obtain reliable results from measurements of a given chemical species in a sample. During chemical analysis, some analytical wastes are produced [5]. It is the analytical chemist's responsibility to manage these wastes, or, following the principles of green chemistry, to prevent their production [6]. For example, by placing an analytical device in *in-line*, *on-line*, or *at-line* modes [4], the analysis can be performed without sample collection. With direct-injection mass spectrometry (MS), virtually all steps, except the final determination, can be omitted when volatile organics are determined in gaseous samples [7]. Determination of trace volatile analytes in complex gaseous mixtures is possible due to the high sensitivity and selectivity of recent mass spectrometers. Various systems have been developed for specific applications in environmental (particularly atmospheric) chemistry, plant chemistry, and food and industrial analysis.

The sample-preparation step is considered the most polluting in the analytical procedure [8], as it may involve the use of toxic chemicals and/or volatile solvents during operations mentioned in Fig. 2. Solvents used in analytical chemistry are high purity, and their manufacture requires more material and higher energy input than technical-grade solvents. Recently, much attention has been given to reducing the environmental hazards of sample-preparation techniques. Various extraction systems, based on miniaturized liquid-liquid extraction (LLE) [9], solid-phase extraction (SPE) and solid-phase microextraction (SPME) [10], headspace (HS) analysis, membrane techniques [11] or the use of alternative solvents [12], have been introduced. The National Environmental Methods Index (NEMI) defines the method as green if chemicals used in the procedure are not listed in the Toxic Release Inventory list as being persistent, bioaccumulative and toxic or being hazardous, the pH during analysis is within the 2–12 range and the amount of waste produced is less than 50 g [13]. According to this definition, the methods that we present are green. The application of direct chromatographic techniques is a step forward in reducing the environmental impact of chromatographic analyses.

3. Gas-chromatography techniques

The introduction of the sample (usually water but also water-ethanol mixture) directly into the chromatographic capillary column used not to be recommended. Water is considered to cause increased column bleeding, especially when polar stationary phases are applied, so a dense, non-polar column stationary phase and dense, polar, cross-linked phases are used. Recent developments in the quality of column stationary phases and novel methods of cross-linking have improved resistance to deterioration caused by water. The on-column introduction of environmental water may cause problems with column performance, especially when the water has high salt content, and may decrease detector sensitivity. Deactivated precolumns therefore have to be installed in front of the analytical column to prevent inorganic salts and organic non-volatile compounds from entering the column. The deactivated column also serves as a retention gap, which provides space for the