

Letter to Editor

Some Remarks on Gas Chromatographic Challenges in the Context of Green Analytical Chemistry

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Abstract

As researchers involved in chromatography for 30 years we would like to present three approaches of implementation of principles of green chemistry into gas chromatography.

Introduction

There is no doubt that our lives have been improved by chemistry. However, activities of chemists and chemical engineers, both in industry and in laboratories, can also adversely affect the quality of the natural environment. It is easy to find several environmental problems as familiar examples of chemistry gone wrong. The growing public concern over protecting our environment has led us to introduce regulations to limit pollution and exposure to hazardous chemicals and materials. Such a situation obligates the chemists to change the attitude to their activities. Generally, their work should link the design of chemical products and processes with their impacts on human health and the environment. In this respect the essential duties of the chemical community can be considered in two main directions:

- improving the level of pro-environmental awareness at all levels of training (schools, universities and industry), which should result in preparation of specialists capable of handling and solving common environmental problems,
- changing chemical activity into a such way that it will be conducted in an environmentally friendly manner.

Recently, a significant increase of such actions has been observed and the term *Green Chemistry* has been introduced to describe them [1]. Green chemistry encompasses all aspects and types of chemical processes that reduce negative impacts on human health and the

environment. Green chemistry standards have become alternatives to the traditional pollute-and-clean-up practice.

The activity of analytical chemists in laboratories, i.e. through uncontrolled disposal of chemical waste, used reagents, etc., may also exert (however to a lesser extent) a negative influence on the environment. Therefore, further development of green chemistry should also comprise the development of green analytical chemistry.

The specific principles of chemical practice related to sustainable development are summarized as the Twelve Principles of Green chemistry [2], proposed in 1998. They can be found elsewhere, for example at the home-page of the American Chemical Society (www.acs.org/education/greenchem/principles.html) or in the Journal of Chemical Education [3].

Considering these principles it is easy to indicate the directions which will decide about the "green" character of analytical chemistry [4]. The following should be treated as the top priorities:

- eliminating or minimizing the use of chemical reagents, particularly organic solvents, from analytical methods,
- eliminating from analytical procedures chemicals with high toxicity and ecotoxicity,
- reducing steps demanding much labor and energy, in particular analytical methods (per single analyte).
- reducing the impact of chemicals on human health.

Gas Chromatographic Challenges

The main demands for analysts using chromatographic methods wishing to implement the principles of green analytical chemistry are as follows:

- utilization - as much as possible - of so-called direct chromatographic analysis, which permits us to determine analytes in a sample without any pretreatment or sample preparation

- reduction of labor and energy consumption, e.g. reducing sample preparation time when direct chromatographic analysis is not possible

- elimination or reduction of the amount of solvent from sample preparation steps applied before final chromatographic analysis

- conducting all operations with solvents in a hermetic systems

- reducing matrix interferences

- reducing chromatographic run time

- reducing the need for reanalysis

- integration of steps of analytical procedures, i.e. by using hyphenated techniques.

Implementation of principles of green chemistry into gas chromatography can be performed in many ways. First of all, eliminating or minimizing the amount of solvent in sample preparation techniques before final chromatographic analysis is highly recommended. Therefore, techniques using gas and supercritical fluids for extraction of many pollutants are very popular. Also, the importance of fast chromatography, especially with field-portable instrumentation, is quickly gaining attention. Coupling of gas chromatography with techniques having high identification ability, e.g. with mass spectrometry, (GC/MS) has gained prominence because confirmation can be achieved in the same step as analysis with second dimension of information. This provides increased confidence in the result in conjunction with increased effectiveness.

Solventless Sample Preparation Techniques

Typical methods for sample preparation of different environmental samples usually involve liquid-liquid or liquid-solid extraction with an organic solvent often followed by clean up and preconcentration steps. These methods are time consuming and costly in the amount of solvent required. Greater concern over the disposal of usually toxic solvents and their impact on the environment has led towards cleaner extraction methods. Such methods are commonly described as solventless sample preparation techniques [5]. Three approaches are strongly recommended among these techniques, i.e. gas extraction and membrane-based techniques and supercritical fluid extraction.

Gas extraction techniques are the most widely used for isolation of volatile pollutants from different matrices, mainly due to the fact that they can be considered as proecological (solvent-free) methods of isolation and enrichment. Furthermore, most versions of these techniques provide the required sensitivity (up to ppt level)

and can be automated by connection with gas chromatography. Static and dynamic headspace techniques have frequently been used in practice during last ten years. One dynamic version, i.e. purge and trap (PT) is broadly recommended by the U.S. EPA and is widely accepted as the method of choice for routine analysis of volatile organic compounds in water. Static headspace microextraction is also becoming very popular mainly because it does not need such sophisticated instrumental construction as the PT technique. Recently, different membrane-based techniques, like membrane inlet mass spectrometry (MIMS) and purge-and membrane mass spectrometry (PAM MS) have also been proposed.

Supercritical fluid extraction (SFE) has many advantages over conventional extraction methods:

- it requires far less time to achieve extraction

- the solvent used, usually carbon dioxide, is non-toxic, available in high purity at low cost

- solvation characteristic of typical supercritical media can be altered by changing either the pressure or temperature of the fluid.

SFE, unlike conventional extraction techniques, does not require preconcentration steps and offers the possibility of eliminating clean-up steps often required in other extraction methods before detection. Supercritical fluids have become popular extraction media for different types of analytes from matrices like human and animal tissues, sediments, fly ash, sewage. As application ranges are being extended, interest in SFE is increasing.

Preconcentration of Pollutants Followed by Thermal Desorption

A standard method for the measurement of volatile organic compounds in workplace or environmental air involves sampling polluted air on a suitable sorbing agent, followed by recovery of the sample by solvent or thermal desorption [6].

Advantages of thermal desorption versus conventional solvent extraction include 1000-fold improvement in detection limits, no chromatographic interference from solvent or solvent impurities, enhanced sample throughput and lower cost per analysis. Another benefit is that thermal desorption is a very straightforward gas extraction process. Considering these advantages it can be stated that thermal desorption fulfills all requirements of introducing principles of green chemistry into chromatographic analysis. Its use in practice still becomes more popular also due to the fact that commercial systems are now available which meet all basic criteria and offer numerous features for simplifying and enhancing the operator's work.

High-Speed (fast) Gas Chromatography

Since the introduction of gas chromatography in 1952, there have been unceasing efforts to improve separation speed [7]. Reduction of overall analysis time provides

significant savings in time and money. The use of fast chromatography can be especially attractive for laboratories where many routine samples are analyzed on a daily base. It can also be beneficial in situations where a short time-to-result is needed.

The main routes toward faster separation include, amongst others:

- decreasing the inner diameter of the capillary columns
- fast temperature programming
- application of shorter columns
- working at turbulent flow
- vacuum outlet operation
- working above optimal carrier gas velocities.

Recently, high speed separation is performed on columns that consist of a bundle of 900-2000 microcapillaries of small (20-40 μm) internal diameter, referred to as polycapillary or microcapillary columns (MC). Such a bundle allows one to eliminate the deficiencies associated with the use of capillary and packed columns while the advantages of both are preserved. The use of these columns enables fast separation of large samples injected

and an exceptionally high range of velocities of the carrier gas at which the column retains its high efficiency.

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