Journal of Chromatography A, 1207 (2008) 1–16

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Review

Fast gas chromatography for pesticide residues analysis

Milena Dömötörová [a,b], Eva Matisová [a,*]

[a] Department of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 81237 Bratislava, Slovak Republic
[b] Department of Toxic Organic Pollutants, Slovak Medical University, Limbová 12, 833 03 Bratislava, Slovak Republic

ARTICLE INFO

Article history:
Received 3 June 2008
Received in revised form 7 August 2008
Accepted 11 August 2008
Available online 22 August 2008

Keywords:
Fast gas chromatography
Pesticide residue analysis
Multiresidue analysis

ABSTRACT

The importance of method development in the area of pesticide residues analysis is apparent from legislative requirements continuously decreasing the maximum acceptable concentration levels in food and water. This covers also contribution in the science in the field of ultra-trace analysis of organic pollutants in complex mixtures. Analysis time is one of the most important aspects that should be considered in the choice of analytical methods for routine application. With this fact, fast gas chromatography (GC) has acquired a real importance in the pesticide residue analysis. This paper provides an overview of fast GC methods for analysis of pesticide residues in variety of matrices at ultra-trace concentration levels. Emphasis is put on the development in the last 6 years.

Contents

1. Introduction

Pesticide is a general term that includes a variety of chemical and biological products used to kill or control pests such as rodents, insects, fungi and weeds [1]. Adverse effects on human health of pesticide residues remaining in food after they are applied to food crops are generally known: acute neurologic toxicity, chronic neurodevelopment impairment, possibly dysfunction of the immune, reproductive and endocrine systems or cancer and many other. In the European Union (EU) approximately 320,000 tonnes of active substances are sold every year, which accounts for one quarter of the world market [2].

Residues in fruit and vegetables, cereals, processed baby food and foodstuffs of animal origin are controlled through a system of statutory maximum residue limits (MRLs). MRLs are defined as: 'The maximum concentration of pesticide residue (expressed as milligrams of residue per kilogram of commodity (mg/kg)) likely to occur in or on food commodities and animal feeds after the use of pesticides according to good agricultural practice (GAP)' [3]. There are various organizations, that set MRLs, such as European Commision (EC), Codex Alimentarius or national governments in Australia, Canada, Japan, USA, etc. Individual limits for different active substance/food commodity combinations are being set. As an example around 30,000 different MRLs have been set by EC [4]. MRLs vary ordinarily within the interval 0.0008–50 mg/kg

* Corresponding author. Tel.: +421 2 5932 5283; fax: +421 2 5292 6043.
E-mail address: eva.matisova@stuba.sk (E. Matisová).

0021-9673/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2008.08.063

[5], typically between 0.01 and 10 mg/kg for adult population. The lower values of MRLs are set for baby food—EC specified the MRL of 0.010 mg/kg [6], the lowest levels are set for particular special residues [7]. In drinking water, the permissible maximum residue level in EU is 100 ng/L, in the case of some persistent chlorinated pesticides the limit is set to 30 ng/L [8]. Analysis close to these above-mentioned levels corresponds to the analysis at ultra-trace level. Scientifically valid methods of analysis at low concentration levels—currently still often very close to limits of quantification (LOQs) are essential for surveillance/compliance programs established with the terminal goal to minimize the hazards and the risks to health and achieving more sustainable use of pesticides.

The most efficient approach to pesticide analysis involves the use of chromatographic methods. Gas chromatography–mass spectrometry (GC–MS) with electron impact (EI) ionization and the combination of liquid chromatography (LC) with tandem mass spectrometers (LC–MS/MS) using electrospray ionization (ESI) are identified as techniques most often applied in multi-residue methods for pesticides at present [9]. For GC-amenable semivolatile pesticides GC methods are still preferred over LC methods due to higher resolution. Especially fast GC techniques satisfy the present-day demands on faster and cost-effective analysis. Although the foundations of faster GC were laid down already in 1960s, rapid development came up parallelly with perfection in chromatographic instrumentation together with data processing in 1990s. Nowadays, fast GC can be performed on commercial gas chromatographs, which are standardly equipped with high-speed injection systems, electronic gas pressure control, rapid oven heating/cooling and fast detection. Several reviews were published, which overview theory, methods, instrumentation and application of fast GC: practical fast GC [10], fast GC in trace analysis [11], fast GC with mass spectrometric (MS) detection [12], fast GC in food analysis [13]. Methods for analysis of pesticide residues are reviewed mainly from the point of view of sample preparation: in plant material [14], fruit and vegetables [15], residues in baby food [16].

This review starts with a brief general introduction to fast GC. Then the attention is devoted to the specificity of pesticide residues analysis as well as problems associated with analysis of pesticides in general. Some space is devoted to sample preparation mainly from the point of view of time requirements and feasibility for fast GC. The main part of the review is devoted to published papers applied to fast GC in the analysis of pesticide residues and they are classified according to the main GC speeding-up strategies. Examples of real-life analysis are also presented.

2. Fast GC

The primary objective of GC separation is to achieve the desired resolution of compounds of a given mixture in the shortest possible time. According to the classification of types of faster GC analyses the analysis time of fast GC is in minutes range, very fast GC in seconds and ultra fast GC in sub-seconds range [17]. The usual peak widths at half height are 0.2–3 s in fast GC, 30–200 ms in very fast GC and 5–30 ms in ultra-fast GC, which is due to its low efficiency not applicable in practice. Definitions based solely on run time miss the important aspects of peak separation and peak capacity [18], while the definition based on peak width takes into account separation power per time and therefore seams to be more reasonable. Speeding up GC analysis provides unquestionable benefits toward conventional GC, such as higher laboratory throughput, reduced GC operating costs, and better analytical precision by possibility of more replicate analyses. There is a number of ways to push the speed of capillary GC analysis faster, and they can be classified into three general routes toward faster GC separation [10,11]:

(a) minimization of the resolution to a value just sufficient (by reduction of the column length; usage of above optimum carrier gas velocity; higher isothermal temperature; higher initial/final temperature and higher temperature programming rates, or conversion of isothermal GC to temperature programmed GC; pressure/flow programming; columns with lower film thickness),
(b) maximization of the selectivity of the chromatographic system (by usage of more selective stationary phase or application of coupled columns, usage of two-dimensional (2D) GC), or detection (by predominant utilization of MS detection), and
(c) implementation of a method that reduces analysis time at constant resolution (by reduction of column inner diameter (I.D.), usage of hydrogen as carrier gas, application of vacuum-outlet conditions).

Approaches applied in fast GC of pesticide residues are discussed in detail individually as well as instrumental demands necessary for the used techniques.

3. Particularities and difficulties of pesticides analysis

All separate steps which build up whole chromatographic process: extraction, cleaning up, pre-concentration, injection, separation, detection, even data evaluation are adjusted according to the specific demands in the pesticide residues analysis. The two special essential requirements of pesticide residue analysis are the following: high sensitivity and multiresidual character of the method.

Continuous look for pesticides less persistent and toxic for the human being leads to increasing number of registered pesticides. At the same time less persistent pesticides are designed to decompose faster in order to lessen the possibility of accumulation in the soil and in living organisms. Together with the tendency to reduce the absolute amount of applied pesticides this leads to the continuous shift to the lower analyte concentration in a sample and thereby need for methods able to reach lower limits of detection (LODs) and LOQs.

According to the status list of all active pesticide substances on the EU market [5] more than 1100 pesticides are currently registered. These substances belong to more than 100 chemical classes. Benzoylureas, carbamates, organophosphorous compounds, pyrethroids, sulfonylureas, or triazines are the most important groups [9]. Analysis of pesticide residues covers also pesticide metabolites and degradation products. Multiresidual methods (MRMs) provide the capability of determining different pesticide residues in a single analysis. Multiresidue procedure deals with a wide variety of physico-chemical properties of pesticides of different chemical families. The choice of analyzed pesticides is oriented mainly towards actually produced and/or currently banned persistent registered and regulated pesticides as well as their important metabolities included in residue definition. Several extensive studies describe simultaneous determination of 118–300 residues [19–22]. Today MRMs able to analyze samples with an unknown or doubtful pesticide treatment history are increasingly needed. Most real-life samples analyzed in monitoring and enforcement programs have unknown history but the labs have been usually using targeted methods (SIM or MS/MS). Current trend is to use a non-targeted approach (full scan analysis) for data acquisition, even though the data processing is still targeted (based on a given list of residues).