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UV-MALDI mass spectrometric quantitation of uracil based pesticides in fruit soft drinks along with matrix effects evaluation



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ABSTRACT

This study focused on the development of the accurate and precise quantitative method for the determination of pesticides bromacil (1), terbacil (2), lenacil (3), butafenacil (4) and flupropacil (5) in fruit based soft drinks. Three different types of drinks are bought from market; huddled orange fruit drink (100%) (I), red-oranges (II) and multivitamin drink containing strawberry, orange, banana and maracuja (III). Samples were analyzed “with” and “without” pulp utilizing LC-ESI (or APCI) MS/MS, HPLC-ESI-(or APCI)-MS/MS and UV-MALDI-Orbitrap-MS methods. The effect of high complexity of the food matrix on the analysis was discussed. Study focuses on the advantages of the UV-MALDI-Orbitrap-MS method compared to the traditionally involved GC alone or hybrid methods such as GC-MS and LC-MS/MS for quantification of pesticides in water and soft drinks. The developed method included the techniques performed for validation, calibration and standardization. The target pesticides are widely used for the treatment of citrus fruits and pineapples, but for soft drink products, there are still no clear regulations on pesticide residues limits. The matrix effects in the analysis of fruit drinks required implementation of the exact standard reference material corresponds to the variety of food matrices. This paper contributed to the broad analytical implementation of the UV-MALDI-Orbitrap-MS method in the quality control and assessment programs for monitoring of pesticide contamination in fruit based sodas.

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Abbreviations: ANOVA, analysis of variance; AOELs, acceptable operator exposure levels; ADIs, Acceptable daily intake; APCI, atmospheric pressure chemical ionization (mass spectrometric method); B3LYP, Becke, three-parameter, Lee–Yang–Parr quantum chemical method (functional); B3PW91, quantum chemical method (functional); COZY, (homonuclear) correlation spectroscopy (NMR processing mode); DHA, 2,4-dihydroxy benzoic acid; DHB, 2,5-dihydroxy benzoic acid; ESI, electrospray ionization (mass spectrometric method); GC, gas-chromatography; GP, gas-phase; G, quartet–guanine quartet; Glu, glucose; Hex, hexose; HMBC, (heteronuclear) multibond correlation spectroscopy (NMR processing mode); HPLC, high performance liquid chromatography; HSQC, heteronuclear single quantum coherence (NMR processing mode); LODs, concentration limit of detection (analyte); LOQs, concentration limit of quantitation (analyte); LC, liquid chromatography; LMW, low molecular weight (analytes); McL, McLafferty rearrangement (mass spectrometric term); MLODs, concentration method detection limit (instrumental); MLOQs, concentration method quantitation limit (instrumental); MALDI, matrix/assisted laser desorption ionization (mass spectrometric method); MS, mass spectrometry; M06-2X, Meta hybrid GGA quantum chemical method (functional); MS/MS, mass spectrometry in a tandem mode of operation; NMR, nuclear magnetic resonance; PCM, polarizable continuum model (quantum chemical method); PO, polynomial order; RA, relative abundance; RTs, retention times; Suc, sucrose; TOF, time-of-flight (mass spectrometric method); UV, ultraviolet (irradiation)

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1. Introduction

The elaboration of highly precise analytical protocols for pesticide screening for environmental and foodstuffs monitoring purposes occupied a prominent position in quality control programs, due to widespread usage of pesticides in the agricultural practice. The maximum pesticide residue in variety of foods matrices, their metabolites and/or degradation products are strictly regulated, due to their neurotoxic and potentially carcinogenic effect (Zhu and Li, 2002; Kruithof and Martijn, 2013; Acher et al., 1994; Hapeman et al., 1997; Golan et al., 2012; Garcia-Reyes et al., 2008; Chen et al., 2011; Ouyang et al., 2013; Song et al., 2009, 2012; Gilbert-Lypez et al., 2010; Lavagnini et al., 2011; Liu et al., 2012). Attention is drawn to heavily consumed fruits, vegetables and drinking water. Particularly important are the studies on uracil-based pesticides, which were/are largely, used in agricultural practice for treatment of citrus fruit, but for which has no clear regulation. The application of European Directives for drinking water to fruit juices admissible maximum pesticide exposure ϵ 0.1–0.5 mg.L⁻¹ for entire amount of the contaminating chemicals (Verordnung (EG): 91/414/EEC/1991.07.15, 396/25.02.2005, 39/EU/06.22.2010). Considerable efforts have been resulted to development of analytical protocols for determination of pesticides in water and soft fruit drinks, based primarily on relative quantification. They widely involved chromatographic and variety of

hybrid methods. The non-polar pesticides are usually detected by GC, whether alone or in hybrid version GC–MS, while the polar ones—through the LC–MS/MS method. Recent reports on LC–TOF–MS revealed the perspectives of this method for control of pesticides in foodstuffs matrixes (Ibacez et al., 2011; Frycak et al., 2002; Perez-Bendito and Rubio, 1999). In all these studies, the evaluation of quality assurance is focused only on determination of overall error associated with “analytical measurements”. However for a reliable analytical quantitation of real analytical foodstuffs matrixes, the subdivision of different stages of control process and the evaluation of the errors at each of these stages are compulsory, because of (i) the complex foodstuffs matrix-effect difficult for the estimation of sampling bias. This is the most problematic component, due to the absence of exact standard (or certified) reference materials, representative to variety of foodstuffs matrixes. Usually as individual standards are employed the commercially available in high purity objects of interest such 1–4 (Scheme S1). In our study, the stock solutions of individual standards are prepared. Therefore, the rather lack of certificated reference materials altered the metrology, nevertheless of the precision and accuracy of the instrumental method used; (ii) the widely employed hybrid instrumentation may alter the systematic error of measurements, due to the strong dependence of the chromatographic separation of analyte mixture from the experimental conditions (Laurent et al., 1988; Karlsson et al., 2013). Therefore the common error of measurements for hybrid methods are determined by the chromatographic separation stage, due to the high precision of the MS measurements defined by the high (ultra-high) resolving power. Since often the complex foodstuff mixture and structural similarity of analytes caused overlapping of chromatographic peaks, the developments of methods for direct assay on the base only of the mass spectrometry are of emergency. The methodological MS developments, due to its instrumental flexibility, variety of ionization methods, and sample preparation techniques, enable the implementation of highly precise analytical protocols for direct assay, applicable to each type of foodstuffs matrixes, in homogeneous and heterogeneous phases. Therefore the generally great and robust advantages of the MS as the instrumental method may be employed at a maximal level, thus ensuring the meaningful analytical information at analyte concentrations to *attomol*, respectively. These characteristics of the variety of MS methods are beyond the capability of other widely distributed instrumental physical methods for foodstuffs analysis. Particularly the obtained method performance parameters are beyond ADIs and AOELs of studied pesticides of 0.12 and 0.4 mg kg⁻¹ bw day⁻¹ (Ibacez et al., 2011; Frycak et al., 2002). The shown concentration range is significantly higher for the MS concentration MLODs, involving all available ionization and detection methods. Particularly UV–MALDI–Orbitrap–MS methods have additional advantages consisted on its capability for direct assay of liquid, semi-liquid and solid-state samples, including imaging techniques for individual molecule distribution screening. It is characterized with ultra-high resolving power allowing direct assay of high complex analyte mixture without the sample pre-treatment steps such extraction, fast measurement time, and step limited number of sample preparation pre-treatments. The latter is associated with the preparation of the sample for physical measurements. These characteristics significantly improved the analytical method performance parameters towards systematic and random errors. It is worthy to note that for very complex analyte mixtures the chromatographic selectivity improvements have been performed. They utilized usually mixed stationary phases, tandem columns with different selectivity and column switching devices, respectively. However for analysis of halogenated pesticides such as **1**, **2**, **4** and **5**, the application of the complex switching columns decrease the selectivity and increased the measurement time and cost. For foodstuffs, where the pesticides have polar and non-polar properties, the column-type alters overall separation. The tandem usage of polar and non-polar columns

decreases the selectivity of polar column. This means however, that hybrid techniques can be counterproductive for the overall method performance parameters. Furthermore can fail the clear distinguish between structurally similar analytes such **1** and **2** in the presence of organic matrixes in heterogeneous systems such studied direct huddled fruit drinks with fruit pulp. It is important to note that the studied 100% drinks are relatively less complex than those products, containing 25–50 % fruit content, where have additionally foodstuffs common ingredients such additives as carbohydrates, vitamins, colorants, and more. The development of foodstuffs standards depends on the matrixes. It is a sole individual choice according to the nature of the monitoring problem. Therefore a variety of standard materials for pesticide assessment, representative to given foodstuffs matrix complexity, require a modeling and simulations of (a) sampling complexity and (b) testing of instrumentation diversity, thus establishing the factors, which most influenced the analytical data variability. For these reasons the study is focused on halogenated pesticides **1**, **2**, **4**, and **5** as well as non-halogenated derivative of same uracil-group substances, able to evaluate the advantages and limitations of traditionally utilized GC, GC–MS and LC–MS/MS methods for soft drink pesticide regulations (Moreno et al., 2008; Rasmussen and Minter 2013; Butz and Stan, 1995) as well as the sole application of UV–MALDI–MS one. Nevertheless that **1** and **2** are banned for Europa; their extensive application in few countries in the past still needs the meaningful analytical protocols for determination in water. Thus, in series of our on-going studies on the elaboration of highly precise analytical MS protocols for environmental and foodstuffs contamination assessment and analysis of drugs of abuse (Sukul et al., 2013; Ivanova and Spiteller, 2012, 2013b; Jaeger et al., 2013; Banerjee et al., 2007; Monkiedje and Spiteller, 2002; Hartmann et al., 1998; Spiteller, 1987, 1985, 2012), the LC–MS/MS, HPLC–ESI (or APCI)–MS/MS and/or UPLC–ESI (or APCI)–MS/MS methods are mainly utilized. For accurate quantitation of agricultural contaminations in waters, soils, and/or foodstuffs, the MALDI ionization method (Ivanova and Spiteller, 2013a, 2013b; Jaeger et al., 2013) as above shown has series of unique instrumental advantages. Its conceptually different quantitation procedure, than the routine one used in hybrid LC–MS/MS, HPLC–ESI (or APCI)–MS/MS and/or UPLC–ESI (or APCI)–MS/MS methods, however, need a systematic development. Therefore, the study ensures quality of analytical protocol and allows implementation of high quality analytical standard reference materials according to variety of the foodstuffs matrixes, particularly those for the soft drinks with pulp. The reported full validation assess the key method performance parameters such reproducibility, area ration of calibration standards of foodstuffs matrix analytes, accuracy, repeatability, representativeness and recovery, linearity, dynamic range and low concentration LODs of **1–5** that can be accurately quantified in the presence fruit pulp of **I–III**, respectively. The reported method performance parameters demonstrated additionally the advantages of UV–MALDI–MS versus variety of hybrid LC–MS/MS and GC–MS methods. In addition it allows direct pesticide quantitation in market products.

2. Experimental

2.1. Physical measurements

HPLC–MS/MS measurements are performed on TSQ 7000 instrument (Thermo Fisher Inc., Rockville, MD, USA), using mobile phase compositions 0.1% v/v aqueous HCOOH, 0.1% v/v HCOOH in CH₃CN or the same concentration of HCOOH in solvent mixture CH₃OH:CH₃CN (1:1) respectively. A triple quadrupole mass spectrometer (TSQ 7000 Thermo Electron, Dreieich, Germany) equipped with an ESI 2 source is employed as well. The operation conditions are: capillary temperature 180 °C; sheath gas 60 psi, corona 4.5 μA and spray voltage 4.5 kV. The dissolved sample in CH₃CN (1 mg mL⁻¹) is injected in ion

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