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English Version

**Food analysis - Determination of pesticide residues by LC-MS/MS - Tandem mass spectrometric parameters**

Analyse des produits alimentaires - Détermination des résidus de pesticides par CL-SM/SM - Paramètres de spectrométrie de masse en tandem

Lebensmitteluntersuchung - Bestimmung von Pestizidrückständen mit LC-MS/MS - Parameter für die Tandem-Massenspektrometrie

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## Foreword

This document (CEN/TR 15641:2007) has been prepared by Technical Committee CEN/TC 275 "Food analysis - Horizontal methods", the secretariat of which is held by DIN.

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## Introduction

Pesticide residue analysis employs multi methods involving extraction of residues from foods and clean up of the extract to obtain as many pesticide residues as possible in the purified extracts. Afterwards the extracts can be analysed by different kinds of instruments.

The hyphenation of liquid chromatography (LC) and tandem mass spectrometry (MS/MS) has become one of the most universal, but selective and sensitive analysis techniques for identification and quantification of pesticide residues in extracts of foods.

For the ionization of the analytes (M) in LC-MS/MS, electro spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) interfaces are most commonly used. Depending on the selected polarity of the ionization, protonated or deprotonated molecular ions like  $[M+H]^+$  or  $[M-H]^-$  are generated. Using ESI, relatively stable adducts (clusters) of the analytes (M) and components of the mobile phase like ions (e.g. ammonium, sodium or potassium ions) or solvent molecules (e.g. methanol) can be additionally formed. To obtain a high yield of quasi molecular ions and therefore to increase the sensitivity of the measurement these clusters have to be broken. When using ESI the formed adducts are accelerated by a potential (e.g. declustering potential or cone voltage) in the ion source at atmospheric pressure. Due to collision with neutral gas molecules the clusters (adducts) are broken in the ion source. Under certain conditions some adduct-ions formed are stable (e.g. with ammonium cation  $[M+NH_4]^+$ ). It should be mentioned, however, that ammonium adducts are usually not generated in the APCI-mode and that their formation when using ESI strongly depends on the concentration of ammonium ions in the LC mobile phase. Adduct ions like  $[M+NH_4]^+$  can also be used alternatively for quantification if they were shown to provide reproducible signals. Sodium adducts are usually not suitable for quantitative analysis as their formation and decomposition tends to be highly irreproducible.

The selective determination of each target compound is performed by acquisition of characteristic product ions of the precursor ion (quasi molecular ion or adduct) in the 'selected reaction monitoring' (SRM). Decomposition of the precursor ions in the collision cell is induced by collision with molecules of the collision gas (nitrogen or argon). The collision energy (CE) necessary for fragmentation is a very substantial parameter of the MS/MS optimization for maximum sensitivity.

If LC-MS/MS measurement should be used not only for quantification but also for confirmation of positive findings, at least two SRM transitions have to be recorded.

## 1 Scope

This Technical Report lists mass spectrometric parameters which are useful for the application of European Standards for the determination of pesticide residues in foods of plant origin that use LC-MS/MS, such as the standards in preparation:

prEN 15637 "Foods of plant origin — Determination of pesticide residues using LC-MS/MS following methanol extraction and clean up using diatomaceous earth"

prEN 15662 "Foods of plant origin — Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning by dispersive SPE — QuEChERS-method"

To facilitate the determination of active substances and/or metabolites using LC-MS/MS, Table 1 specifies the precursor ions and product ions suitable for quantification, which can be used independently of the type of triple quadrupole mass spectrometer. However, using an ion trap mass spectrometer other product ions can be generated or at least the relative intensities of the ions are different to triple quadrupole instruments. Furthermore, the additional parameters declustering potential (DP), collision energy (CE), relative retention times and an approximate classification of detection sensitivity are presented in Table 1. These were derived using the API 2000<sup>1)</sup> and should be applicable at least for other instruments of the API type (Applied Biosystems).

## 2 Analyte specific parameters for selective reaction monitoring of pesticides

### 2.1 General

All values indicated in Table 2 were acquired using the above mentioned LC-MS/MS system under the experimental conditions as outlined in 2.2. Comparative investigations showed that these parameters can be transferred simply on instruments of other types of the same manufacturer or after adjustment also on devices of other manufacturers (see in 2.3)

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<sup>1)</sup> Instruments of the API type are products supplied by Applied Biosystems (Foster City, CA, USA). This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.