Analytical methods for pesticide residues in rice

Lucía Pareja, A.R. Fernández-Alba, Verónica Cesio, Horacio Heinzen

Rice consumption has increased worldwide over recent decades, as it has become one of the most common foods. Although the analysis of environmental samples coming from rice areas has been well documented, there is less information regarding the analysis of pesticide residues in rice-grain samples.

Rice (paddy, brown and white) can be considered a complex matrix, leading to difficulties in the application of the different multiresidue methods described in the literature. This review addresses and compares the principal extraction and clean-up methodologies [e.g., liquid-liquid extraction, solid-phase extraction, pressurized-liquid extraction, QuEChERS (quick, easy, cheap, effective, rugged and safe), gel-permeation chromatography and supercritical-fluid extraction – with QuEChERS-based methods being the most frequently employed].

Traditionally, the determination of pesticide residues in rice has been based on gas chromatography with mass spectrometry (MS). But the application of new classes of pesticides has driven laboratories to increase the use of liquid chromatography with tandem MS. The limits of detection and quantification are in the ranges 0.09–90 μg/kg and 1–297 μg/kg, respectively, for the methodologies reported. These values agree with the current internationally-accepted maximum residue limits (MRLs).

Based on the European Union (EU) database, more than 3000 analyses of pesticide residues in rice have been performed by official EU laboratories over the past decade. Of these, 6% reported pesticide residues above the MRLs.

Physico-chemical properties can explain the occurrence of pesticides in rice commodities: lipophilic pesticides are frequently found in brown rice, whereas fungicides are mainly found in milled rice. Carbendazim, malathion, iprodione, tebuconazole, quinclorac and tricyclazole are the pesticides most frequently found in white rice, while buprofezin, hexaconazole, chlorpyrifos and edifenphos are most commonly found in paddy rice.

Pesticide-residue concentrations can be affected during rice processing – with concentrations generally lower in the final products. However, few studies focusing on primary processing have addressed the setting of precise values applicable for the processing factors.

Keywords: Chromatography; Extraction; Mass spectrometry; Maximum residue limit; Pesticide; Pesticide-residue analysis; Pesticide-residue occurrence; Processed rice; Rice; Sample treatment

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1. Introduction

Cereal crops comprise more than 60% of agricultural production worldwide. Among cereals, rice, wheat and corn are the three most important. Since 1990, harvested rice has expanded by about 0.4% a year, and the average yield of the crops increased by about 2% [1]. The increase in productivity per hectare is due to the development of a technological package that, with some differences from place to place, is universally applied. The basis of this methodology relies on the intensive use of agrochemicals (e.g., fertilizers, acaricides, insecticides, fungicides and herbicides).

Rice is an annual grass (Gramineae) that belongs to the genus *Oryza*, which includes 20 wild species and two cultivated species, *Oryza sativa* and *Oryza glaberrima*. *Oryza sativa* is grown all over the world while *Oryza glaberrima* has been cultivated in West Africa for the last ~3500 years [2]. Rice is grown under many different conditions and production systems, but submerged in water is the most common method used worldwide. Rice is harvested as a covered grain in which the kernel or endosperm is encased in a protective husk or hull [3]. The hull provides security against many insects and a barrier to reduce the rapid change in moisture content of the kernel when changes in humidity occur. Harvested rice is commonly known as rough or paddy rice and is 20% hull and 80% brown rice. The composition of brown rice is 3% bran,

 0165-9936/$ - see front matter © 2010 Published by Elsevier Ltd. doi:10.1016/j.trac.2010.12.001

4% germ layer (which gives brown rice its color) and 93% endosperm. The inside of the rice grain, hard and white, is generally called white rice. Table 1 shows the composition of brown rice [3].

After harvesting and drying, paddy rice is subjected to the primary milling operation which includes de-husking (hulling) as well as the removal of bran layers (polishing) before it is consumed. In this process, the rice obtained after hulling and milling is called raw rice, generally called polished or white rice. The process has to be accomplished with care to prevent excessive breakage of the kernel and to improve recovery of paddy white rice. At the processing plant, the rice is cleaned and hulled to obtain brown rice. If white rice is desired, the brown rice is milled to remove the outer bran layers. Three main types of rice are produced and marketed, paddy, brown and white rice, so we have to consider them from an analytical point of view.

During rice processing, different by-products are produced (e.g., husk, bran and broken rice), depending upon the rice mill [3,4]. These by-products are used as common ingredients in horticultural, livestock, industrial, household and food products [4]. The parboiled rice is produced from paddy rice, the rice being soaked and then steam cooked. This process does not allow the kernel to swell during cooking and the moisture level does not exceed 40%. The starch granule is cooked (technically gelatinized), but not allowed to swell. The rice is then dried while still in the paddy form and passed through a standard milling preprocess to remove hull and bran [5,6]. Fig. 1 shows the scheme for processing rice.

Rice is cultivated in a humid, temperate environment so fungi, insects and mites can affect its production. More than 70 insect species have been recorded as rice pests, and weed growth, which can be prolific, is one of the major constraints on crop yields causing seriously reduced production or even blocking it [7]. For these reasons, several kinds of pesticides, insecticides, fungicides and herbicides are used to prevent weed growth and to protect crops against pest damage. The types of pesticide used in rice crops depend on the country not only because the legislation but also because of the weather and the conditions of the production system which are important during the selection of the pesticides to be applied. Sometimes, due to bad agricultural practices while applying these chemicals [8], or different legislations between countries [9], residues of several pesticides can be found in rice, not only affecting the quality of rice but also threatening human health and the environment [8,10].

Good agricultural practices need to be applied when growing rice and controlling pests [8,11], so, in order to protect consumers' health, monitoring programs have been implemented for the determination of these chemicals in food [7,11,12].

Table 1. Composition of brown rice

	Protein (%)	Fiber (%)	Fat (%)	Starch (%)	Ash (%)	Others (%)
Endosperm	7.8	0.4	0.5	90.2	0.6	0.4
Bran	15.2	10.7	20.1	16	9.6	28.4
Germ	20.2	3.5	21.6	2.4	7.9	44.4

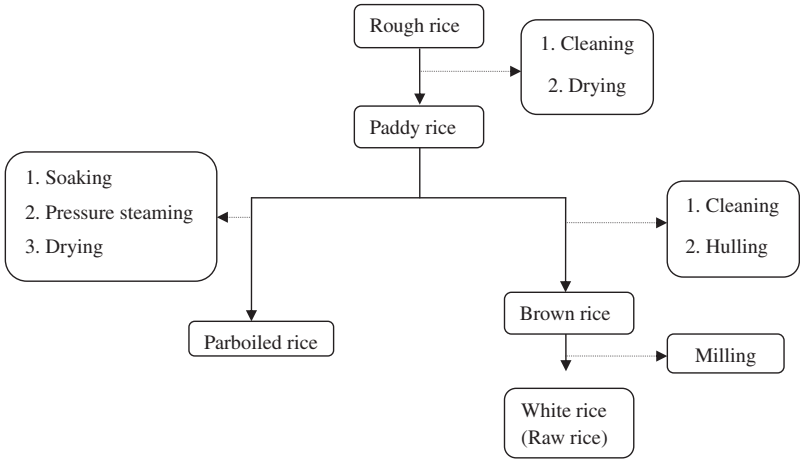

Figure 1. Scheme of rice processing.