Optimization of the operating conditions of solid sampling electrothermal vaporization coupled to inductively coupled plasma optical emission spectrometry for the sensitive direct analysis of powdered rice

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HIGHLIGHTS

- 4-mg aliquots of rice powder can be accurately analysed in 87 s by SS–ETV–ICP-OES.
- The total analysis time, including grinding, weighing and analysis is 5 min.
- As accurate results are directly obtained as with ICP-MS following acid digestion.
- Detection limits of 0.01–6 ng g^{-1} were achieved in the solid, depending on the element.
- Al, As, Co, Cu, Fe, Mg, Pb, Se and Zn levels in organic brown and white rice are reported.

GRAPHICAL ABSTRACT
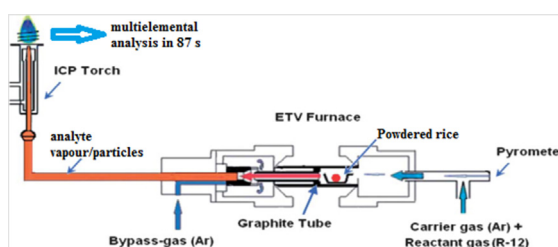
ABSTRACT

Two different approaches were used to improve the capabilities of solid sampling (SS) electrothermal vaporization (ETV) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) for the direct analysis of powdered rice. Firstly, a cooling step immediately before and after the vaporization step in the ETV temperature program resulted in a much sharper analyte signal peak. Secondly, point-by-point internal standardization with an Ar emission line significantly improved the linearity of calibration curves obtained with an increasing amount of rice flour certified reference material (CRM). Under the optimized conditions, detection limits ranged from 0.01 to 6 ng g^{-1} in the solid, depending on the element and wavelength selected. The method was validated through the quantitative analysis of corn bran and wheat flour CRMs. Application of the method to the multi-elemental analysis of 4-mg aliquots of real organic long grain rice (white and brown) also gave results for Al, As, Co, Cu, Fe, Mg, Se, Pb and Zn in agreement with those obtained by inductively coupled plasma mass spectrometry following acid digestion of 0.2-g aliquots. As the analysis takes roughly 5 min per sample (2.5 min for grinding, 0.5–1 min for weighing a 4-mg aliquot and 87 s for the ETV program), this approach shows great promise for fast screening of food samples.

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1. Introduction

With over 40,000 different varieties [1], rice, a semi-aquatic grass plant grown in every continent except for Antarctica [2], is a staple food for nearly 3 billion people [3]. Because of its exposure to both soil and water, rice can uptake several elements. Past studies have shown that the various varieties of rice can contain both toxic and essential elements. In particular, noticeable amounts of As, Cr, Pb, Se and V have been reported [4]. This is not surprising, as contamination of agricultural soils with several metals and metalloids can result from aerial deposition, industrial sewage tainting the water used for irrigation, the use of fertilizers and chemicals, etc. [5]. Several of these elements, including As, Cd, Cr, Hg, Pb and Ni, may be harmful to humans, as some of their chemical forms are either mutagens and/or carcinogens [6]. Over time, exposure to these mutagenic and/or carcinogenic species can thus lead to serious and lasting health effects. Ascertaining rice safety for human consumption is thus essential to prevent such health problems.

To determine if rice contains a potentially problematic level of toxic elements, various techniques have been used following acid digestion: flame atomic absorption spectrophotometry (AAS) [7], graphite furnace AAS (GFAAS) [8], inductively coupled plasma (ICP) optical emission spectrometry (OES) [7], ICP mass spectrometry (MS) [9,10] and/or total reflection X-ray fluorescence [7]. However, using a digestion method is time-consuming, in addition to necessitating dangerous chemicals [4,7–10] and potentially leading to contamination or analyte loss. Furthermore, the conventional nebulization system in ICP spectrometry introduces only 2–5% of the sample solution into the plasma, the rest going down the drain, which is quite wasteful [11]. For risk assessment purposes, a faster and greener analysis method would be beneficial.

Direct solid analysis would eliminate the digestion step altogether, along with any concurrent contamination or analyte loss as well as the dilution that is unavoidable following digestion. Solid sampling (SS) has been used for the analysis of rice in combination with GFAAS [12], instrumental neutron activation analysis (INAA) [7,8], laser-induced breakdown spectroscopy (LIBS) [13] and synchrotron-based confocal micro-X-ray fluorescence [14]. However, INAA and synchrotron-based techniques are not widely available, LIBS is not automated and GFAAS is not applicable to the simultaneous determination of numerous elements. One automated approach that is quick and simple, but has not yet been applied to the direct analysis of rice, is SS electrothermal vaporization (ETV) coupled to ICP-OES [15–17]. With SS–ETV–ICP-OES, the sample introduction efficiency is typically close to 80%

[16,18], which is a huge improvement compared to what is achieved with a conventional nebulization system. Furthermore, because only a few mg of sample are typically loaded onto graphite boats that are then placed in the furnace, many experiments can still be conducted when only a small sample size is available [19]. However, issues of representative sampling may arise with the use of such small aliquots. For instance, during past work on plant samples, the relative standard deviation (RSD) was as low as 3% [17] and as high as 34% [18]. While the analysis of rice products was carried out before by ETV–ICP-OES, slurry sampling [20,21] or an extraction [22,23] was first done, which involved additional steps, in turn decreasing sample throughput and increasing the sources of error. Only one study used SS–ETV for the analysis of rice but in combination with atomic fluorescence spectrometry [24].

Yet according to previous work done on the application of SS–ETV–ICP-OES to the analysis of a variety of samples, including some plants, close matrix-matching is not required for calibration, which may be done with aqueous solutions or using increasing amounts of CRMs, including graphite [25]; so, the approach should be applicable to the analysis of rice. The goals of this work were to optimize SS–ETV–ICP-OES for the fast, sensitive and accurate multi-elemental determination of both toxic and essential elements in powdered rice, and to demonstrate the accuracy of the approach for the analysis of organic long grain rice samples, through comparison with an independent approach: acid digestion followed by analysis by ICP-MS. The necessity of internal standardization with an Ar emission line was also checked, as a similar approach in ICP-MS, using Ar_2^+ as internal standard, could correct, in some cases, for the non-linearity induced by matrix effects in the analyte mass response curve [26]. Internal standardisation with an Ar emission line has been helpful for the accurate analysis of clays and soils by SS–ETV–ICP-OES [15], which are however more complex matrices than rice.

2. Experimental

2.1. Reagents

Three certified reference materials (CRMs) from the National Institute of Standards and Technology (NIST) were used: NIST 1568a Rice Flour for external calibration using increasing masses of CRM (i.e., 0.4, 0.8, 1.6, 2.0, 2.4, 2.8, 3.3 and 3.9 mg) to establish an 8-point calibration curve for the various analytes; NIST 8433 Corn Bran and NIST 8437 Hard Red Spring Wheat Flour as samples to

Table 1
SS–ETV–ICP-OES instrumental conditions.

ARCOS lateral view ICP-OES	
Plasma RF power (kW)	1.4
Ar plasma gas flow rate (L min^{-1})	13.00
Ar auxiliary gas flow rate (L min^{-1})	2.0
Signal scan mode	Transient
Sampling rate (Hz)	10
Integration time (ms)	10
ETV 4000C	
Ar carrier gas flow rate (L min^{-1})	0.3
Ar bypass gas flow rate (L min^{-1})	0.4
CCl$_2$F$_2$ reaction gas flow rate (mL min^{-1})	5

Temperature program	Furnace temperature (°C)	Time (s)
Initial	21	
Desolvation/pyrolysis	300	30
Cool down	21	10
Vaporization	2200	22
Cool down	21	15

Table 2
ICP-MS (Varian 820MS) operating conditions.

Parameter	Range of optimization	Optimal setting
Ar plasma gas flow rate (L min^{-1})		18.0
Ar auxiliary gas flow rate (L min^{-1})		1.75
Sample uptake rate (mL min^{-1})		0.8
Plasma RF power (kW)	1.3–1.5	1.4
Ar sheath gas flow rate (L min^{-1})	0–0.10	0.04
Ar aerosol carrier gas flow rate (L min^{-1})	0.7–1.2	1.0
H$_2$ CRI skimmer gas flow rate (mL min^{-1})	0–100	60
Sampling depth (mm)	5–7	6.4
Dwell time (ms)		10 ms
Monitored ions		^{24}Mg$^+$ ^{27}Al$^+$ ^{31}P$^+$ $^{32-34}$S$^+$ ^{39}K$^+$ ^{54,56,57}Fe$^+$ ^{59}Co$^+$ ^{55}Mn$^+$ ^{63,65}Cu$^+$ ^{66,68}Zn$^+$ ^{75}As$^+$ ^{76,78}Se$^+$ ^{110,111,114}Cd$^+$ $^{206-208}$Pb$^+$