



Statistical mixture design development of digestion methods for Oyster tissue using inductively coupled plasma optical emission spectrometry for the determination of metallic ions

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ARTICLE INFO

Article history:

Received 20 April 2009

Received in revised form 10 July 2009

Accepted 13 July 2009

Available online 21 July 2009

Keywords:

Statistical mixture design

Simplex centroid design

Biological samples

Metallic ions

Atomic emission spectrometry

ABSTRACT

The quantitative determination of chemical elements in organic or biological samples is an important analytical problem. Normally the elements to be determined in the organic matrix must be transformed into a simple inorganic form. A digestion method by heating on a block digester has been developed for the determination of Al, As, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, V and Zn in Oyster tissue by ICP OES. A simplex centroid statistical mixture design has been used to study the effects of changing HNO₃, HCl and H₂O₂ reagent proportions on the digestion of these samples. Response surface and principal component analyses show that the species Ca, Cd, Cu, Fe, Mg, Mn and Zn have very similar analytical tendencies under this experiment. By means of mixture modeling maximum recoveries for these ions were predicted using 19%, 18% and 63% of the HCl, HNO₃ and H₂O₂ pseudocomponent mixtures, respectively. This corresponds to 21.4%, 30.8% and 47.8% of the HCl, HNO₃ and H₂O₂ commercial solutions. Furthermore the As, Co and V ions present large recoveries for these mixtures as well. The Al and Ba ion recoveries are seen to be independent of the mixture proportions. The analysis of Oyster tissue reference material (SRM 1566b – NIST) under optimized conditions at the selected wavelengths resulted in ion recoveries between 90% and 100%.

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1. Introduction

Decomposition methods of biological samples are generally executed using two or more reagents because their different chemical properties can be exploited for the complete destruction of the organic material. Nitric and sulfuric acids, used individually or together with hydrogen peroxide are common digestion mediums. A reliable decomposition method that results in the complete solubilization of the biological sample while retaining the volatile components, reducing the contaminants, having low blank readings as well as an acceptable analytical frequency is one of the most critical steps of a spectrochemical analytical technique [1–4].

Biological materials rich in proteins and fats require high decomposition temperatures or the use of concentrated oxidizing mineral acid or a mixture of an oxidizing acid with hydrogen peroxide in open or closed systems with conventional or microwave heating [3].

Microwave (MW) radiation has become an analytical tool for sample decomposition. The use of high pressure flasks and oxidizing acids results in faster digestion permitting the processing

of a larger number of samples while eliminating losses of volatile species. This technique, however, is sensitive to several factors such as sample mass, acid type, reagent proportions, temperature, pressure and heating time. Different researchers have employed MW ovens or steel bombs for the digestion of biological materials although sample mass and acid volumes were as small as possible to avoid a very acidic final solution as well as for safety reasons.

In these solutions trace elements are preferably determined using mass spectrometry with inductively coupled plasma (ICP-MS) [5] or atomic absorption spectrometry with electrothermal atomization (ET AAS) [6–8] but atomic emission spectrometry [9,10] can also be used.

Some researchers describe the use of acidic or alkaline solubilization [11,12] in open systems [13–16], with larger sample masses and reagent volumes than those used in closed systems, for the determination of trace elements in addition to major elements, although these processes are slow and inadequate to determine volatile elements.

Based on the above considerations the objective of this study is to optimize mixtures of an oxidizing (HNO₃) and non-oxidizing (HCl) acids and an auxiliary oxidizing agent (H₂O₂) to determine macro- and micro-constituents in Oyster tissue using block digester heating under reflux (cold finger).

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Unfortunately the optimum mixture of these components cannot be determined from chemical principles or existing information. For this reason statistical mixture designs are employed in this work to determine the mixture proportions that result in maximum percentage recoveries of the 12 metals from the organic material by inductively coupled argon plasma optical emission spectrometry (ICP OES) [17–20]. These designs are especially appropriate for this study since they not only permit a determination of the linear blending properties of each solution but also the second and third order synergic and antagonistic interaction effects among the mixture components for each of the metallic elements investigated.

2. Experimental

2.1. Reagents and solutions

All the solutions were prepared with analytical reagent grade and ultra pure water, obtained by a Milli-Q system (Millipore, USA, with a conductivity of $0.054 \mu\text{S cm}^{-1}$). All the glassware and plastic flasks used were cleaned with a neutral detergent (5%, v/v), dilute nitric acid (10%, v/v for 24 h) and then with deionised water.

Multielement standards of Al, As, Ba, Ca, Cd, Co, Cu, Fe, Mg, Mn, V and Zn were prepared by dilution of $1000 \mu\text{g L}^{-1}$ standard solutions (Merck) of the elements. Analytical curves were made using the following concentrations of the analytes: (i) 0.5; 1.0; 2.0; 4.0; $6.0 \mu\text{g mL}^{-1}$ for Al, Cu and Fe; (ii) 0.02; 0.04; 0.10; 0.20; $0.40 \mu\text{g mL}^{-1}$ for As, Ba, Cd, Co, Mn, and V; (iii) 5.0; 10; 15; 20; $40 \mu\text{g mL}^{-1}$ for Ca, Mg and Zn.

2.2. Sample digestion

The solutions for each point of the mixture design were prepared weighing approximately $0.5000 \pm 0.0001 \text{ g}$ of reference material (SRM 1566b – NIST) in a digestion tube and adding volumes of 37% (v/v) HCl and 65% (v/v) HNO_3 , as listed in Table 1. The tubes were put in a TECNAL model TE 040/25 block digester. Cold finger condensers with water refrigeration were attached to the tubes. The system remained in operation overnight, at a temperature of 50°C . After this step 30% (w/v) H_2O_2 was added and the temperature gradually raised until about 140°C , with digestion occurring for 4 h at this temperature. After digestion the tubes were taken off the block digester and cooled to room temperature. The solutions were then transferred to a 25.0 mL volumetric flask with the volume being completed with ultra pure water [21]. The Al, As, Ba, Ca, Cd, Co, Cu, Fe, Mn, Mg, V and Zn concentrations were determined at the selected wavelengths shown in Table 2.

2.3. Statistical mixture design

Mixture properties are governed by reagent proportions and not by the total quantity of each reagent. The mixture proportions are

Table 2

Instrument operating conditions for the determination of metallic elements in Oyster tissue (SRM 1566b-NIST).

Sample flow rate (mL min^{-1})	1.0
Radio frequency power (kW)	1.4
Principal argon flow rate (L min^{-1})	15
Auxiliary argon flow rate (L min^{-1})	0.5
Nebulization flow rate (L min^{-1})	0.6
Read delay (s)	30
Auto integration (s, min.–max.)	1–5
Radial observation height (mm)	15
Replicates	3
Wavelengths (nm)	Al I: 396.152; As I: 188.977; Ba II: 455.403; Ca II: 315.887; Cd II: 226.502; Co II: 228.616; Cu I: 324.754; Fe II: 238.204; Mg II: 279.077; Mn II: 257.610; V II: 292.402; Zn I: 213.856;
Background correction	2 points

not independent of one another since

$$f_{\text{HCl}} + f_{\text{HNO}_3} + f_{\text{H}_2\text{O}_2} = 1$$

where the f values are the volume fractions of the commercial grade acids. Since digestion is not recommended using pure acid or peroxide solutions only ternary mixtures of these solvents were investigated. To facilitate the statistical interpretation of the mixture models the component proportions were converted to pseudocomponents using the usual equation:

$$x_i = \frac{f_i - L_i}{1 - \sum L_i}$$

where L_i are the lower limits of the proportions of the components used in the mixture design, and f_i are the volume proportions. The subscript i represents HCl, HNO_3 and H_2O_2 . The volumes of HCl, HNO_3 and H_2O_2 solutions used to make the mixtures and the corresponding pseudocomponent values are included in Table 1. Fig. 1 shows the compositions of the 10 mixtures investigated here. The vertices correspond to the pseudocomponent mixtures of the commercial solutions: (1) 10% HCl, 20% HNO_3 and 70% H_2O_2 , (2) 70% HCl, 10% H_2O_2 and 20% HNO_3 and (3) 10% HCl, 10% H_2O_2 and 80% HNO_3 . Since the pseudocomponents are linearly related to the volume proportions, model interpretation in terms of pseudocomponents is easily converted into laboratory values.

Mixture models are determined for each of the metallic ions being analyzed. The recovery value for each ion, y , is expressed as a function of the mixture pseudocomponents by linear, quadratic and special cubic models incorporated in the equation:

$$y = b_{\text{HCl}}x_{\text{HCl}} + b_{\text{HNO}_3}x_{\text{HNO}_3} + b_{\text{H}_2\text{O}_2}x_{\text{H}_2\text{O}_2} + b_{\text{HCl-HNO}_3}x_{\text{HCl}}x_{\text{HNO}_3} + b_{\text{HCl-H}_2\text{O}_2}x_{\text{HCl}}x_{\text{H}_2\text{O}_2} + b_{\text{HNO}_3-\text{H}_2\text{O}_2}x_{\text{HNO}_3}x_{\text{H}_2\text{O}_2} + b_{\text{HCl-HNO}_3-\text{H}_2\text{O}_2}x_{\text{HCl}}x_{\text{HNO}_3}x_{\text{H}_2\text{O}_2} + e$$

Table 1

Volume proportions and pseudocomponent values for the mixtures of the statistical design shown in Fig. 1.

Mixture	V_{HCl}	V_{HNO_3}	$V_{\text{H}_2\text{O}_2}$	x_{HCl}	x_{HNO_3}	$x_{\text{H}_2\text{O}_2}$
1,11	3.0	1.0	1.0	0.8333	0	0.1667
2,12	0.5	4.0	0.5	0	1	0
3,13	1.0	1.0	3.0	0.1667	0	0.8333
4,14	0.5	2.3	2.2	0	0.4167	0.5833
5,15	2.2	2.3	0.5	0.5833	0.4167	0
6,16	2.0	1.0	2.0	0.5	0	0.5
7,17	1.6	1.7	1.7	0.3888	0.2222	0.3888
8,18	2.8	1.1	1.1	0.7777	0.0283	0.1950
9,19	1.1	2.8	1.1	0.1950	0.6117	0.1950
10,20	1.1	1.1	2.8	0.1950	0.0283	0.7777

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