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Tu31 COMPARATIVE STUDY OF THE ANALYTICAL CHARACTERISTICS OF THREE RESINS MODIFIED WITH CHELATING AGENTS FOR THE PRE-CONCENTRATION OF METALS IN NATURAL WATERS. Margarita Villanueva, Faculty of Chemistry, University of Havana, Zapata and G, El Vedado, C.P 10400 Havana, Cuba, villa@fq.uh.cu; Bárbara Luna, Ramón Pomés, National Center of Scientific Researches, C. P. 6414, Havana, Cuba; Yoelis Rodríguez, Center of Miner and Metallurgical Researches, Havana, Cuba; Mario Pomares, Institute of Material and Reactives, University of Havana, Cuba, and Alfredo Sanz Medel, Faculty of Chemistry, University of Oviedo, Julian Clavería No. 8, Oviedo, Asturias, Spain

The importance of the determination of trace metal concentrations in natural water samples is increasing in contamination monitoring studies. Because of extremely low concentrations of metals, a preliminary concentration step is usually necessary before their determination. For this purpose, various pre-concentration/separation methods have been widely used.

In recent years, solid phase extraction technique with column has found increasing application for the preconcentration of trace metal ions and reduction of matrix interferences. The resins are modified with different functional groups, which improve the selectivity for the separation and pre-concentration of elements in complex matrix or for the analysis of a large sample volume. This technique has been combined with flow analysis and flow-injection analysis [1-5]. In this work, a comparative study of the analytical characteristics of three resins modified with chelating agents for the pre-concentration of Cd, Cu, Pb, Ni, Zn and their determination in natural waters with atomic spectroscopy was developed.

Three columns packed with three different chelating resins were investigated. The dimensions of the columns were 4 cm of length and 3 mm of inner diameter (Omni firm). The selected systems were Diethyldithiocarbamate-C₁₈, Kelex 100[7-(4-ethyl-1-methyloctyl-8-hydroxyquinoline)]-C₁₈, TSK Toyopearl (8-hydroxyquinoline immobilized on a vinyl copolymer). "Off-line" and "on-line" experiments were developed. A simple flow-injection system was used for the "on-line" experiment. Flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS) were used for the optimization of sorption parameters and final determination, respectively.

The effects of concentration and volume of eluent; pH of the solution, sample volume and the sampling and elution rates on the chelation process were studied. Application of these materials for the pre-concentration and removal of metal ions from natural waters was also described. The analytical performance of the three chelating resins and the type of modification produced during their preparation were compared. Finally, the results demonstrated that TSK resin was the best one for quantitative recuperation of all elements.

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Tu34 ACID VAPOR PARTIAL DIGESTION OF BIOLOGICAL SAMPLES IN A FOCUSED MICROWAVE: MULTI-ELEMENT DETERMINATION BY ICP OES WITH AXIALLY-VIEWED CONFIGURATION. Lilian C. Trevizan, Ana Rita A. Nogueira*, and Joaquim A. Nóbrega, Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, São Carlos, SP, 13560-970, Brasil, djan@terra.com.br, *Embrapa Pecuária Sudeste, São Carlos, SP, Brasil

Sample preparation is an important step before instrumental measurements. Emphasis has been placed on the development of fast and contamination-free methods for determination of trace elements. Vapor-phase partial digestion is an alternative procedure for sample preparation, which allows the simultaneous purification of the acid, reduces the risk of contamination and improves detection limits by reducing analytical blanks. In this work, an acid vapor partial digestion method was proposed using a focused microwave oven (STAR-System 6, CEM, NC, USA) operating at atmospheric pressure. A laboratory-made PTFE support vessel equipped with four sample cups was adapted to fit on the microwave glass vessel. Method accuracy was checked by using bovine liver certified reference material (NIST 1577b, MD, USA). Samples were directly weighed (50 mg) into PTFE cups followed by addition of 150 µl H₂O₂. The mixture was exposed during 25 min to acid vapor steaming from 15 ml of concentrated HNO₃ placed in the bottom of the glass vessel. The acid vapor was generated at 115°C. The resulting suspension was diluted with 0.14 mol l⁻¹ sub-boiled HNO₃ to a final volume of 3 ml. Aluminum, Cu, Fe, Mg, Mn, Zn, and the residual carbon content (RCC) were determined by inductively coupled plasma optical emission spectrometry (VISTA AX, Varian, Australia) with axially-viewed configuration. Table 1 shows the results obtained with the proposed method.

Table 1. Determination of Al, Cu, Fe, Mg, Mn and Zn (mg kg⁻¹) in bovine liver (n = 3)

Element	Certified	Determined
Al	3*	1.45 ± 0.28
Cu	160 ± 8	140 ± 12
Fe	184 ± 15	117 ± 26
Mg	601 ± 28	540 ± 7
Mn	10.5 ± 1.7	8.48 ± 0.11
Zn	127 ± 16	117 ± 6

* non-certified value

Except for Al, element recoveries were between 64% and 111% and RCC's in the digestates were 25 ± 5% (n = 3). As an additional advantage of the proposed method, up

to 24 samples can be simultaneously prepared when using a 6-cavity focused microwave.

Tu35 EFFECT OF NITRIC ACID CONCENTRATION ON CLOSED-VESSEL MICROWAVE-ASSISTED DIGESTION OF PLANT MATERIALS. Geórgia C.L. Araújo*, Mário H. Gonzalez*, Ana Rita A. Nogueira*, and Joaquim A. Nóbrega, Grupo de Análise Instrumental Aplicada, Departamento de Química, Universidade Federal de São Carlos, São Carlos, SP, Brasil, anarita@cnpse.embrapa.br; * Embrapa Pecuária Sudeste, Caixa Postal 339, 13560-970, São Carlos, SP, Brasil

An ideal sample digestion procedure should be fast and generate digestates with physical and chemical characteristics compatible with the analytical technique used for analytes measurement. Frequently aggressive conditions are adopted to reach quantitative decomposition of organic compounds in plant materials. At high temperature and pressure in a closed vessel microwave-assisted procedure severe reaction conditions can be attained without using an elevated amount of oxidant acids. Most works described in the literature did not investigate systematically this possibility and thus there is room to improve microwave-assisted procedures considering the amounts of acids employed and the consequent acid concentration of the digestates. The study developed dealt with the closed vessel microwave-assisted digestion of four species of *Paspalum* genera, a native Brazilian forage used for bovine feeding, using a combination of nitric acid and hydrogen peroxide. All experiments were performed employing an Ethos 1600 microwave system (Milestone, Germany) equipped with 10 PFA fluoropolymer closed vessels, and with pressure and optical fiber temperature sensors. The effect of nitric acid concentration on digestion efficiency was tested for solutions (2.0 mL) containing 2.0, 3.0, 5.0, 7.0, and 14 mol L⁻¹ plus 1 mL of hydrogen peroxide (30% v v⁻¹). All experiments were carried out using a 5-step heating program with the maximum temperature set at 240°C. Subsequently, five heating programs with different temperatures were evaluated by keeping the acid concentration at 2.0 mol L⁻¹. The digestion efficiency was assessed by determining residual carbon content (RCC), Al, Ba, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn by inductively coupled plasma optical emission spectrometry with an axial-view configuration (Vista, Varian, Australia). The obtained results did not indicate any pronounced effect of acid concentration on RCC, which varied from 5 to 15 mg L⁻¹. The analytes were accurately determined without any appreciable effect caused by RCC on emission intensities. It can be concluded that *Paspalum* can be efficiently digested using diluted nitric acid solution in spite of its original carbon content around 45% m m⁻¹. In all experimental conditions adopted the temperature- and pressure-digestion time curves showed the same profiles indicating that different acid concentrations were effective to generate proper conditions when used in closed vessels heated by microwave radiation. The remaining acid concentration in the digestates before diluting varied from 1.6 to 5.6 mol L⁻¹ depending on the acid concentration of the digestion solution.

Tu38 ELEMENTAL ANALYSIS OF BIOLOGICAL SAMPLES BY ICP OES AFTER COMBUSTION IN AN OXYGEN BOMB. Gilberto B. Souza*, Instituto de Química

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Combustion with oxygen in a sealed bomb has been used to convert solid and liquid combustible samples into soluble forms for chemical analysis [1-2]. In this system, the organic matter is oxidized to carbon dioxide and water during combustion and the volatile components formed by burning are trapped in an absorption solution. An oxygen combustion bomb-ion chromatography method was applied for elemental analysis in organic compounds, fuel and hazardous wastes with indirect photometric detection [3-4]. In the present work, a rapid sample preparation method is proposed for decomposition of milk powder, bovine tissues, and plant materials containing certified contents of the analytes. The combustion was carried out in a commercial ParrTM stainless steel oxygen bomb (300 mL) at an oxygen pressure of 25 atm. The bomb was fired via an electrical discharge through a platinum wire, which was placed in a stainless steel capsule containing the sample (500 mg). Most of the samples were decomposed within 5 min, including a cooling step. A water-soluble tertiary amine 10% v/v solution (CFA-C) was used as absorption medium and the inorganic elements Ca, K, Mg, Na, P, S, and Zn were recovered with the bomb washings and determined in a simultaneous inductively coupled plasma optical emission spectrometer (ICP OES, Vista, Varian) with radial view configuration. The ICP OES was operated with a concentric nebulizer coupled to a cyclone type nebulization chamber. Most of the elements recoveries in the samples were between 95 and 100% and the certified and found contents exhibited a fair agreement at a 95% confidence level. The procedure was extended for determining iodine in milk samples spiked with potassium iodide prior combustion. The goal was to evaluate the volatilization and collection of iodine in CFA-C medium and its determination by ICP OES with axial view configuration (I 182.978 nm). All recoveries were around 95-105% and the instrumental detection limit was 1.5 mg L⁻¹. The combustion procedure is rapidly applied and for an element as iodine any losses caused by volatilization in open systems and any undesirable effect caused by acid medium are avoided.

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Th01 INORGANIC FINGERPRINTING OF CRUDE OILS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Teresa C.O. da Fonseca, *Petrobras Research Center (CENPES), 21949-900 Rio de Janeiro, Brazil, tcris@cenpes.petrobras.com.br; Norbert Miekeley, Carmem L. Porto da Silveira, Department of Chemistry,