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Concentration of Total Al, Cr, Cu, Fe, Hg, Na, Pb, and Zn in Commercial Canned Seafood Determined by Atomic Spectrometric Means after Mineralization by Microwave Heating

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The concentration of total Al, Cr, Cu, Fe, Hg, Na, Pb, and Zn in commercial canned seafoods (tuna, sardine, jurel, ark clams, mejillons, and common cockles) frequently consumed by the Venezuelan population was spectrometrically evaluated. Flame atomic absorption spectrometry (Fe and Zn), flame atomic emission spectrometry (Na), cold vapor atomic absorption spectrometry (Hg), and electrothermal atomization atomic absorption spectrometry (Al, Cr, Cu, and Pb) were the techniques of choice. Before spectrometric analysis, samples were mineralized by microwave heating, using either Parr-type high-pressure bombs (for Hg and Pb only) or closed vessels with pressure relief valves (for the other metals). Recoveries (95–105%), precision studies (RSD < 3%), and analyses of NIST and NIES standard reference materials demonstrated the reliability and accuracy of the analytical methodologies employed in this study. Metal concentrations were higher in mollusks (edible portion) than in fish (muscle tissue), because bivalves bioconcentrate metals in their tissues. Common cockles showed higher concentrations (μg/g of dry weight) of Al (1168 ± 175), Cu (4.0 ± 0.2), Fe (1117 ± 26), Na (35.9 ± 1.2 mg/g), and Pb (1.3 ± 0.1). Mejillons presented the highest Zn concentration (191 ± 23 μg/g), while the highest Cr was found in ark clams (1.2 ± 0.3 μg/g). Two brands of Venezuelan canned tuna showed Hg concentrations (μg/g) ranging from 1.1 to 1.4, above the Action Level of 1 μg/g of Hg set by the FDA. These data can be used for referential purposes to judge and control the quality and safety of this type of food.

INTRODUCTION

Industrial processes have resulted in an increased concentration of metals in water. These metals may be taken up by marine fauna and make their way into the food chain. Most marine foodstuffs are canned, being thus more available for the consumption of humans living away from sea sites (Bressa et al., 1988; Colina and Romero, 1989; Chung and Tsai, 1991; Oduoza, 1992). Aluminum (Al), mercury (Hg), and lead (Pb) are toxic metals that may occur in canned seafood (Pennington, 1987; Colina and Romero, 1989; Oduoza, 1992). On the other hand, chromium (Cr), copper (Cu), iron (Fe), sodium (Na), and zinc (Zn) are essential for humans and are supplied in the food (Demir et al., 1990). The concentration of these metals in canned seafoods varies, depending on the type and origin of the food, pH of the product of the cans, oxygen concentration in the headspace, quality of inside lacquer coating of the cans, storage time, as well as temperature and humidity of storage place (Oduoza, 1992). Independent of the source, the determination of these metals is of paramount importance to help assess the quality and purity of food (Cuthbertson, 1989). Most countries have established regulatory guidelines for the maximal metal concentrations allowed in seafood. Therefore a definitive need exists for the monitoring of metal concentrations in canned seafood using reliable analytical procedures.

In the determination of total metals in seafood, the transformation of the solid sample into solution is an important pretreatment step to be considered in order to avoid serious underestimations of the analyte (Colina and Romero, 1992). For this purpose, several decomposition procedures have been recommended, depending on the kind of sample, the sample size, and the elements of interest. Many of these procedures require considerable time, are very laborious, and need constant supervision during operation. Recently, there has been great interest in using microwave heating to speed up the mineralization of a variety of biological materials. To achieve this, samples are commonly pretreated by using microwave-assisted pressurized acid mineralization, carried out in closed vessels with relief valves (Kuss, 1992; Romero et al., 1992). Microwave-heatable Parr-type high-pressure bombs are more effective for the retention of volatile analyte elements (e.g., lead and mercury), thus preventing metal losses by volatilization during microwave digestion. Additionally, the risk of contamination is decreased when pressure reactors are employed.

The most widely used techniques for the determination of metals in seafoods are flame atomic absorption spectrometry (FAAS; Fe and Zn) (Tahán et al., 1994a,b), flame atomic emission spectrometry (FAES; Na) (Tahán et al., 1994b), cold vapor atomic absorption spectrometry (CVAAS; Hg) (Tahán et al., 1993a,b), and electrothermal atomization atomic absorption spectrometry (ETA-AAS; Al, Cr, Cu and Pb) (Granadillo et al., 1994; Tahán et al., 1994a). These spectrometric techniques are preferred because of their low detection limits, the mea-

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Table 1. Instrumental Conditions for the Spectrometric Determination of the Metals under Consideration (Tahán et al., 1993, 1994a,b; Granadillo et al., 1994)

metal	technique	wavelength (nm)	atomization mode	pyrolysis[a] temperature (°C)	pyrolysis[a] time (ramp/hold) (s)	atomization[a]	analytical isoformer[b]
Al[c]	ETA-AAS[d,e]	309.3	wall	700 1500	5/10 5/5	2300	0.01 M nitric acid
Cr[f]	ETA-AAS[g,e]	357.9	wall	1650	10/5	2650	0.01 M nitric acid
Cu[c]	ETA-AAS[d,e]	324.7	wall	900 1200	10/5 5/5	2200	0.01 M nitric acid
Fe	FAAS	248.3	air/acetylene flame				0.01 M nitric acid
Hg	CVAAS	253.6	absorbance measured in peak height; measurement time 45 s; nitrogen carrier gas pressure 255 kPa				sodium tetrahydroborate (3% m/v)
Na	FAES	589.0	air/acetylene flame				0.01 M nitric acid
Pb[h]	ETA-AAS[i,e]	283.3	platform	600[j] 600	30/15 0/10	2000	0.5 mg/L of palladium + 2% m/v of citric acid
Zn	FAAS	213.9	air/acetylene flame				0.01 M nitric acid

[a] Temperatures given represent the digital settings on the control panel of the HGA-500 temperature programmer. Internal Ar flow: 0 mL/min. Maximum power heating used. Holding time was 5 s. For Al, Cu, and Pb, two-step pyrolysis procedures were used. [b] Term taken from Granadillo and Romero (1993). [c] In uncoated graphite tubes. [d] For 20-μL injections of the test portions mixed with the analytical isoformer; deuterium arc background correction. [e] Integrated absorbance measured. [f] In pyrolytic graphite-coated graphite tubes. [g] For 10-μL injections of the test portions. [h] In pyrolytic graphite-coated graphite tubes with pyrolytic graphite platforms. [i] For 10-μL injections of the test portions and of the isoformation solution via the alternate volume mode of the autosampler; deuterium arc background correction. [j] Internal alternate gas: air at 300 mL/min. CVAAS, cold vapor atomic absorption spectrometry; ETA-AAS, electrothermal atomization atomic absorption spectrometry; FAAS, flame atomic absorption spectrometry; FAES, flame atomic emission spectrometry.

surements are precise, accurate and can be done rapidly, and their relatively low operating costs. In the present study we evaluated spectrometrically the concentrations of total Al, Cr, Cu, Fe, Hg, Na, Pb, and Zn in commercial canned seafoods (i.e., fish and mollusks), frequently consumed by the Venezuelan population and also exported, as a way to ascertain the food quality for human consumption; some of the products considered were imported from Chile and Spain. Before spectrometric analysis, samples were mineralized by microwave heating. It should be emphasized that fish and mollusks constitute an important component of the country's diet and are therefore of considerable interest for health and commerce. In addition, the metal concentration of canned seafood may be used to establish environmental and/or storage contamination.

EXPERIMENTAL PROCEDURES

Reagents. All chemicals used were of analytical reagent grade. The metal stock solutions (ca. 1000 mg/L) were prepared from Titrisol concentrates from Merck (Darmstadt, Germany), made with the following salts: $AlCl_3$, $CrCl_3$, $CuCl_2$, $FeCl_3$, $Hg(NO_3)_2$, NaCl, $Pb(NO_3)_2$, and $ZnCl_2$. Standard solutions were freshly prepared by serial dilution of the stocks with grade I (as established by the American Society for Testing and Materials, ASTM, ca. electrical resistivity > 16.6 MΩ/cm at 25 °C) (ASTM, 1977) triply distilled, deionized water; nitric acid purchased from Riedel-de Haën (Hannover, Germany) was added to produce a 0.01 M nitric acid concentration. Metal spikes used for recovery studies were taken from diluted solutions of the Titrisol concentrates. The sodium tetrahydroborate solution (3% m/v) was prepared by dissolving sodium tetrahydroborate powder (Riedel-de Haën) in appropriate amounts of grade I ASTM triply distilled, deionized water. The palladium nitrate stock solution was prepared by mixing together 1 g of $Pd(NO_3)_2$ (from Aldrich Chemical Company, Milwaukee, WI) with 1 mL of concentrated nitric acid, leaving for about 15 min without stirring, and finally diluting to 100 mL with grade I ASTM triply distilled, deionized water; an intermediate solution of palladium (40 mg/L) was prepared by dilution of 866 μL of the palladium stock solution up to 100 mL with 0.01 M nitric acid. A composite Pd–citric acid analytical isoformer was produced for Pb and contained 0.5 mg/L of Pd + 2% m/v of citric acid; this composite solution was prepared as follows: 1.25 mL of the intermediate palladium solution and 2 g of citric acid (Riedel-de Haën) were diluted to 100 mL with 0.01 M nitric acid.

For accuracy evaluation, the following standard reference materials were used: Albacore Tuna (NIST RM 50) and Oyster Tissue (SRM 1566a) from the National Institute of Standards and Technology (Gaithersburg, MD), Tea Leaves (NIES no. 7) and Rice Flour (NIES no. 10) from the National Institute for Environmental Studies (Ibaraki, Japan). These materials were mineralized as stated below to provide aqueous solutions whose final concentrations were within the range of the metal concentrations expected in the seafoods analyzed. Extreme care was exercised to avoid contamination of samples and solutions from dust, tap water, glassware, chemicals. Sample manipulation, solution preparation, and instrumental measurements were conducted in a clean room with Class-100 work area.

Apparatus. A Perkin-Elmer Model 2380 atomic absorption spectrometer with a Perkin-Elmer Model HGA-500 graphite furnace atomizer and a deuterium arc background corrector (Norwalk, CT) were used for the ETA-AAS determination of total Al, Cr, Cu, and Pb according to methods reported previously (Tahán et al., 1993a, 1994a,b; Granadillo et al., 1994). All ETA-AAS data were obtained using either standard (uncoated) graphite tubes (for Al and Cu), pyrolytic graphite-coated graphite tubes (for Cr), or pyrolytic graphite-coated graphite tubes with standard pyrolytic graphite platforms (for Pb). A Perkin-Elmer Model 460 spectrometer was used for the FAAS determination of total Fe and Zn (Tahán et al., 1993a, 1994b), for the FAES determination of Na (Tahán et al., 1993a, 1994b) and for the CVAAS determination of total Hg (Tahán et al., 1993a,b); in this last case, a Perkin-Elmer Model MHS-10 mercury/hydride system was attached to the spectrometer to generate the mercury vapors. The instrumental conditions used for the metals included in this study are shown in Table 1. The drying temperature used for all metals and matrices evaluated by ETA-AAS was 120 °C; these conditions were optimized on the basis of time–temperature studies using the standard reference materials cited already. The light sources were single-element hollow-cathode lamps whose operating parameters (current and spectral bandwidth) were those given by the manufacturer, except for the spectral bandwidth of Pb, set at 0.2 nm to overcome a background interference probably due to an overcompensation of the background absorption by the deuterium arc background corrector, as reported elsewhere (Navarro et al., 1989). Argon was employed in the graphite furnace as external and internal gas, and the flow of the latter was interrupted during atomization. For Pb, pyrolysis under an oxygen atmosphere was achieved using air as internal alternate gas during the first pyrolysis step, as shown in Table 1.
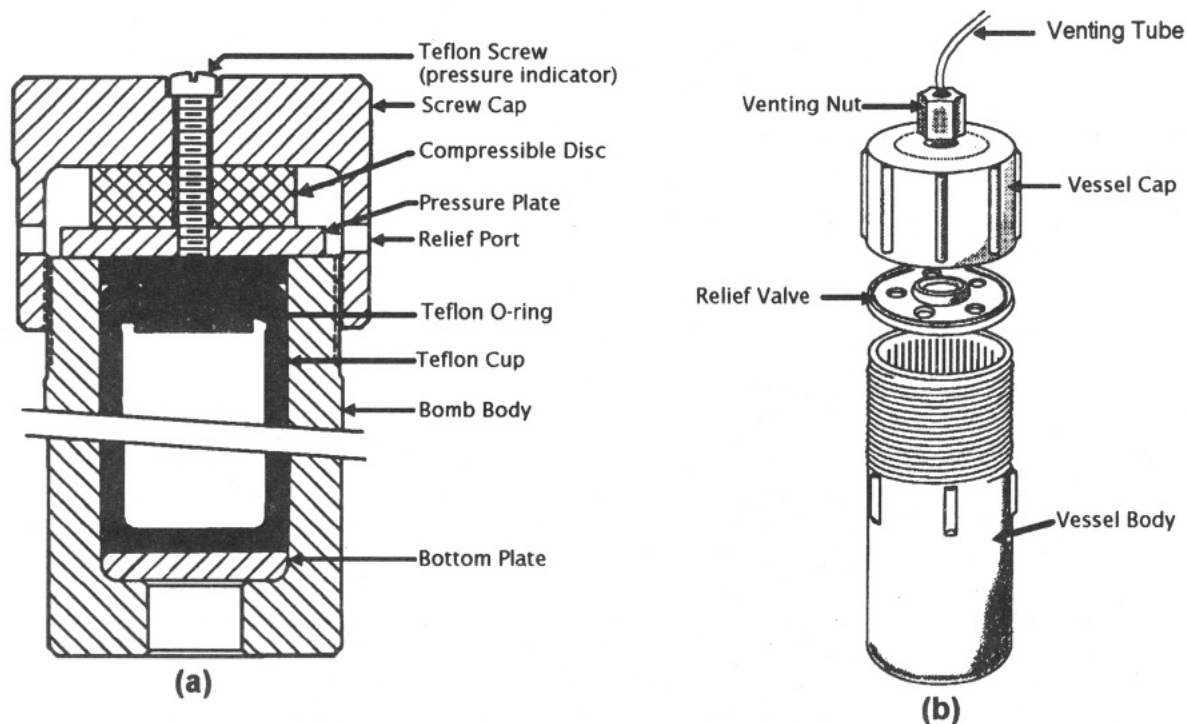
Figure 1. High pressure reactors: (a) 45-mL microwave digestion bomb and (b) 120-mL microwave digestion vessel with pressure relief valve.

The commercial canned seafoods were freeze-dried in a Labconco Model 6 liter lyophilizer (Kansas City, MO), kept at −52 °C for 24 h. Mineralizations were performed with Parr Instrument Company (Moline, IL) 4782 microwave acid digestion bombs (for Hg and Pb only) and with 120 mL Teflon PFA (a tetrafluoroethylene with a fully fluorinated alkoxy side chain) microwave digestion vessels with pressure relief valves (for the other metals). The casing of the microwave acid digestion bomb is made from microwave-transparent polymer; the PTFE crucible has a 45 mL capacity and is sealed by a PTFE O-ring between the cup and the cover (Figure 1a). The closed vessel digestion system (Figure 1b) consists of a vessel body, safety pressure relief valve, vessel cap, venting nut, and venting tubing; this vessel system is designed to operate at internal pressures up to 120 psig. Above 120 psig the safety valve will open, allowing the system to vent into a collection container, thus lowering the pressure inside the vessel. The valve then reseals allowing pressure to again increase. This automatic venting is a safety feature of the closed vessel system to ensure that vessel rupture due to the excessive pressure, will not occur. For mineralization purposes, both high-pressure systems were irradiated in a CEM Model MDS-81D laboratory microwave oven (Matthews, NC), consisting of a microwave drying system (operated at 2450 MHz) with an analyst-selectable power output of 0−600 W in 1% increments, a microwave cavity with a variable speed exhaust fan, a programmable microprocessor based digital computer, teflon-coated cavity, exhaust tubing, and standard screen rotating turntable.

Samples. Forty cans of each type of seafood (total wet weight 3−4 kg/type) were taken at random from markets and retail outlets and kept at ambient temperature until homogenization occurred. Canned samples were drained of fluid (as normally done by the consumer before eating) before pooling and blending. Samples were lyophilized, ground, mixed, and kept in polyethylene bags at 4 °C until analysis. Determinations were done in pentuplicate. All metal data presented below are reported on a dry weight basis.

Procedures. For Hg and Pb, the mineralization procedures are described elsewhere (Tahán et al., 1993a,b, 1994a). Briefly, not more than 100 mg of lyophilized test portion (or standard reference material) and 2.5 mL of concentrated nitric acid were put into a 45 mL microwave acid digestion bomb, and were irradiated for 70 s at 100% power of the microwave oven (equivalent to 600 W and 2450 MHz) for complete mineraliza-

tion. After cooling to ambient temperature, the digestion solution was transferred into a 10-mL volumetric flask and diluted to volume with 1 M nitric acid−1 M perchloric acid solution. For the other metals (Tahán et al., 1993a, 1994a), approximately 1 g of lyophilized test portion (or standard reference material) and 15 mL of concentrated nitric acid were put into a 120-mL microwave digestion vessel with pressure relief valve and the vessel cap was torque closed with the use of an automatic capping station (CEM); routinely, 10 samples and two blanks were placed on the turntable, inserted in the oven and irradiated for 10 min at 100% power for complete mineralization. After cooling to ambient temperature, the content was transferred quantitatively into a 25-mL polypropylene volumetric flask and diluted to volume with grade I ASTM triply distilled, deionized water. Blanks were prepared with the same reagents, without the samples, undergoing the microwave mineralizations. Mercury determination by CVAAS was done as follows: an aliquot of the sample digestion solution (volume ranged between 3 and 4 mL depending on mercury concentration) was placed into the generator vessel of the mercury/hydride system. Sodium tetrahydroborate solution was added and the mercury vapors generated were directed to the optical cell. The absorbance reading was taken at the maximum value reached. Before the spectrometric determinations of the other metals, the mineralized samples were diluted with 0.01 M nitric acid at different ratios depending upon the metal under study (Granadillo et al., 1994; Tahán et al., 1993a, 1994a,b): Al, 4-fold; Cr, 2-fold; Cu, 4-fold; Fe, 10-fold; Na, 1000-fold; Pb, 4-fold; and Zn, 100-fold. For the ETA-AAS analyses, either 10-μL (for Cr) or 20-μL (for Al and Cu) aliquots of diluted test portions under analysis (or aqueous standards) were injected into the graphite tubes. For Pb, 10-μL aliquots of diluted test portions and 10 μL of the analyte isoformation solution, containing 5 ng of Pd and 200 μg of citric acid, were injected in sequence onto the platforms. Two-step pyrolysis procedures were used for the ETA-AAS determinations of Al, Cu, and Pb (Table 1). For Fe and Zn (FAAS), and for Na (FAES), diluted samples and aqueous standards were directly aspirated into the air−acetylene flame.

RESULTS AND DISCUSSION

Metal contamination during the freeze-drying process was not revealed in carefully performed blank tests. In general, drying by lyophilization produced no metal

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Table 2. Analytical Figures of Merit for the Spectrometric Determination of Metals in Canned Marine Food Products (Tahán et al., 1993a,b, 1994a,b; Granadillo et al., 1994)

metal	calibration curve[a]	correlation coefficient	linear range (μg/L)	standard error of the estimate $(S_{y,x})_{(s)}$	standard deviation of intercept (s)	standard deviation of slope (s·L/μg)	detection limit[b] (μg/L)	characteristic mass[c] (pg)	precision RSD[d] (%)
Al	$y = 0.0050x - 0.0004$	0.9999	100	0.002	0.0012	0.00003	0.5	19 (10)	1.0
Cr	$y = 0.0090x + 0.0004$	0.9999	50	0.001	0.0014	0.00010	0.03	5 (3.5)	2.3
Cu	$y = 0.0244x + 0.0005$	1.0000	50	0.002	0.0011	0.00004	0.3	3 (8)	1.9
Fe	$y = 0.0325x + 0.0015$	0.9998	6[e]	0.002	0.0010	0.00040	70	0.09[f] (0.13)	3.3
Hg	$y = 0.0010x$	0.9999	200[g]	0.001		0.00005	53	4 (5)	2.4
Na	$y = 1.3333x - 0.6600$	0.9983	30[e]	1.633	1.4910	0.07700	20	0.50[f] (0.70)	2.7
Pb	$y = 0.0034x - 0.0002$	0.9999	50	0.003	0.0001	0.00002	0.1	13 (12)	2.2
Zn	$y = 0.2490x + 0.0099$	0.9997	1[e]	0.004	0.0050	0.00410	100	0.02[f] (0.02)	1.8

[a] x and y are the analyte concentration (μg/L for Al, Cr, Cu, and Pb; mg/L for Fe, Na, and Zn; ng for Hg) and the absorbance value (integrated absorbance for Al, Cr, Cu, and Pb; absorbance reading for Fe, Na, and Zn; peak height absorbance for Hg), respectively. [b] Defined as three times the standard deviation of the blank. Values for diluted solutions. [c] Amount of analyte, in picograms (pg), required to give an absorbance of 0.0044 (1% absorption). Characteristic masses in parentheses for Al, Cu, and Pb were taken from Slavin and Carnrick (1985); for Cr, from *Analytical Methods for Furnace AAS* (1984); for Hg, from *Analytical Methods for Atomic Absorption Spectrometry* (1982). [d] Average RSD, for real samples only. Triplicate samples; seven runs each analysis. [e] In mg/L. [f] Characteristic concentration defined as the concentration, in mg/L, required to give an absorbance of 0.0044 (1% absorption). Values in parentheses were taken from *Analytical Methods for Atomic Absorption Spectrometry* (1982). [g] In ng.

losses, similar to results reported by Colina and Romero (1989, 1992) for fish, and loss of water of 66% (tuna), 63% (sardine), 54% (jurel), 68% (ark clams and mejillons), and 52% (common cockles); metal losses were determined from recoveries of the metal spikes added to test portions of commercial seafoods undergoing lyophilization. During sample pretreatment, Hg and Pb losses by volatilization were eliminated by carrying out the microwave mineralization in sealed bombs (Figure 1). The reliable determination of total Hg by CVAAS in canned seafoods from undigested samples was not feasible, as the presence of organic matter is a source of interference, as reported already (Tahán et al., 1993a,b); in this sense, Hg quantification by CVAAS can be accomplished only if the destruction of the organic matter is efficiently achieved (i.e., by microwave mineralization), to a point where Hg is liberated from its chemical bonding (i.e., to protein sulfhydryl groups). It should be emphasized that sample masses larger than 100 mg tended to activate the safety release mechanism of the Parr 4782 high-pressure digestion bomb (Figure 1a) by blowing out the relief disc to compensate for the excessive pressure build up, with corresponding losses of Hg and Pb (Tahán et al., 1993b). The two mineralization procedures used in the present study allowed the elimination of concomitant substances and produced suitable digestion solutions for spectrometric analyses; both procedures were fast and convenient to process large number of samples by shortening the total analysis time. Additionally, the digestion procedures made it possible to determine eight metals sequentially in the same digest.

The term analytical isoformer, coined by Granadillo and Romero (1993) instead of the traditional term chemical modifier, was recently proposed because it suggests the process actually accomplished by the modifier, namely analyte isoformation, and it connotes the chemical and/or physical actions that the modifier performs on the analyte element and/or on the matrix under study (Granadillo et al., 1994). With exception of Hg and Pb, the analytical isoformer employed for the metals considered in this work was solely 0.01 M nitric acid; this circumstance decreased the risk of contamination and avoid multistep analytical procedures (Tahán et al., 1994a; Granadillo et al., 1994). Preatomization losses of Al, Cr, Cu, Fe, Na, and Zn were not observed. For Pb, volatilization losses of the analyte element in the graphite furnace were controlled by using Pd-induced isoformation in conjunction with the carbon-reducing effect achieved by the addition of citric acid, as reported recently by Granadillo and Romero (1993).

The blanks of the Pd(NO$_3$)$_2$ and citric acid used were below the ETA-AAS detection limit for Pb (0.1 μg/L; see Table 2). The spectrometric quantification of Hg by CVAAS, in the mineralized test portions, was straightforward (Colina and Romero, 1989,1992; Tahán et al., 1993a,b).

Table 2 shows the analytical figures of merit for the spectrometric determination of Al, Cr, Cu, Fe, Hg, Na, Pb, and Zn in samples of tuna, sardine, jurel, ark clams, mejillons, common cockles, oyster tissue, tea leaves, and rice flour, mineralized by microwave heating (Tahán et al., 1993a,b, 1994a,b; Granadillo et al., 1994). Precision was evaluated in the real samples under consideration. Except for Hg, three aliquots of each material (ca. 1–5 mL) were analyzed (five runs each analysis) using the described methods; for Hg, triplicate analyses were performed. For all metals, precision (RSD) was better than 3%, for both the within- and between-run (day-to-day) analyses (Table 2), which can be considered adequate for these types of analytical evaluations of real samples. The characteristic masses and characteristic concentrations presented in Table 2 are in good agreement with values reported in the current literature (*Analytical Methods for Atomic Absorption Spectrometry*, 1982; *Analytical Methods for Furnace AAS*, 1984; Slavin and Carnrick, 1985). Accuracy was tested by analyzing four standard reference materials, supplied by two international agencies (NIST and NIES), and results are given in Table 3. The reliability of the analytical methods was further assessed through recovery studies, done by triplicate spectrometric determinations of the metals under consideration in three tuna samples and in three sardine samples; the range of recovery was 95–105%. The method of standard additions was also used for metal quantification as well as for the evaluation of the effect of nonspectral interferences by comparing their slopes with those of aqueous calibration graphs in 0.01 M nitric acid; this method yielded graphs with slopes statistically indistinguishable from those of the aqueous standard calibration graphs. This implied the absence of nonspectral interferences in the spectrometric analyses and permitted the use of either the calibration graphs or the standard addition method quantification. Calibration graphs prepared with aqueous standards were preferred for the quantification of metals and, therefore, were used throughout. Altogether, the above analytical figures of merit indicate that the spectrometric methodologies used in this research were precise, accurate, and interference-free, providing full analytical confidence to the reported metal data.

Table 4 shows the dry weight concentration data for

Table 3. Accuracy of the Spectrometric Determination of Metals in Standard Reference Materials

reference material	metal	mean concentration ± 1 SD (µg/g of dry wt)	
		certified value	measured value
NIST RM 50 Albacore tuna	Hg	0.95 ± 0.10	0.92 ± 0.10 n = 7
NIST SRM 1566a oyster tissue	Hg	0.0642 ± 0.0067	0.0631 ± 0.0099 n = 8
NIES no. 7 tea leaves	Al	775 ± 20	762 ± 2 n = 6
	Cr	0.15[a]	0.22 ± 0.04 n = 8
	Cu	7 ± 1	6 ± 1 n = 6
	Na	1.0 ± 0.1[b]	1.0 ± 0.2[b] n = 8
	Pb	0.8 ± 0.3	0.8 ± 0.1 n = 10
NIES no. 10 rice flour	Fe	13 ± 1	12 ± 2 n = 6
	Zn	22 ± 1	21 ± 1 n = 7

[a] Provisional value. [b] In mg/L of diluted sample. n = Number of test portions analyzed; triplicate analyses of each portion were made.

Al, Cr, Cu, Fe, Hg, Na, Pb, and Zn found in the six marine species studied, namely tuna, sardine, jurel, ark clams, mejillons, and common cockles, presented in canned form to the consumer. Metal concentrations were higher in mollusks (edible portion) than in tuna, sardine and jurel (fish muscle tissue). This is a result of the feeding mechanism by filtration that bivalves have, bioconcentrating metals in their tissues, even when levels of these metals in seawater are not excessive (Merian, 1994). Consequently, ark clams, mejillons, and common cockles are adequate biological monitors of pollution of the aquatic environment, properly reflecting the environmental contribution of toxic metals

(Colina and Romero, 1992). Common cockles showed higher concentrations (µg/g) of Al (1168 ± 175), Cu (4.0 ± 0.2), Fe (1117 ± 26), Na (35.9 ± 1.2 mg/g), and Pb (1.3 ± 0.1) than those of ark clams and mejillons, probably because of the smaller size of the former. The concentration of Cr, Cu, Fe, Na, and Zn in any of the canned products studied could result from two factors: (i) the metal concentration naturally present in the seafood and (ii) the extent of contamination from the can which stored the food. Mejillons presented the highest Zn concentration (191 ± 23 µg/g; Table 4) probably due to the fact that this metal is increased naturally in this marine species. The metal contributions from the can and the food may be identified by an adequate comparison with similar seafood but not canned. It is important to state that metal concentrations found in samples of mollusks come mainly from visceral tissues which are subsequently discarded in the industrial process of canning. For instance, De Gregori et al. (1992) reported a substantial decrease in the Cu and Cd concentrations (µg/g) of Chilean canned mollusks without visceral tissue (Cu, 1.8 ± 0.1; Cd, 2.1 ± 0.1) with respect to the fresh product with visceral tissue (Cu, 2.4 ± 0.2; Cd, 4.6 ± 0.7), while the visceral tissue alone had Cu and Cd concentrations (µg/g) of 8.5 ± 0.1 and 20 ± 2, respectively. This circumstance must be carefully considered when the sources of any particular metal under study is to be established in the canned food. Independent of the origin, however, all these metals are ingested as a whole by consumers who eat these types of canned seafood.

Existing legislation suggests an upper limit of 2 µg/g for Pb in canned foods. The levels of Pb obtained in this work were not above this specified limit but there is a high probability that such toxic level could gradually accumulate above recommended limits in canned foods and consequently in the tissue of consumers (Oduoza, 1992). In fact, automobile combustion of tetraethyllead-containing gasoline still represents the main source of Pb pollution in Venezuela (ca. >90%) (Granadillo et al., 1995). We must stress that Pb is a lethal toxicant that

Table 4. Dry Weight Metal Concentrations (Mean ± 1 SD; µg/g) Found in Several Commercial Canned Seafoods Evaluated Spectrometrically (Ranges Are in Parentheses)

sample [trademark]	metal							
	Al	Cr	Cu	Fe	Hg	Na[a]	Pb	Zn
tuna, Thunnus alalunga [Eveba][b]	11 ± 1 (10–12)	UD[f]	1.3 ± 0.7 (0.9–1.8)	61 ± 2 (58–63)	1.2 ± 0.1 (1.1–1.2)	18.0 ± 0.2 (17.9–18.2)	UD	16 ± 1 (15–16)
tuna, Thunnus alalunga [Oriente][b]	5 ± 1 (4–5)	UD	1.5 ± 0.2 (1.1–1.6)	140 ± 3 (138–145)	1.3 ± 0.1 (1.2–1.4)	17.9 ± 1.2 (17.1–18.7)	UD	16 ± 1 (15–18)
tuna, Thunnus alalunga [Margarita][b]	18 ± 5 (13–23)	UD	2.1 ± 0.4 (1.8–2.4)	105 ± 4 (102–110)	0.4 ± 0.1 (0.3–0.5)	26.5 ± 0.6 (26.1–26.9)	0.5 ± 0.1 (0.4–0.5)	21 ± 1 (20–22)
tuna, Thunnus alalunga [California][b]	4.0 ± 0.1[c] (0.2–0.5)	0.4 ± 0.1[c] (0.3–0.4)	2.2 ± 0.1 (2.0–2.3)	326 ± 94 (235–430)	0.2 ± 0.1 (0.1–0.3)	31.4 ± 0.7 (30.6–32.0)	0.5 ± 0.1 (0.4–0.6)	21 ± 1 (19–22)
sardine, Sardinella anchovia [Margarita][b]	96 ± 8 (90–102)	0.3 ± 0.1 (0.2–0.3)	1.5 ± 0.1 (1.4–1.6)	157 ± 3 (155–159)	UD	15.7 ± 0.7 (15.2–16.3)	0.5 ± 0.1 (0.4–0.6)	20 ± 1 (18–21)
jurel, Caranx crysos [San Pedro][d]	9 ± 3 (7–11)	0.3 ± 0.1 (0.2–0.3)	2.1 ± 0.4 (1.8–2.4)	49 ± 2 (47–50)	UD	24.7 ± 0.7 (24.1–25.1)	UD	26 ± 1 (25–27)
ark clams, Arca zebra [Margarita][b]	83 ± 4 (80–86)	1.2 ± 0.3 (1.0–1.6)	5.9 ± 0.3 (5.6–6.2)	160 ± 6 (154–165)	UD	29.8 ± 1.1 (29.1–30.6)	1.2 ± 1.0 (0.5–1.8)	52 ± 1 (51–55)
mejillons, Perna perna [Albo][e]	122 ± 11[c] (110–135)	0.9 ± 0.2[c] (0.7–1.2)	2.6 ± 0.2 (2.3–2.8)	147 ± 5 (140–150)	0.3 ± 0.1 (0.2–0.4)	35.8 ± 1.9 (33.4–37.7)	0.4 ± 0.1 (0.3–0.5)	191 ± 23 (172–215)
common cockles, Acantothcardia echinata [Albo][e]	1168± 175 (1044–1291)	0.11 ± 0.03 (0.08–0.14)	4.0 ± 0.2 (3.8–4.4)	1117 ± 26 (1099–1136)	0.2 ± 0.1 (0.2–0.3)	35.9 ± 1.2 (34.7–37.2)	1.3 ± 0.1 (1.2–1.4)	41 ± 3 (39–42)

[a] In mg/g. [b] Product from Venezuela. [c] In ng/g. [d] Product from Chile. [e] Product from Spain. [f] UD = Undetectable by spectrometric means (ETA-AAS for Cr and Pb; CVAAS for Hg).

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should be excluded from the diet, particularly that of children (Wixson and Davies, 1994). This was of particular concern for ark clams (1.2 ± 1.0 µg/g of Pb) and common cockles (1.3 ± 0.1 µg/g of Pb).

Mercury in fish and mollusks occurs almost entirely as methylmercury. This is a highly toxic compound and chronic exposure to it can induce mental retardation and death. As a result, the U.S. Food and Drug Administration (FDA) has set an Action Level of 1 µg/g (wet weight) for Hg concentration in fish (Driscoll et al., 1994). Two brands of Venezuelan canned tuna analyzed in the present study (i.e., Eveba and Oriente) showed Hg concentration of 1.2 ± 0.1 µg/g and 1.3 ± 0.1 µg/g, respectively, well above the level recommended by FDA, representing a potential health threat.

Average Al concentration reported for canned seafoods is <3 µg/g (Pennington, 1987). We found much higher concentrations for Al (µg/g), in sardine (96 ± 8), ark clams (83 ± 4), mejillons (122 ± 11), and common cockles (1168 ± 175). Aluminum is an important human toxin that may induce severe neurological disorders in nonuremic individuals (Flaten and Garruto, 1991). It is well known that Al affects several enzymes and other biomolecules relevant to Alzheimer's disease; it is present in senile plaques and neurofibrillary tangles (Flaten and Garruto, 1991). Additionally, we have found firm evidence of Al-induced pathological dysfunctions in hemodialyzed individuals (Romero, 1991).

As a corollary, we believe that it is safer and wiser to have Al, Hg, and Pb refined to the lowest possible levels in food. In conclusion, metal data presented were reliably obtained by using spectrometric techniques after microwave mineralization. These data can be used for referential purposes to judge and control the quality and safety for human consumption of commercial canned seafood.

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