

Determination of Lead in Mexican Candy and Flavored Salt Products

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ABSTRACT

This analysis of lead in Mexican candy and flavored salt products is predicated on the collection of a sample that is representative of the lot being tested. Two significant analytical challenges are posed by these products: preparation of a representative analytical sample (i.e., one that can provide a sufficiently homogenous analytical portion for subsequent digestion and analysis) and ensuring reliable quantitation in matrices with high salt content. In this work, a novel procedure was developed to prepare homogeneous analytical samples from kg quantities of product and a pre-digestion step. Smaller subsamples from this step were then subjected to microwave digestion and subsequent analysis via Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). Quality control (QC) data showed good reproducibility between replicate subsamples and good recoveries from sample spikes. Despite the expected interferences due to high salt levels in the samples, the use of a matrix modifier and appropriate furnace conditions surmounted these potential effects. The results from samples analyzed by both GFAAS and Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) compared very favorably. This study demonstrates appropriate methods for obtaining highly reproducible results that can serve as the basis for regulatory action.

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INTRODUCTION

In the early to mid-1990s, nurse practitioners for the California Childhood Lead Poisoning Prevention Program identified Mexican candy products that appeared to be associated with excessive childhood lead exposures. At that time, the primary issue appeared to be the presence of lead in candy wrappers [1]. Since that time there have been numerous analytically significant results where the lead content is apparently unrelated to the wrapper. In April 2004, a series of articles in the Organic County Register in California reported high levels of lead in imported Mexican candy products and potentially toxic levels of lead in a number of chili-based products [2-7]. Earlier FDA analyses of these products were plagued by an inability to obtain reproducible results from separate portions of a particular sample. Although these results were in part due to the extreme variability of lead in the products, this variability “restrained” potential regulatory actions. Clearly, development of appropriate methods for this application that can achieve both good precision and accuracy is a priority for FDA.

Definitive information on the specific source(s) of lead contamination in these products is not available at this time. The major ingredient in lollipops, sucrose, does not appear to be contaminated. Past and present findings suggest that the origin of the lead contamination is largely associated with at least two common ingredients in many Mexican candies (i.e., chili and alt). Lead contamination has been found in other types of candies including tamarind-based and tejocote-based candy in lead-glazed ceramic jars, and some tamarind, tejocote, and chocolate-based candy with and without chili. Several Mexican candy manufacturers have concluded that the chili additives were being contaminated during the open-air drying process. Other potential sources of this contamination might be the grinding process involved in preparation of chili powder, or the possible use of lead arsenate as a pesticide agent.

At the present time, a variety of Mexican candy and salt-based products appear to contain analytically significant but highly variable amounts of lead. We suspect that the lead contamination is caused by small particles that have relatively high levels of lead. This variability is not only *between* lots of the same product but *within* individual items from the same lot. In general, these types of products are very difficult to grind or blend in a fashion that will yield a suitably homogenous composite sample. Although the use of grinding large quantities of these products was attempted as a means for sample homogenization, this was unsuccessful in producing a homogeneous sample from which a smaller subsample (0.5-1.0 g) could be removed for subsequent analysis to yield acceptable levels of precision.

The scope of this work was the development of a suitable sample workup procedure for determination of lead in a variety of hard and soft candy, powdered candy products, and fruit candy products, especially those containing chili and salt as major ingredients. The primary goal of this procedure was to produce a homogeneous composite and therefore an analytical portion that can be sampled repetitively with the expectation of accurate and precise analytical results.

EXPERIMENTAL

The types of products included in the scope of this work can be categorized as follows. These category types were predicated on whether their physical nature after the addition of water would result in product consistency such that all particulate matter was either suspended or not suspended.

Type I Products: Semi-solid or soft candy (e.g., chocolate-based, fruit-based, including tamarind, tejocote, apple, etc.) with or without chili or other visible particulate ingredients (i.e., Chaca-Chaca, Pelon-Pelon Rico)

Type II Products: Hard candy (including suckers) with or without visible particulate ingredients (chili) either in the candy or on the surface of the candy (i.e., Vero brand Rabaniditas suckers)

Type IIA Products: Hard candy (including suckers) with supplemental *but separate* salt and chili (i.e., Vero brand Super Rabaniditas)

Type III Products: Powdered sugar or flavored salt products with or without other particulate ingredients, e.g., chili (i.e., Brinquitos - flavored, acidified, sugars; Pica Limon - flavored, acidified salt).

The general analytical procedure used to obtain reproducible measurements of lead in high salt candy products is similar to the approach used for canned foods described by Jones and Boyer [8]. Further details on this procedure are described in a draft method [9] which will be incorporated into future versions of the EAM. The general steps in this procedure are as follows.

1. Blending/mixing of this composite sample with water and/or nitric acid
2. For those samples that would suspend, pre-digestion of a rather large (40 g) sample portion
3. Microwave digestion of an aliquot equivalent to approximately 0.5 g of the product
4. GFAAS and ICP-MS analysis

Blending of Composite Sample

A 1 kg composite sample and an equivalent mass of deionized water (for Type I products) or 10% nitric acid (Type II products) were placed in a large sized Nalgene polymethylpentene mixing vessel. The mixture was covered and left overnight to facilitate softening/dissolution of the product. In some cases, heating was required to assist in this process. The resulting mixture was blended in a 6 L stainless steel bowl of a Robot Coupe RSI 6Y food chopper until a visually homogeneous mixture was obtained. In the case of chocolate-based products, smaller amounts of water were required to avoid formation of water-insoluble fat layer. In the case of Type II, IIA, and III products, the mixture was subjected to an additional blending step using a high-shear type Brinkmann Polytron mixer to facilitate homogenization of remaining particulate materials in the mixture. It should be noted that although some candy additives such as silicon dioxide and titanium dioxide may not be completely dissolved after this treatment process, this process provides a mixture that is homogeneous with respect to lead content and stable enough to allow selection of a subsample for subsequent digestion and analysis.

Predigestion of Subsample

For sample types giving stabile suspended particulates, a 40 g portion of the blended composite sample and 20 mL of nitric acid were placed in a beaker. The beaker was covered with a watch glass and digested on a hot plate at approximately 100°C until the sample was solubilized. In some cases, additional nitric acid was required to achieve complete or near complete solubilization. At this point, the weight fraction of the candy in this mixture was determined using the formula below.

$$WF = m_s/m_n \quad \text{where}$$

WF= sample mass fraction

m_s = mass of analytical sample treated (g)

m_n = final net mass of the analytical sample, water, and acid (g)

Microwave Digestion of a Analytical Sample

The digestion procedure is detailed in EAM 4.3 [10]. In brief, an amount of the sub-sample equivalent to 0.5 g of untreated candy was removed using the WF computed above. It should be noted that larger masses of products with high-sugar contents may exceed the capacity of the microwave digestion vessel. A Teflon XP1500 digestion vessel was used with the operating conditions specified in Table 1 for simultaneous processing of up to 12 samples.

Table 1. Conditions used for microwave digestion.

Stage	Max power	%	Ramp Time	PSI control	Temp	Hold Time
1	300 W	100	5 min	800 psi	130°C	0 min
2	1200 W	100	20 min	800 psi	200°C	3 min

GFAAS Analysis

The GFAAS analysis procedure is likewise detailed in EAM 4.3 [10]. These analyses were performed using a Varian model SpectrAA 880Z instrument. Standard “cookbook” parameters were employed, including a wavelength of 283.3 nm, bandpass of 0.5 nm, and Zeeman background correction. Each solution analyzed included 10 µL of the sample, 10 µL of deionized water, and 3 µL of a 1% NH₄H₂PO₄ matrix modifier solution to suppress premature volatilization of lead in the form of PbCl₂. GFAAS temperature program parameters include 200°C dry stage, 825°C ash stage, 1750°C atomization stage, and a 2300°C clean stage. Given that the samples contained high salt contents, a standard addition-based method was used for quantitation. Here, lead was quantified by spiking a sample extract with three different levels of lead and computing the original concentration using linear regression.

ICP-MS Analysis

The same sample extracts used for GFAAS analyses were diluted for subsequent analysis via ICP-MS. The ICP-MS analysis procedure followed draft FDA guidelines for analysis of metals in dietary supplements [11]. The analyses were performed using a Agilent ICP-MS model 7500c equipped with a Cetac model ASX-510 autosampler, a Neslab water chiller model M-75, a Babbington nebulizer, a Peltier-cooled spray chamber, an octopole collision/reaction cell, and ICP-MS ChemStation software. Lead was detected using the sum of the intensities for the three major lead isotopes (²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb) to account for isotopic variation in the samples and

standards. Lead standards of concentrations of 0.1, 0.5, 1.0, and 10 ppb were prepared and analyzed. Internal standard-based quantitation was employed using ^{209}Bi to account for drift in instrument response and possible suppression of lead ionization. Although suppression of ^{209}Bi signal was observed in some of the samples, when the samples were diluted further this suppression was minimized and the use of the internal standard-based quantitation corrected for this type of matrix effect.

RESULTS AND DISCUSSION

While a number of different products were analyzed, results corresponding to those which had concentrations greater than 0.1 mg/kg are reported here. Table 2 gives a compilation of these results and provides mean and percent relative difference (%RD) from replicate analyses via GFAAS. Two of the products were found to exceed the 0.5 mg/kg (ppm) regulatory limit for lead. The highest concentration of lead detected was 0.890 mg/kg. The precision of the analyses was quite good considering the heterogeneity of the product, with %RDs generally less than 10% with the largest being 14%, and represent a significant improvement on the generally poor reproducibilities noted in earlier analyses. These values demonstrate the suitability of the sample preparation techniques in obtaining a homogenous subsample for analysis.

Table 2. Summary of results from analysis of lead in various Mexican candy products. All results are in units of mg/kg. REPL. 1 and REPL. 2 refer to replicate analyses of same subsample. %RD denotes percent relative difference.

NO.	SAMPLE #	PRODUCT	REPL. 1	REPL. 2	MEAN	%RD	
1	273457	candy with chili flavored salt	0.223	0.212	0.218	5%	
2	277228	candy with chili flavored salt	0.100	0.096	0.098	4%	
3	277238	candy with chili flavored salt	0.950	0.831	0.891	13%	
4	279316	chili flavored salt	0.095	0.107	0.101	12%	
5	279327	chili flavored salt	0.182	0.210	0.196	14%	
6	281154	lollipop with chili flavored salt	0.105	0.105	0.105	0%	
7	281161	candy with chili flavored salt	0.404	0.381	0.393	6%	
8	281822	candy with chili flavored salt	0.228	0.217	0.223	5%	
9	282038	lollipop with chili flavored salt	0.108	0.104	0.106	4%	
10	285321	lollipop with chili flavored salt	0.323	0.334	0.329	3%	
11	285433	chili flavored salt	0.700	0.674	0.687	4%	
					Mean	0.313	7%
					Min	0.098	0%
					Max	0.890	14%

A manufacturer of some of these candy products formally challenged the GFAAS results from other non-FDA labs and disputed the validity of the analytical methods employed here based on the knowledge that high salt levels can result in matrix effects and poor quantitative results. While it is indeed true that GFAAS analyses may be adversely affected by spectral interferences in the presence of matrices containing high levels of salt, additional QC data indicate that these allegations are unfounded with respect to the results reported here. It should be noted that the primary anticipated effect of salt on modern GFAAS instruments with Zeeman background

correction is *under-reporting* of analyte concentrations, not *over-reporting* as the industry complaint contended. While GFAAS analyses of these products in FDA and in non-FDA labs using instruments other than the Varian 880Z model employed in this study have indeed experienced difficulties in achieving good recoveries, they have been able to obtain acceptable results by employing different GFAAS conditions and more complex matrix modifiers. However, the major reason for the poor precision in analyses of these products was the use of small sample masses and the lack of a means of producing a homogenous sample composite.

In this study, specific quality assurance (QA) and QC procedures were followed to ensure high quality data. This included the use of standard operating procedures (SOPs), analysis of replicate samples to assess precision, analysis of a reference material (RM) to assess accuracy, and analysis of spiked samples to assess accuracy of quantitation in the sample matrix. Samples of a reference material (RM8433 Corn Bran, with lead content of 0.140 +/- 0.034 mg/kg) were analyzed along with each batch of samples, and the percent recoveries for these were in the expected range of 80-120%. Table 3 shows results from analyses in which the same samples were spiked with known amount of lead prior to the sample workup procedure. The percent recoveries were quite good, with a range of 88 to 124% with a mean percent recovery of 106%.

Table 3. Percent recovery data from spikes of lead into the subsamples.

NO.	SAMPLE #	PRODUCT	% RECOVERY
1	277230	candy with chili flavored salt	121%
2	279327	chili flavored salt	98%
3	280326	candy with chili flavored salt	100%
4	281161	candy with chili flavored salt	124%
5	281829	lollipop with chili flavored salt	88%
6	282038	lollipop with chili flavored salt	97%
7	282067	lollipop with chili flavored salt	109%
8	286351	chocolate candy	119%
9	287118	lollipop with chili flavored salt	101%
	Mean		106%
	Min		88%
	Max		124%

An additional set of validation studies using ICP-MS was performed on some of the same subsamples. ICP-MS, while also prone to interferences, is not subject to the many spectral interferences which can occur in GFAAS. Table 4 shows a comparison of results from these two methods. The results compare very well, with %RD (assuming ICP-MS results as the “true” value) less than 12% with no significant determinate error evident.

Table 4. Comparison of GFAAS and ICP-MS results on the same subsamples. All results are in units of mg/kg.

NO.	SAMPLE #	PRODUCT	GFAAS	ICP-MS	%RD
1	277238	chili flavored salt	0.890	0.972	-8%
2	279316	chili flavored salt	0.101	0.090	12%
3	285321	lollipop with chili flavored salt	0.328	0.309	6%

The regulatory status of a candy product containing lead is based on the both the levels found in the product and the intended intake of the product. Since no specific limits have been established in the U.S. for lead in food products, each decision has been based on an *ad hoc* evaluation. In the recent past, FDA viewed candy products that exceeded 0.5 mg/kg, a previous Food Chemical Codex (FCC) standard for sugar, as being potentially violative (note the current FCC standard for sugar is 0.1 mg/kg). More recently, FDA has included the serving size listed on the label of a product label into its considerations. Accordingly, when the total lead exceeds 10 µg per serving, *regardless* of the lead concentration in the product, regulatory action is considered.

While estimates of serving size portions and typical amounts of product consumed are fairly well established for U.S. candies, the typical consumption rates (amount and frequency) of some ethnic products such as Mexican candies and flavored salt products are not. Although the serving sizes denoted on the labels for flavored salts were typically ~1 g, actual amounts of these products ingested by children based on field observations ranged from 10-20 g. The corresponding intake of lead are of concern given the relatively high concentrations of lead detected in some of these products as noted above coupled with the fact children are consuming multiple serving portions on a daily basis. For this reason, the state of California has passed a health advisory [12] and Los Angeles County is considering a ban on importation of products known to contain high levels of lead [13]. Based on this work, FDA supported the detention of this particular product.

Independent of past or current policy in regard to lead, the demonstrated precision and accuracy of each set of sample results is an important consideration in the regulatory evaluation process. The data presented here clearly indicate that high quality results can be obtained even from the most problematic samples.

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