attack as seen in Figure 5a–b appeared to be very localized (arrows) and may not remove all the hemicellulose.

The action of sodium chlorite is to oxidize the lignin of a plant cell wall without extracting carbohydrates from cellulose and hemicellulose. Figure 5c shows the cell wall of sodium chlorite delignified wheat straw. The cell wall showed no disruptions and appeared to be evenly extracted. After trifluoroacetic acid hydrolysis, cellulose is collected in a crucible, dried, and weighed. Figure 5d illustrates wheat straw TFAA with typical cellulose sheets (arrows).

The use of detergents in analyzing for fiber in feeds and forages offered quick, easy, and repeatable methodology; however, possible losses and complications have been described. The chemical action of acid detergent appears to be unsatisfactory for yielding a fraction of only cellulose as the major carbohydrate component; however, it does provide a repeatable measure of fiber in animal rations. The alditol acetate derivatization system for feeds and forages can be used to analyze for cellulose, hemicellulose, hemicellulose sugars, and uronic acids and lignin and offers additional structural information about the fiber components in the plant cell wall.

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Sample Preparation and the Determination of Lead in Chewing Gum by Nonflame Atomic Absorption Spectrometry

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A procedure for the dissolution of chewing gum by combined wet and dry ashing is described. Lead concentrations in ten varieties of chewing gum are determined by the heated graphite tube atomizer technique of atomic absorption spectrometry.

Recent chemical literature reveals an increasing interest in the determination of trace concentrations of essential and nonessential elements in foods and other agricultural products. The elucidation of the exact roles played by these elements in various biological systems is far from complete. The advances of the past decade in the development of extremely sensitive, yet relatively inexpensive, instrumentation such as the electrothermal atomizers in atomic absorption spectrometry have made trace-level analysis widely accessible (Syty, 1974). A particularly useful and thorough review of the methods and techniques used in the determination of metals in foods has been published recently (Crosby, 1977).

An extensive search of the analytical literature has yielded no published methods for the determination of heavy metals in chewing gum. Apparently, this material has not been examined by either atomic absorption or by other modern spectrometric methods of analysis. It became, therefore, the purpose of this study to develop a method for the determination of trace concentrations of lead in gum by atomic absorption with electrothermal atomization. Lead was selected as the first element to be tested because of its health hazard to children at dietary amounts above 300 μg/day (King, 1971).

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It is of interest to note the chemical composition of chewing gum. Gutta, the all trans isomer of rubber is formed by *Palaguium gutta* and *Mimusops balata*, among other tropical plants. Chicle, which makes the chewing of gum possible, is synthesized by *Archras sapota*, an evergreen tree native to Mexico and Central America (Bonner and Varner, 1965). Crude chicle contains gutta, resin, arabin, sugar, calcium, and different soluble salts (Strausbaugh and Core, 1977). In the manufacturing of chewing gum, the crude product is purified and sterilized and flavorings and sugar are added. Chicle is also mixed with jelutong or pontianak, a coagulated latex containing polyisoprene, to produce bubblegum. The annual consumption of chicle and jelutong in the United States ranges between 1000–2000 tons of each material (Archer and Audley, 1973).

EXPERIMENTAL SECTION

Apparatus. The Perkin-Elmer Model 460 atomic absorption spectrophotometer, equipped with the Perkin-Elmer heated graphite atomizer Model 2000, was used for all measurements. The instrument was operated in the "peak height" mode, with other instrument settings as specified by the manufacturer's operating manuals (Perkin-Elmer, 1976, 1977). The Perkin-Elmer Intensitron lead hollow cathode lamp provided the 217.0-nm analytical line. Data were recorded on a Sargent-Welch Model SRG recorder. Chewing gum samples were ashed in a muffle furnace. Ten-microliter aliquots of solutions were injected into the graphite tube atomizer by means of a variable 5–50-μL Finnpipette with pretreated disposable pipet tips.

Reagents. Distilled water was purified by passage through a mixed-bed ion-exchange resin. High-purity Ultrex nitric acid (J. T. Baker Chemical Co.) was used throughout. The listed lot analysis of this acid included a lead concentration of 1.00 μg/L. This produced a blank signal much below the detection limit at the dilution levels used.

A commercial 1000 μg/mL Pb standard solution (Fisher Scientific Co.) was used, and dilute standards were prepared by appropriate dilution with 0.10 N HNO_3. Dilute standard solutions were prepared fresh daily, each piece of volumetric glassware being always reserved for the same Pb concentration as that which had been contained in it previously. Since the walls of volumetric flasks and pipets were thus conditioned to a given level of Pb in the solution, this tended to minimize adverse effects of solution interaction with container walls.

Procedure. In order to reduce the risk of contamination, only new glassware and porcelain casseroles were used in this study. All the glassware and casseroles were initially cleaned with detergent, followed by rinsing with distilled water and by thorough rinsing with distilled–deionized water. They were then soaked for 24 h in concentrated HNO_3, followed by three rinses with distilled–deionized water and by drying in the oven. The disposable plastic pipet tips were similarly soaked in acid and rinsed, followed by drying in a vacuum dessicator.

A weighed sample, consisting of an entire stick of gum, was placed in a precleaned covered casserole and ashed for 4 h at 500 °C in the muffle furnace. Upon cooling, 1 mL of concentrated Ultrex nitric acid was added and the residue was dissolved and then slowly evaporated to dryness on a hot plate. The residue was then ashed again at 500 °C for 2 h. After cooling, 1 mL of concentrated Ultrex nitric acid was added and the sample was diluted with water to 25 mL in a volumetric flask.

Ten-microliter aliquots of prepared sample solutions were injected into the HGA, alternated with frequent injections of the standards. The concentrations of Pb in the chewing gum samples were evaluated by direct comparison to a calibration curve and by the method of standard addition. A fresh calibration curve was prepared daily. The method of standard addition was carried out as follows: 5 mL of the sample solution was mixed with 5 mL of a standard of sufficiently high concentration to cause an approximate doubling of the Pb content in the sample.

RESULTS AND DISCUSSION

Sample Hydrolysis. Neither wet ashing alone nor dry ashing alone were found to oxidize the sample adequately to permit complete dissolution. When a stick of gum was placed in 10 mL of concentrated HNO_3 and allowed to stand for 24 h, the gum remained virtually unaffected. Placing a stick of gum in a muffle furnace and heating for 24 h at 500 °C resulted in incomplete oxidation, as evidenced by the presence of numerous black and grey particles which failed to go into solution upon acidification and dilution.

A combination of the wet and dry ashing procedures yielded a suitable sample preparation technique. It was found that most chewing gum samples dissolved completely if following the initial ashing of the dry stick of gum, the following was done: the sample was cooled; 1 mL of concentrated HNO_3 was added; the sample was dissolved, evaporated to dryness on the hot plate, reashed in the muffle furnace; the ash redissolved in 1 mL of concentrated HNO_3 and diluted to volume in a 25-mL volumetric flask. Following the second ashing period the residue had the appearance of a pure white crystalline powder, without any black or grey particles.

In a few instances, all the final white ash did not dissolve in the 1 mL of concentrated HNO_3, followed by dilution with water. However, in these instances, when the remaining residue was dissolved in another 1-mL portion of HNO_3 and diluted to volume in a 25-mL volumetric flask, no lead signal was detected in this solution. Thus, the single 1-mL aliquot of Ultrex nitric acid seems adequate for the final dissolution step. Only nitric acid was tested for dissolution of the sample in order to avoid the difficulties associated with the use of other acids. Perchloric acid is known to be incompatible with analysis of the sample digest by atomic absorption with electrothermal atomization. Sulfuric acid is undesirable because of its high boiling temperature and the possibility of adsorption of lead on some insoluble compounds which form in the presence of H_2SO_4 (Crosby, 1977).

A series of chewing gum samples were prepared with progressively shortened duration of the first ashing. It became apparent that ashing for less than 4 h resulted in incomplete combustion because the sample was still glowing red when removed from the furnace. Similarly, if the duration of the second ashing was less than 2 h, dark particles remained in the casserole and failed to dissolve upon addition of nitric acid.

The white ash remaining in the casserole following the successful sample treatment dissolved readily in 1 mL of HNO_3, followed by dilution with water, but it did not dissolve either in deionized water alone or in 0.10 N HNO_3.

Selection of Instrumental Operating Parameters. The settings recommended by the Perkin-Elmer instrument manuals (Perkin-Elmer Corporation, 1976, 1977) were used for the wavelength, slit setting, lamp current, drying, charring, and atomization temperatures. The nitrogen flow was not interrupted during atomization because the sensitivity was adequate. Suitable durations for the drying (125 °C), charring (500 °C), and atomization

Table I. Variability of Lead Concentration in One Brand of Chewing Gum

pack and stick no.	weight, g	absorbance[a]	concn of spiking standard, μg/mL of Pb	absorbance[a] after spiking	Pb concn, μg/g
A-1	3.1679	0.059	0.100	0.111	0.286
A-2	3.1658	0.034	0.0600	0.062	0.166[b]
A-3	3.1050	0.051	0.100	0.103	0.265
A-4	3.2120	0.038	0.0600	0.063	0.205
A-5	3.1104	0.044	0.100	0.105	0.213
				av	0.242
				16% = rel. SD	
B-1	3.2321	0.036	0.0500	0.061	0.161
B-2	3.2080	0.030	0.0500	0.058	0.136
B-3	3.2321	0.033	0.0500	0.055	0.166
B-4	3.1753	0.035	0.0500	0.057	0.174
B-5	3.1356	0.025	0.0500	0.052	0.126
				av	0.153
				14% = rel. SD	

[a] Each entry represents an average of at least three repeated injections. [b] An error was made during preparation; the result is excluded from calculations.

Table II. Concentration of Lead in Ten Brands of Chewing Gum

brand	wt of stick, g	calibration curve[a] wt of Pb per stick, μg	calibration curve[a] wt of Pb per gram, μg/g	standard addition[a] wt of Pb per stick, μg	standard addition[a] wt of Pb per gram, μg/g	% difference
no. 1	2.9911	0.189	0.063	0.215	0.072	−13
no. 2	2.8250	0.840	0.297	0.761	0.269	9.9
no. 3	8.0420	0.541	0.067	0.641	0.080	−18
no. 4	3.1386	0.460	0.147	0.488	0.155	−5.3
no. 5	2.2078	0.726	0.329			
no. 6	1.7910	1.12	0.625	1.14	0.634	−1.4
no. 7[b]	3.1753	0.600	0.189	0.610	0.192	−1.6
no. 8	3.2086	0.874	0.272	1.07	0.333	−20
no. 9	3.1912	1.11	0.348	1.37	0.438	−21
no. 10	2.7374	0.806	0.294	1.04	0.357	−19
av		0.727	0.263	0.815	0.281	−9.9

[a] All injections of samples and standards were repeated at least three times and averaged. [b] Represents an average for nine sticks of gum from two packs.

(2300 °C) steps were determined by operating the instrument in the continuous mode and allowing sufficient time for the pen to return to the base line between the heating steps. This resulted in the drying step being set at 20 s, the charring step at 30 s, and the atomization step at 10 s.

Although the absorption signal dropped to zero following the charring peak and preceding the atomization peak, molecular absorption interference was detected for several samples when the wavelength was switched to the nonabsorbing lead line at 280.2 nm. Adjusting the charring temperature up to 700 °C and the charring time up to 80 s did not significantly decrease the peak caused by molecular absorption. The background correction feature of the A.A. instrument eliminated all absorption at 280.2 nm. Similarly, at the 217.0-nm analytical wavelength no molecular absorption was observed with the background corrector turned on. The background corrector was used throughout this study.

Double lead atomization peaks were observed, as expected from the reports of other workers (McLaren and Wheeler, 1977). These double peaks were observed for the chewing gum samples but not for the aqueous standards. The first peak was consistently the highest and it was the one measured. After the instrumental settings had been optimized, the instrument was no longer used in the continuous mode. Instead, it was operated in the "peak height" mode which measures only the highest absorbance obtained during the atomization cycle.

Calibration Curve and Sensitivity. Making 10-μL injections throughout, the calibration curve proved linear up to 0.250 μg of Pb/mL. All the chewing gum samples tested yielded Pb concentrations below 0.05 μg/mL when each stick of gum was diluted to a final volume of 25 mL as described above.

Sensitivity, as indicated by the slope of the calibration curve, was 0.15 ng^{-1}. Defining the detection limit as that quantity which yields a signal twice the size of the average deviation from the mean yielded a detection limit of 2.7 × 10^{-2} ng of Pb, given the 10-μL injection volume.

Reproducibility. Reproducibility was tested by making ten replicate injections of the 0.100 μg/mL of Pb aqueous standard, seven injections of the 3.2194-g sample of gum no. 7 dissolved as described above, and nine injections of the same gum sample spiked with an equal volume of 0.0500 μg/mL of Pb standard. Relative standard deviations were 0.59, 9.5, and 5.8%, respectively. The reproducibility, as well as the signal magnitude, improve slightly when an old graphite tube is replaced by a new one, after the latter is conditioned by several heatings.

Variability of Lead Content within the Same Brand. Lead was determined in the individual sticks of gum in two packages of gum no. 7. The data and results are presented in Table I. There is a difference of approximately 40% in the lead levels in the two packages of the same chewing gum: in the one the average Pb concentration is 0.228 μg/g, and in the other it is 0.153 μg/g. The variations in Pb concentration from stick to stick within the same package were 14 and 16% relative standard deviation from the mean.

Results of Analysis of Several Brands of Gum. In Table II are contained the data and the results of lead determination in ten brands of chewing gum by direct comparison to a calibration curve and by standard addition. The Pb content varied from a low of 0.215 μg to a high of 1.14 μg per stick and from a low of 0.072 μg to a high of 0.634 μg per gram of product. Evaluation of the samples by direct comparison to the calibration curve gave results that averaged 10% below those obtained by standard addition. The percent difference in the two sets of answers ranged from −21 to 9.9%. In view of these differences, evaluation by the method of standard addition is preferred.

SUMMARY

A simple method for the hydrolysis of chewing gum samples was developed and the technique was applied to the determination of lead in ten brands of chewing gum by atomic absorption with electrothermal atomization. On the average, the tested gums contained 0.815 μg of Pb per stick or 0.281 μg of Pb per gram of gum. Future investigations will test the applicability of this sample preparation technique for the determination of trace concentrations of other heavy metals in chewing gum. Preliminary work has shown detectable quantities of several other heavy metals. It will also be of interest to study the extraction of heavy metals from gum under conditions similar to those found in the mouth during the chewing of gum. Even if extraction of Pb into saliva was complete, the detected amounts of Pb are minute compared with the allowable limit of Pb in the diet of 300 μg/day. The lead may originate in the natural products from which the gum

is made or it may enter the product during the manufacturing and packaging steps.

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Cooking Properties of Spaghetti: Factors Affecting Cooking Quality

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The effects of analytical replication, cooking time, and protein quantity and quality on the cooking properties of spaghetti were investigated. Spaghetti cooking quality, as related to cooked weight, cooking loss, and cooked firmness, was determined at specified cooking time intervals. Results showed that replication did not affect analysis and that cooking time was the prime determinant of cooking quality. Protein quantity and quality were also significant factors affecting cooking quality particularly with respect to the maintainance of firmness and cooking stability.

The cooking quality of spaghetti is a measure of its water absorption capacity (cooked weight), cooking loss, and cooked firmness or tenderness. Determination of cooked weight and cooking loss is comparatively simple (Walsh et al., 1971). The objective determination of spaghetti cooked firmness is more difficult. Several techniques have been developed for measuring this quality factor.

Binnington et al. (1939) used a modified Bailey shortometer for measuring the transverse breaking strength of the spaghetti strand and recording tenderness tester for measuring the tenderness of the cooked spaghetti.

Karaesonyi and Borsos (1961) described a torsionmeter for measuring the torsional strength of macaroni and spaghetti.

Walsh (1971) used an Instron Universal Testing Instrument for measuring cooked spaghetti firmness. Cooked spaghetti was placed on a Plexiglas plate and sheared at a 90° angle with a Plexiglas tooth. The work (g cm) used to cut the sample was used as an index of firmness. Statistical analysis of data from replicate determinations showed that the shear test had a high positive correlation ($r = 0.812$) with taste panel scores. Cooking time was 20 min and was selected to place maximum stress on the cooked spaghetti.

Voisey and Larmond (1973) applied the Instron Universal Testing Instrument equipped with tensile test cell, double shear cell, and multiblade test cell. Their results indicated that optimum cooking times for spaghetti ranged from 10 to 18 min and averaged 13 min.

During the spaghetti cooking process the granules imbibe water, swell, and gelatinize. This water penetration and starch gelatinization is dependent on the quality of the surrounding protein network.

According to Holliger (1963), spaghetti containing low protein levels (9%; 14% moisture base (M.B.) imbibed more water and had higher cooking losses than high protein spaghetti (14.1%; 14.0% M.B.). Product shape also affected water absorption and cooking loss. For example vermicelli (diameter 0.9 mm) had a higher water absorption and higher cooking loss than macaroni (diameter 3.6 mm). Holliger also stated (1974) that, in addition to protein content, gluten quantity and quality also influenced pasta product quality.

Sheu et al. (1967) were able to show from reconstitution studies that cooked spaghetti firmness, cooked weight, and cooking loss were primarily affected by the gluten fraction and that starch appeared to have less of an effect on spaghetti cooking quality.

Dahle and Muenchow (1968) noted that protein is an essential structural component of spaghetti and other pasta products. Removal of lipid or protein content adversely affected the retention of amylose. Removal of protein from spaghetti resulted in higher water absorption, higher cooking loss, and greater stickiness, softness, and pastiness.

According to Matsuo and Irvine (1970) the type of gluten in durum wheat had a more pronounced effect on cooking quality than the amount of gluten. A relationship between cooked spaghetti firmness and gluten strength was apparent.

Walsh and Gilles (1971) separated the protein of semolina into albumins, globulins, gliadins, and glutenins. They found that albumin and protein content were negatively correlated with cooking loss and high gliadin content appeared to be related to low cooked weight, low cooked firmness, and high cooking loss.

Irvine et al. (1961) investigated the effect of such factors as wheat type, variety, grade, protein content, particle size, etc. on the farinogram characteristics of semolina. They noted that as protein content increased, dough develop-

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