

COMMUNICATIONS

Determination of Nickel, Manganese, Copper, and Aluminum in Chewing Gum by Nonflame Atomic Absorption Spectrometry

The recently reported method for the hydrolysis of chewing gum was applied to the determination of Ni, Mn, Cu, and Al by nonflame atomic absorption spectrometry. Five samples of two different brands of gum were tested with the following results: $1.5 \times 10^{-4}\%$ Cu in brand A ($2.5 \times 10^{-4}\%$ Cu in brand B), $4.2 \times 10^{-5}\%$ Ni ($4.9 \times 10^{-5}\%$ Ni), $2.7 \times 10^{-4}\%$ Mn ($2.7 \times 10^{-4}\%$ Mn), and $6.1 \times 10^{-2}\%$ Al ($9.0 \times 10^{-2}\%$ Al).

Examination of the research literature reveals only two reports (Boudene, 1977; Fetterolf and Syty, 1979) describing the determination of trace metals in chewing gum. The objective of the present communication is to report the extension of the sample preparation technique used in the determination of Pb in chewing gum by nonflame atomic absorption spectrometry (Fetterolf and Syty, 1979) to the determination of Ni, Mn, Cu, and Al.

EXPERIMENTAL SECTION

Apparatus. The Perkin-Elmer Model 460 atomic absorption spectrophotometer equipped with the HGA-2000 graphite tube electrothermal atomizer was used for all measurements. The instrument was operated in the "continuous" mode during the determination of Cu (the height of the recorded atomization peak was measured), in the "peak height" mode during the determination of Mn and Ni, and in the "peak area" mode during the determination of Al. Other relevant operating parameters are listed in Table I. Data were recorded on a 10-mV strip-chart recorder. Aliquots of solutions were injected into the heated graphite atomizer by means of the variable 5-50 μ L Finnpiquette or the fixed-volume Eppendorf pipets.

Reagents. Commercial 1000 μ g/mL atomic absorption standards (Fisher Scientific Co.) were used, and dilute standards were prepared, using distilled water and sufficient Ultrex nitric acid to make all final solutions 1:100 (v/v) in HNO_3 . All solutions were stored in glass volumetric flasks. The acid blank for standards consisted of 1:100 (v/v) Ultrex HNO_3 in distilled water. The high-purity acid is listed by the manufacturer as containing 0.7 ng/mL Cu, 0.1 ng/mL Mn, <1 ng/mL Ni, and 1 ng/mL Al.

Procedure. The procedure reported earlier (Fetterolf and Syty, 1979) was used for the dissolution of the chewing gum samples. Each sample consisted of a single stick of gum and was solubilized in a final volume of 25.00 mL. The average weight of a stick of gum was 2.7560 g for brand A and 1.8649 g for brand B.

The prepared gum sample solutions were evaluated by both the calibration curve and the standard addition techniques. The spiked solutions were prepared by mixing 0.200 mL of sample with 0.200 mL of an appropriate standard using a micropipet. Fifteen-microliter aliquots of samples and of standards were injected into the HGA for the determination of Al and of Cu, but 30- μ L aliquots were used for Ni and Mn. Two popular brands of chewing

gum were tested (designated brands A and B).

RESULTS AND DISCUSSION

In collecting the data for each metal, all solutions of samples and of standards were tested by making four or five repeated injections. The average deviations from the mean absorbance signals for all the tested solutions yielded the following averages for each metal under the respective experimental conditions: 7.7% for Ni, 6.2% for Al, 1.5% for Mn, and 3.6% for Cu. All measurements of absorbance were made in the linear ranges of the calibration curves. The prevailing experimental conditions permitted the following detection limits: 0.2 ng of Ni (or $7.2 \times 10^{-6}\%$ by weight of Ni in gum, based on 30- μ L injections), 5.6 ng of Al (or $4.0 \times 10^{-4}\%$ Al in gum, based on 15- μ L injections), 0.02 ng of Mn (or $7.2 \times 10^{-7}\%$ Mn in gum, based on 30- μ L injections), and 0.23 ng of Cu (or $1.7 \times 10^{-5}\%$ Cu in gum, based on 15- μ L injections). The detection limit was defined as that amount of metal which yields a signal twice the average deviation from the mean.

The results of analysis of five sticks of two brands of gum are given in Table II. Comparison of the Ni averages indicates that the calibration curve and the standard addition methods of evaluation are equally suitable for the determination of Ni in chewing gum samples. No matrix effect uncompensated for by the background corrector can be detected. The slight variation in Ni content from stick to stick and from brand to brand is of the order of magnitude of the Ni detection limit.

No variation of any significance in Mn content is observed between brands A and B and among the individual sticks of gum. There is only a very slight difference in results obtained by standard addition as compared to those obtained from the calibration curve.

There appears to be significant fluctuation in Cu content among the individual sticks of both brands of gum. Evaluation must be made by the method of standard additions because it raises the results of analysis by an average factor of 1.3 above the values obtained by simple comparison to the calibration curve.

Unlike the behavior of Cu, Mn, and Ni, when the absorbance of Al was recorded continuously while the sample was heated through the drying, charring, and atomization stages, two poorly resolved peaks were observed during the atomization interval. This was observed only with the spiked and unspiked gum samples but not with aqueous standards. The double peak persisted when the wavelength was changed to the 308.2-nm Al line, but no ab-

Table I. Instrumental Parameters Used for the Determination of Aluminum, Nickel, Manganese, and Copper

	Al	Cu	Mn	Ni
wavelength, nm	309.3	324.7	279.5	232.0
slit, nm	0.7	0.7	0.2	0.2
background corrector	ON	ON	ON	ON
drying time/temp	20 s/125 °C	20 s/125 °C	20 s/150 °C	20 s/125 °C
charring time/temp	10 s/1000 °C	10 s/650 °C	10 s/1000 °C	10 s/1000 °C
atomization time/temp	7 s/2700 °C	7 s/2800 °C	7 s/2700 °C	7 s/2700 °C

Table II. Amounts of Nickel, Manganese, Copper, and Aluminum Found in Five Sticks of Two Brands of Chewing Gum

brand A		brand B	
calibration curve	standard addition	calibration curve	standard addition
% Ni			
3.7×10^{-5}	3.9×10^{-5}	3.7×10^{-5}	3.7×10^{-5}
4.1×10^{-5}	4.3×10^{-5}	5.7×10^{-5}	6.2×10^{-5}
4.4×10^{-5}	5.1×10^{-5}	5.0×10^{-5}	5.0×10^{-5}
3.9×10^{-5}	3.5×10^{-5}	4.8×10^{-5}	5.0×10^{-5}
4.7×10^{-5}	4.3×10^{-5}	5.2×10^{-5}	4.8×10^{-5}
av = 4.2×10^{-5}	av = 4.2×10^{-5}	av = 4.9×10^{-5}	av = 4.9×10^{-5}
% Mn			
2.6×10^{-4}	3.0×10^{-4}	2.5×10^{-4}	2.7×10^{-4}
2.3×10^{-4}	2.7×10^{-4}	2.4×10^{-4}	2.7×10^{-4}
2.3×10^{-4}	2.7×10^{-4}	2.4×10^{-4}	2.8×10^{-4}
2.4×10^{-4}	2.5×10^{-4}	2.7×10^{-4}	2.8×10^{-4}
2.2×10^{-4}	2.6×10^{-4}	2.7×10^{-4}	2.5×10^{-4}
av = 2.4×10^{-4}	av = 2.7×10^{-4}	av = 2.5×10^{-4}	av = 2.7×10^{-4}
% Cu			
-	-	1.5×10^{-4}	2.0×10^{-4}
1.1×10^{-4}	1.6×10^{-4}	3.6×10^{-4}	4.4×10^{-4}
1.8×10^{-4}	2.5×10^{-4}	1.2×10^{-4}	1.6×10^{-4}
0.71×10^{-4}	0.92×10^{-4}	1.6×10^{-4}	2.0×10^{-4}
0.78×10^{-4}	1.03×10^{-4}	1.8×10^{-4}	2.3×10^{-4}
av = 1.1×10^{-4}	av = 1.5×10^{-4}	av = 1.9×10^{-4}	av = 2.5×10^{-4}
% Al			
1.5×10^{-2}	5.0×10^{-2}	1.6×10^{-2}	6.0×10^{-2}
1.4×10^{-2}	6.5×10^{-2}	2.6×10^{-2}	10.1×10^{-2}
1.2×10^{-2}	6.5×10^{-2}	3.3×10^{-2}	10.3×10^{-2}
1.4×10^{-2}	7.9×10^{-2}	3.3×10^{-2}	10.6×10^{-2}
1.1×10^{-2}	4.8×10^{-2}	3.6×10^{-2}	8.0×10^{-2}
av = 1.3×10^{-2}	av = 6.1×10^{-2}	av = 2.9×10^{-2}	av = 9.0×10^{-2}

sorbance during atomization was detected at the nearby 312-nm non-Al line, indicating that the double peak is not due to molecular absorbance uncompensated for by the background corrector. Furthermore, the shape and intensity of the double peak remained unaffected by changes in the temperature and duration of either the drying or the charring stages. Thus the possibility of splatter of sample solution away from the center of the tube and toward the cool edges of the tube during the preliminary heating stages appears to be disproved. Consequently, the entire double peak was concluded to represent the atomization of Al and the analytical signal was obtained in the "peak area" mode of the instrument, integrating over the entire atomization cycle.

In the case of Al, evaluation by standard addition yields results that are at least three times higher than those observed from simple comparison to the calibration curve, indicating the presence of a significant matrix effect and pointing to the reliability of only the former method. The extent of the matrix effect can be observed, for example, when 0.200 mL of sample ($A = 0.122$) is mixed with 0.200 mL of 5.00 $\mu\text{g/mL}$ Al standard ($A = 0.323$), and the resulting mixture exhibits an absorbance of 0.076, lower than either of the individual solutions. It is noted that, although

sticks of brand A gum come individually wrapped in aluminum foil and those of B wrapped in paper, the latter brand has a higher Al content.

The detected metals may originate in the natural substances used in the preparation of chewing gum or may enter the product during manufacture and packaging. Even if the extraction of metals into saliva were complete, the detected amounts of metals are minute compared with the known daily requirements and, consequently, must be negligible compared with any recommended limits in the diet which may be established.

LITERATURE CITED

Boudene, C., *Med. Nutr.* 13, 199 (1977); *Chem. Abstr.* 87, 166160y (1977).

Fetterolf, D. D., Syty, A., *J. Agric. Food Chem.* 27, 377 (1979).

Lawrence Kupchella
Augusta Syty*

Department of Chemistry
Indiana University of Pennsylvania
Indiana, Pennsylvania 15705

Received for review October 3, 1979. Accepted February 27, 1980.