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Investigation of Foreign Substances in Food[1]

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KEYWORDS

Food, food contamination, food processing, food technologies, foreign substances, FTIR, Grocery Manufacturers Association (GMA), microanalysis, SEM

ABSTRACT

A foreign substance can be any material allegedly found in a food product that is generally not part of the product formulation. In rare cases a foreign substance could include a natural ingredient added to excess so that it separates from the product. Foreign substances may take the form of mold, bone, fruit pits, herbaceous stems, rocks, insects and other animals, wood, paper, oil, grease, dirt, soil, plastics, metal, and glass (7).

Foreign substances in food can lead to problems for the food industry. When a consumer or a food processor reports finding a foreign substance in a food product, there is a need to determine quickly what it is and where it came from. The food processor needs to determine whether it came from his own operation, from one of his suppliers of packaging and raw materials, or whether the foreign substance came from the consumer who contaminated the food either deliberately or inadvertently. Although the food supply is mostly free of foreign object contamination, the industry faces foreign substance product tampering and recalls, a single one of which can harm a company's reputation and brand name, destroy a business and affect the credibility of the entire food industry.

As of January 1, 2008 the Food Products Association merged with the Grocery Manufacturers Association (GMA). The merged association is now known as Grocery Manufacturers Association (http://www.gmaonline.org/). GMA is of the advocacy, value chain, and science powerhouse for about 360 Food, Beverage and Consumer Products Companies. GMA scientists provide technical assistance to the food industry by investigating foreign substances in foods through GMA's Consumer Claims program.

The objective of a foreign substance examination is to identify the material, the probable sources, and, if possible, whether the foreign substance was in the product when it was processed. Seven categories of foreign substances are discussed here, with two or more case histories in each category. Samples were provided by the food industry.

METHODS

Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM-EDS)

Many foreign substances are received with product residue already removed. These materials are analyzed without further sample preparation and either coated with carbon or left uncoated if charging is not an issue. A Polaron SC7620 Mini Sputter Coater and CA7625 Carbon Accessory were used to coat the samples.

Some foreign substances need to be placed under a stereomicroscope and removed from the product using a metal or plastic probe. They are washed with water or a suitable organic solvent, and air dried prior to analysis. Other foreign materials are too small to remove from the product. They are analyzed while on the surface of the product after air drying the sample. Glass fragments need to be cleaned with dilute acid and washed with distilled water prior to analysis.

Either secondary or backscattered images were obtained with a Hitachi S-3000N SEM. Energy dispersive spectroscopy analysis was done using a Sigma-2 Microanalysis system equipped with a Kevex Quantum Detector (Noran Instruments, Middleton, WI,

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USA). EDS analysis of foreign substances was performed at 30 kV, specimen tilt 29°, working distance 15 mm. The count rate was held at approximately 3,000 cps. Spectra were collected for 100-300 seconds with a dead time of about 25%. Additional information on materials and methods can be found in earlier papers (2,3,4).

Fourier Transform Infrared Spectroscopy

A Nicolet FTIR (Thermo Nicolet, Madison, WI.) equipped with a Magna 560 IR spectrometer was used to analyze foreign substances. The spectra were obtained in the range 550- 4000 cm-1 at 4 cm-1 resolution. The materials were identified using commercial databases using about 16,000 compounds in 14 databases including Toronto Forensics, Georgia State Crime Lab, Hummel Polymer and Additives, Industrial Coatings Food Additives, and Aldrich Condensed and Vapor Phase Libraries. The identification took into account what computer-indicated compounds were the best matches to the LM and SEM microstructure, as well as macroscopic physical properties of materials like solubility, shape, solid versus liquid, and hardness.

Light Microscopy (LM)

Olympus BH2, Nikon Labophot-2, and Bausch and Lomb (Stereo Zoom-5) microscopes were used to locate and occasionally aid in the identification of foreign substances in food.

Spot Tests

Protein and starch in a chocolate bar were confirmed using Coomassie blue and Lugol's solution respectively.

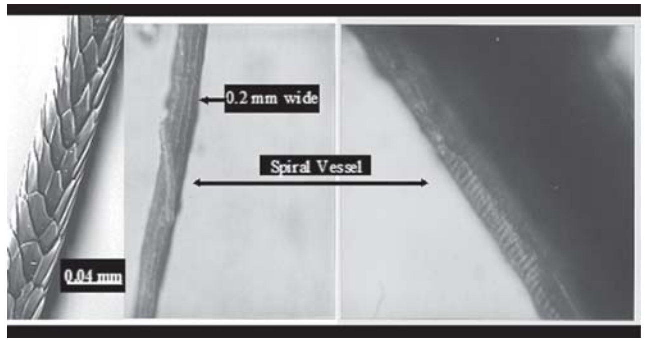

Figure 1: (Left) A animal hair fiber. (Middle) Incident fiber alleged to be a human eyelash. (Right) Spiral vessels in the incident fiber

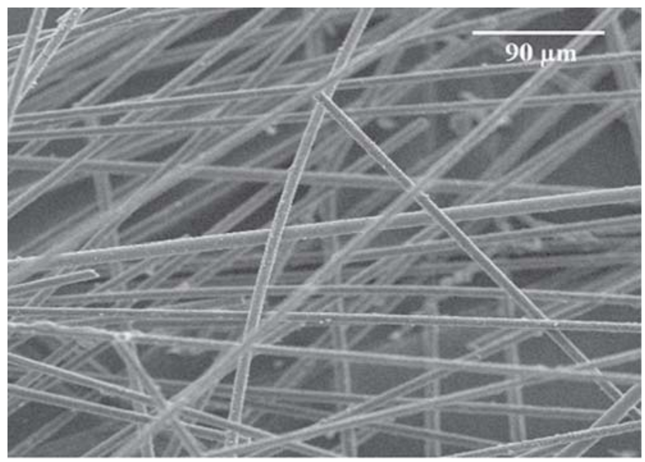

Figure 2: Heat resistant fibers found in a food product.

RESULTS AND DISCUSSION

Mysterious Strands

This category of foreign substances includes fibers composed of plastic, metal, glass, plants, animal and rodent hair, and mold.

The identity of a foreign substance may differ widely from a consumer's identification. The strand in Figure 1 (middle) was submitted by a consumer who said it was an eyelash. The photo on the left shows a typical microstructure of an eyelash. The foreign material is obviously not an eyelash. Using light microscopy, the 0.2 mm wide strand was identified as a plant fiber based on the presence of spiral vessels which are common to all plant materials. The correct identification lessened the seriousness of the complaint and reduced the risk of litigation.

If the exhibit is a food safety hazard, the correct identification helps to resolve the issue expeditiously. The fibers in Figure 2 were submitted as a fiber bundle about 3 inches long. Individual fibers were 0.01-0.03 mm wide. They could not be melted by heating in the flame of a Bunsen burner. The EDS spectrum in Figure 3 shows they are made from carbon and silicon. The silicon was present as a coating on the carbon. They may be silicon carbide-coated graphite fibers intended for use in high temperature applications (6)

Mold sometimes develops in processed food, but these microorganisms form only when the container has been compromised by some type of external abuse. Figure 4 shows representative LM photos of mold at 100x and 500x magnification.

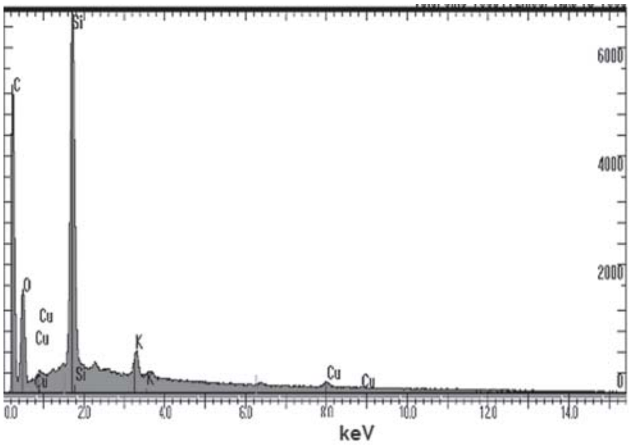

Figure 3: EDS spectrum of the heat-resistant fibers.

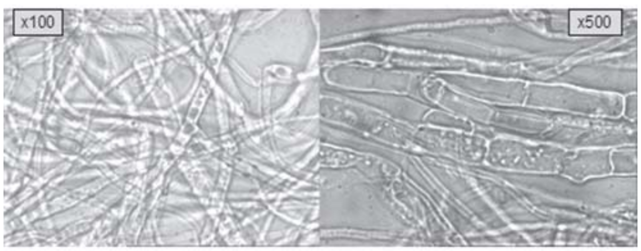

Figure 4: Photo of Mold at 100x and 500 x magnification. Mold sometimes develops in food only when the container has been compromised by some type of external abuse.

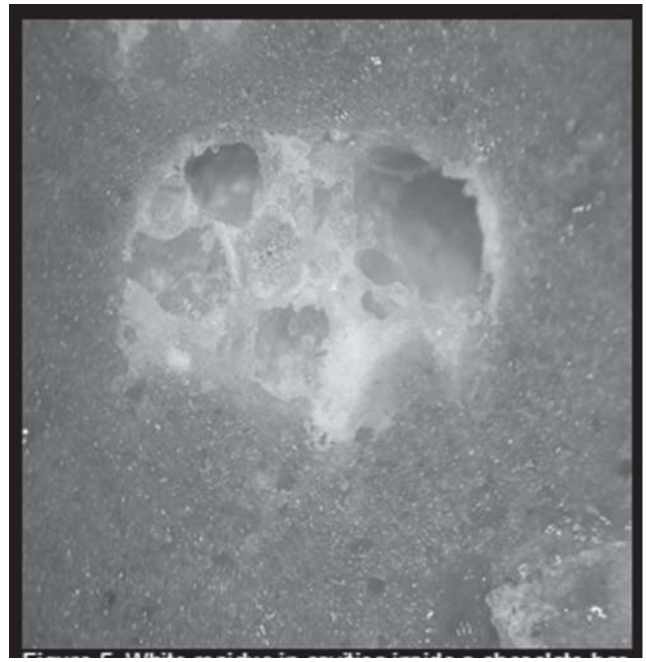

Figure 5: White residue in cavities inside a chocolate bar.

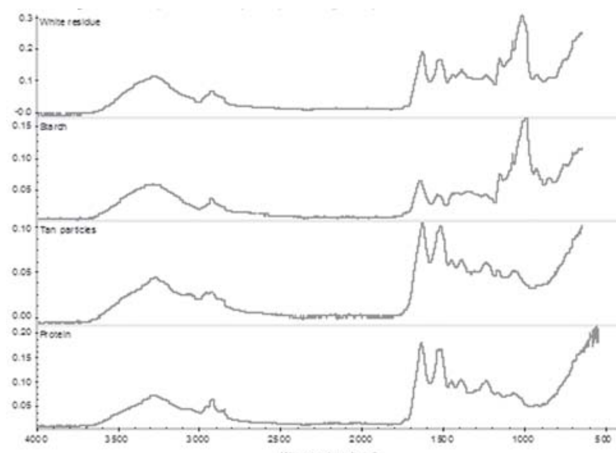

Figure 6: FTIR Spectra of white (starch) and tan (protein) residues in the cavities of the chocolate bar.

Foreign Substances Produced During Food Processing

Occasionally, materials associated with the packing process like metals, glass, paint, or processing aids inadvertently enter the product.

Figure 5 shows white deposits in cavities inside a chocolate bar. Using Lugol's solution, starch was identified by its characteristic black color and was confirmed using FTIR. Using FTIR, tan particles that tested negative for starch, were found to contain protein. Figure 6 shows the FTIR spectra for the starch and protein components compared to standards.

Figure 7 shows a photo of about a 0.2 mm wide particle that caused a fruit juice to become cloudy. The particles are composed of bubbles attached to a solid matrix. Using Commassie Blue stain, the solid matrix tested positive for protein. Using FTIR and SEM-EDS, the bubbles were identified as a silicon-based antifoam agent. Figure 8 shows FTIR spectra for the bubble and an antifoam agent. Figure 9 shows the EDS spectrum for the silicon component.

Figure 10 shows an approximately 0.1 mm long particle that caused a gritty taste in canned chili. Using SEM-EDS, the particles were found to contain silicates of potassium, aluminum and iron. Figure 11 shows the EDS spectrum for the particle. The particles came from the spice used to prepare the chili.

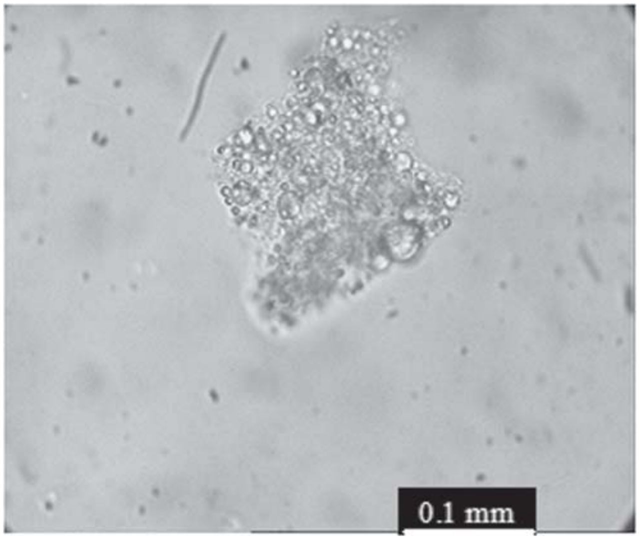

Figure 7: Photo of particles that were found in a fruit juice. They caused the juice to become cloudy. They are about 0.2 mm wide and are composed of bubbles attached to a solid matrix.

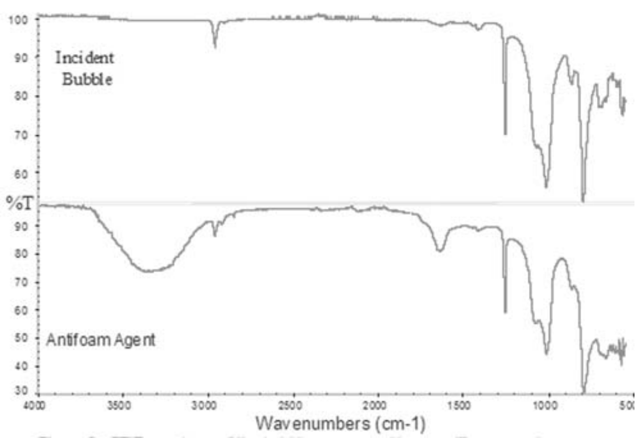

Figure 8: FTIR spectrum of the bubbles compared to an antifoam agent.

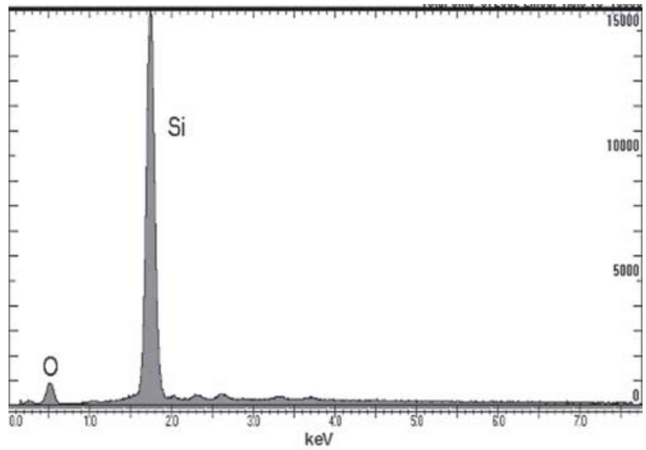

Figure 9: EDS Spectrum of a silicon-based antifoam agent found in chocolate .

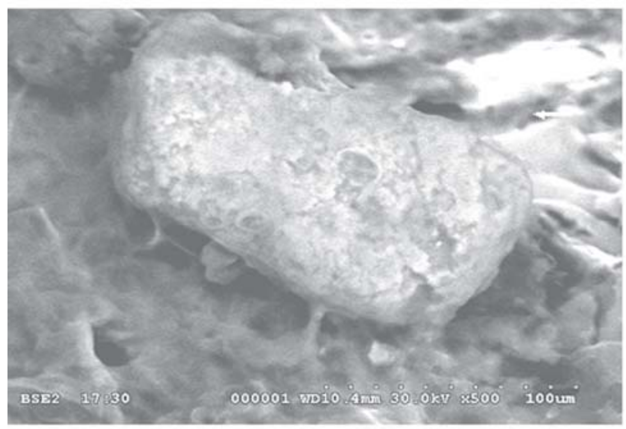

Figure 10: SEM photo of a 0.1 mm long particle found in canned chili.

Glass Fragments

Eight percent of the foreign substances analyzed by the GMA laboratory in 2007 were glass fragments; this is about the same incidence level over the past decade. Container glass accounts for about 50% of the glass fragments. Glass elemental composition plus physical properties like density and shape can be used to identify and help track the source of glass contamination. SEM-EDS can be used to analyze the major elements in glass (2). The analysis is non-destructive and provides a semi-quantitative analysis of glass fragments. Using SEM-EDS, the GMA Laboratory has developed a database comparing glass composition to the source of the glass. With some overlaps container glass, window glass, laboratory ware, automotive, electrical, and architectural glass can be distinguished from each other using SEM-EDS, either by the level of the major elements in the glass or by the presence of elements in one glass but not in another (1, 10). Case histories of glass foreign substance contamination

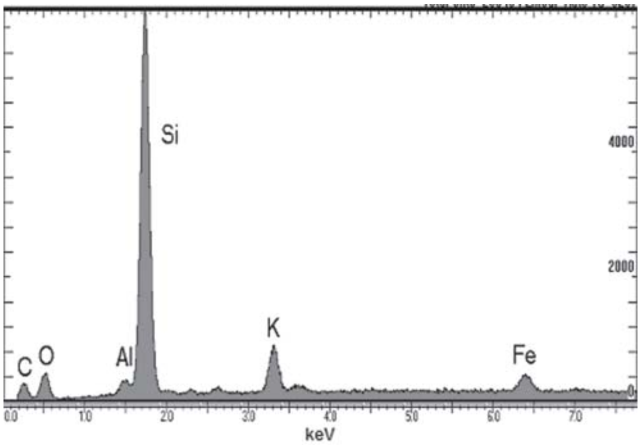

Figure 11: EDS spectrum of the particle from the spice used to prepare chile.

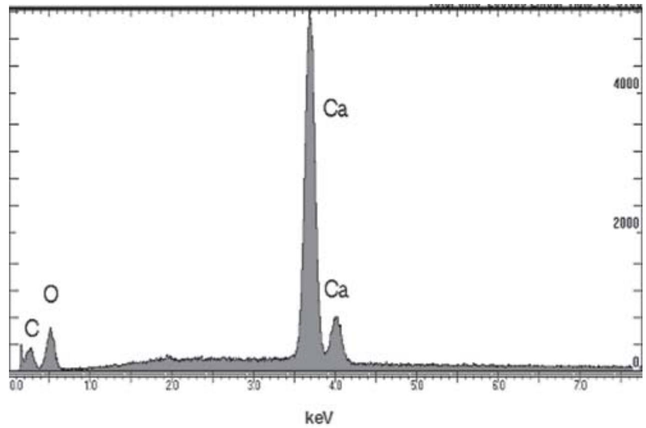

Figure 13: EDS spectrum of the particles found in white grape juice.

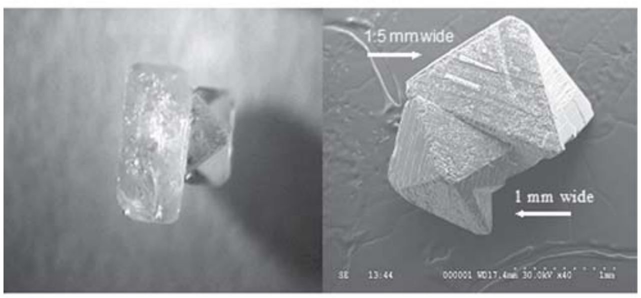

Figure 12: An LM and SEM photo of 2 representative particles found in white grape juice.

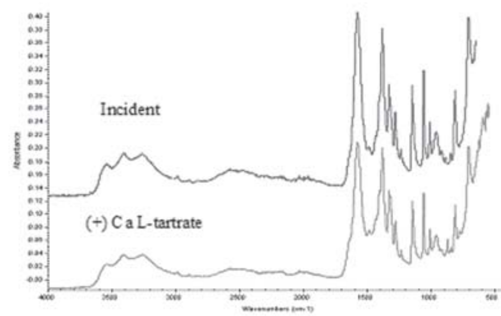

Figure 14: FTIR spectrum of the incident crystals compared to a calcium tartrate reference standard.

have been published earlier. (glass in canned tuna, and canned beets; 2). In the case of foreign substance contamination involving the same type of glass, for example, container glass, trace differences in glass composition in the low parts per million range need to be measured, and SEM-EDS is not useful. A case history of glass foreign substance contamination using a semi-quantitative spectrographic method has also been published (2).

Glass-like Particles

Consumers sometimes mistake glass-like particles for glass. These particles include plastics, cream of tartar, myristic and fumaric acid crystals, rock salt crystals, sugar, struvite (magnesium ammonium phosphate) in canned seafood and anti-caking agents (SiO_2). These materials are easily distinguished from glass using SEM/EDS, LM, and/or FTIR.

Figure 12 shows LM and SEM photos of crystals that were found in white grape juice. Figure 13 shows the EDS spectrum of the particles. Calcium, carbon and oxygen were detected and this suggests the presence of a calcium salt of an organic acid.

Figure 14 shows a good match between FTIR spectra of the unknown crystals and a calcium tartrate standard. Grapes contain both tartaric acid and calcium which occasionally will form crystals in grape juice (8).

Metal Fragments

Metal objects vary in chemical composition and SEM-EDS is an excellent way of determining their composition. Metal foreign substances found in food include: bone, tooth enamel, dental filling, brass rivet, can metal, solder, staples, rocks, coins, needles, straight pins, screws, utility blades, and paint.

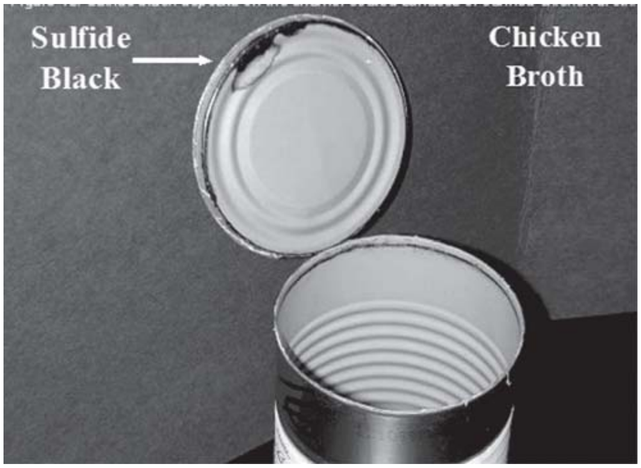

Figure 15: Sulfide black deposits on the enamel-coated surfaces of canned chicken broth.

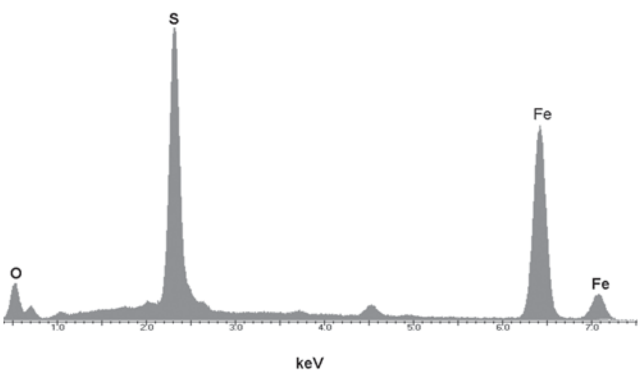

Figure 16: EDS Spectrum of the black deposits on the enamel-coated surfaces of canned chicken broth.

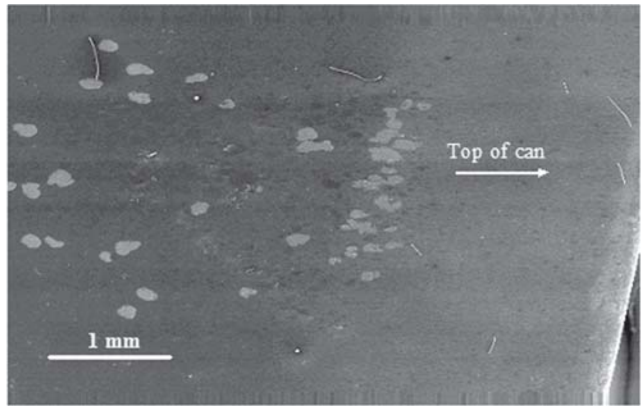

Figure 17: Poor lacquer adhesion under the blackened areas.

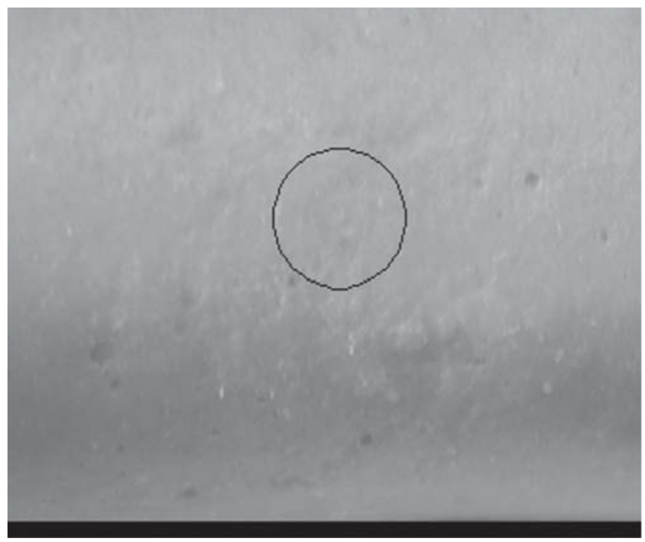

Figure 18: Green discoloration on the surface of sausages.

A key goal of metal foreign substance analysis is to track the source of the material. Figure 15 shows black deposits that formed in the headspace of canned chicken broth shortly after processing and storage. Figure 16 shows the EDS spectrum for the deposit. Iron and sulfur were the major peaks and this suggests that the deposits were composed of black iron sulfide. The source of the sulfur that reacted with the iron was garlic added to the product as a flavor enhancer. Figure 17 shows discontinuities in the organic coating that protected the steel from the can and this was the source of the iron in the deposits. Other SEM-EDS investigations of metal container container-product interactions have been published (2,5).

A green discoloration occurred on the surface of sausages. There were a few green spots on each of the sausage links. Figure 18 shows one of the green spots (inside the circle). The stain was present on the surface of the sausage but not on the casing or in the cross section. Using the backscattered electron detector metal-containing particles, 0.01-0.05 mm, in diameter were detected within the stained area. All the particles contained iron in combination with other elements. Figure 19 shows a 30 μm particle found in the stain. Figure 20 shows its EDS spectrum. The particle contains iron and copper. No iron was found at areas outside the stain. The sausages passed through a salt shower to assist in removing the casings from the meat

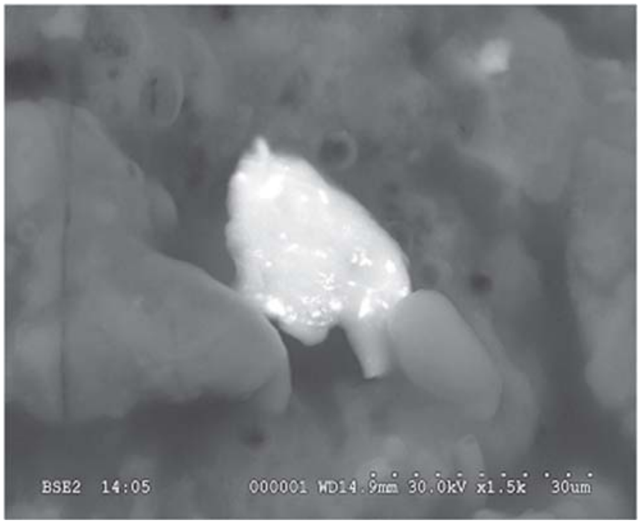

Figure 19: One of several iron-containing particles in the green stain.

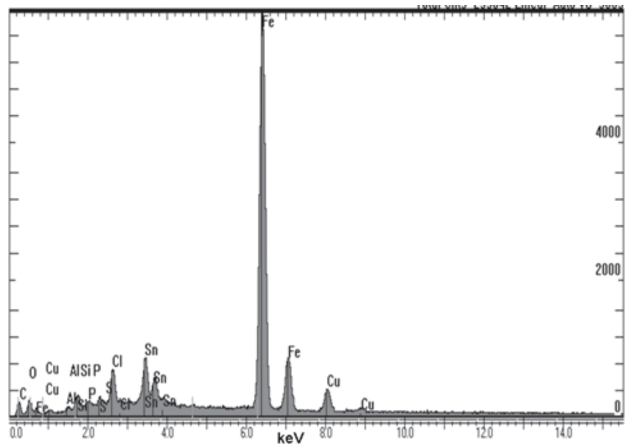

Figure 20: EDS spectrum of the plastic substance found in side clear food package.

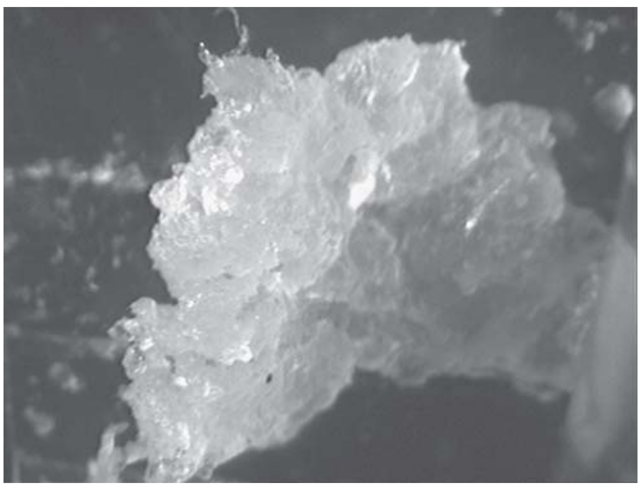

Figure 21: Plastic foreign substance found inside a clear plastic package.

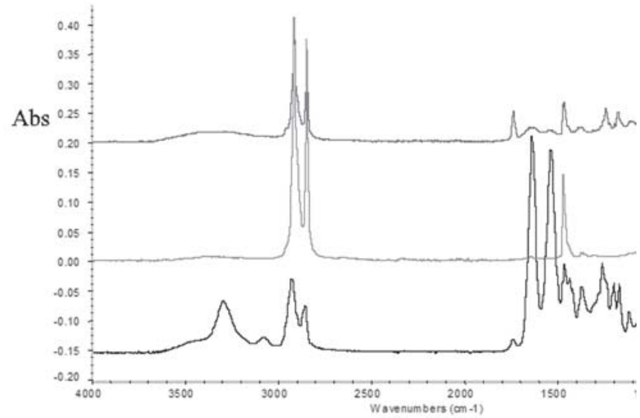

Figure 22: FTIR spectra for the incident plastic, the food contact surface and the outside of the package.

and trace iron contamination was found on individual salt particles. The mechanism for the formation of the green spot may involve oxidation of the meat pigments by interaction with iron from the salt (9). The processor has found the same problem with 2 suppliers of the salt. He'll need to establish specification limit for metal contamination to avoid this problem in the future.

Plastic Pieces

The sources of inadvertent contamination of food by plastic include food packaging and materials associated with the production of the finished product.

Figure 21 shows a plastic foreign substance that was found inside a clear plastic package that contained a food product. Many containers in the lot had the same problem. The material was about 1 inch long x 0.25 inch wide. Figure 22 shows FTIR spectra for a cross section of the incident plastic, the inside, and the outside of the package. This was a laminated package composed of different materials on the inside and outside surfaces. FTIR peaks from the inside and outside materials are present in the spectrum for the incident sample. The incident plastic is a composite of the 2 materials. The making of this package, filling it and heat sealing it was all done by machine. The incident plastic most likely came from excess packaging material left on the heat sealer after the heat-sealing operation.

Cheese sauce packaged in a plastic retort pouch developed a grey discoloration on the food contact surface. Figure 23 shows the grey residue in contact with the cheese sauce and after washing the pouch with water to remove the product. After washing, the grey discoloration and an unknown white substance remained. Figure 24 shows an SEM image of the white material at 180 x magnification. The grey discoloration is not due to particles, but to voids in the white material, up to about 100 microns wide.

Figure 25 shows FTIR spectra for the polyethylene (PE) food contact surface and the polyethylene terephthalate (PET) outside surface compared with the FTIR spectrum of the white residue. The incident material is neither PE nor PET, but its spectrum is a good match for erucylamide (also shown). This compound is a fatty acid amide slip agent used to reduce friction effects in polyethylene film processing. Use of this compound prevents jams in automated packaging equipment. It appears that excessive amounts of this material transferred to the PE during manufacture of the pouch.

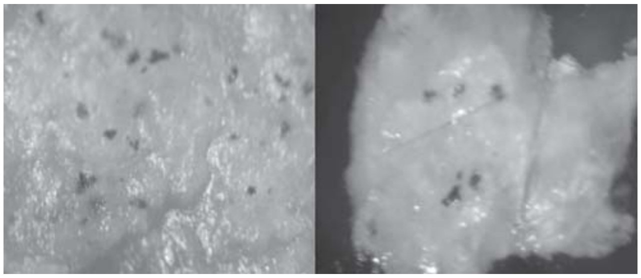

Figure 23: Left photo: Grey discoloration of cheese sauce packaged in a plastic pouch. Right photo: Grey discoloration and a white residue after the washing away the cheese sauce with water.

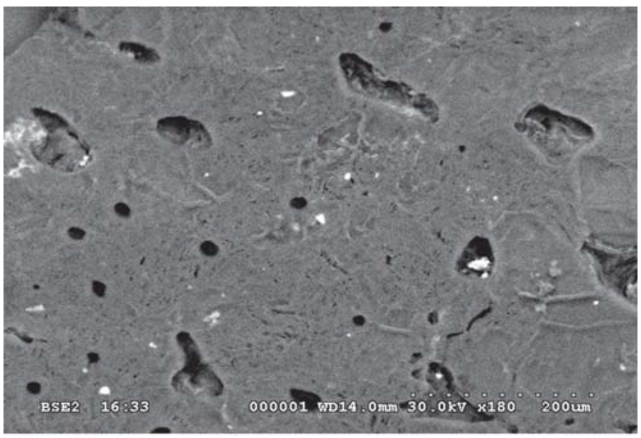

Figure 24: Voids in the surface of the white material.

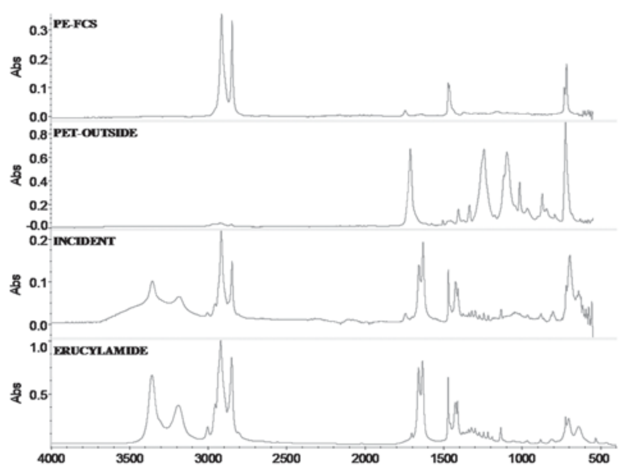

Figure 25: FTIR spectra for the inside and outside surfaces of the package, the incident sample, and erucylamide.

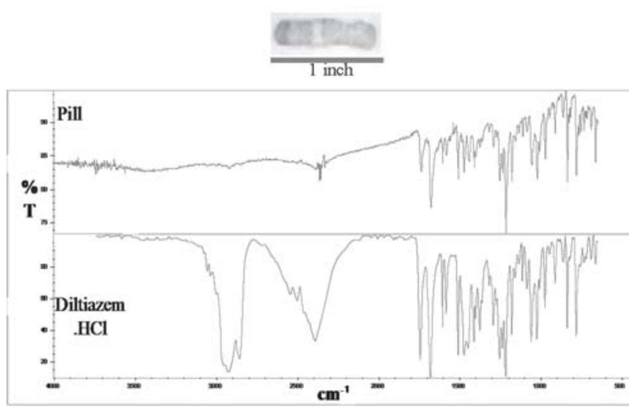

Figure 26: Photo of capsule from a food product, and FTIR spectrum of the incident sample compared to Diltiazem HCl.

Pills

Pills and capsules have been found in processed foods. GMA routinely send pills and capsules to a drug testing laboratory. When a pill is submitted, we usually analyze it by FTIR to see if we can identify the active ingredient. Most times fillers mask the active ingredient. Occasionally SEM-EDS and FTIR can provide useful information to help identify the material.

A food processor submitted a capsule for analysis. We were instructed not to alter the capsule in any way. SEM and FTIR are non-destructive techniques. The EDS spectrum showed that the pill contained both sulfur and chlorine. Figure 26 shows a photo of the capsule and its FTIR spectrum. The closest match from our FTIR database is diltiazem hydrochloride, known by the brand name Cardizem. It contains both sulfur and chlorine. It functions as a calcium channel blocker. The food processor took the capsule to a pharmacy and was able to find a match. It was learned that someone in the claimant's family was taking this medication. The claim was denied. This was a case of product tampering.

CONCLUSION

Food technologists including GMA identify foreign substances and determine where they came from in order to prevent their recurrence. SEM-EDS, FTIR, and LM are valuable tools to investigate foreign substances in food.

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