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# *Food Fraud: Public Health Threats and the Need for New Analytical Detection Approaches*

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The US Pharmacopeia (USP) is an independent, not-for-profit, non-governmental, science-based public-health organization with a rich history of setting public standards since 1820, thus predating the Food and Drug Administration. Of course, most of that history is in pharmaceuticals, medicines and dietary supplements, and we started working on food-testing standards in the *Food Chemicals Codex*<sup>1</sup> (FCC) in 2006. USP is a volunteer-based organization. The information that goes into establishing our standards primarily comes from volunteers in industry and academia, and regulatory agencies, who bring those data to us, and then we have volunteer-cited experts who help to establish and determine whether our methods are suitable for their intended use.

I will discuss economically motivated adulteration (EMA), how it relates to food fraud and the public-health threat. I will talk about gaps in analytical technologies and I'll conclude by describing some of the things that USP is doing to modernize testing methods to deter EMA and fraud.

## ECONOMICALLY MOTIVATED ADULTERATION

I consider EMA to be a subset of food fraud. An expert panel at USP has defined EMA as:

*The fraudulent addition of non-authentic substances or removal or replacement of authentic substances without the purchaser's knowledge for economic gain of the seller.*

The phrase, “without the purchaser’s knowledge,” which isn’t included in other definitions of EMA, is important. With its removal, some people may think that this is what product developers do for a living—finding ways to reduce the costs of food formulations by find-

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<sup>1</sup><http://www.usp.org/fcc/>.

ing replacements for cream, for example, or for meat with soy-protein extender—which is not fraudulent when the product is labeled accurately. Alternative terms are “food fraud” (which we see as a larger term), “food counterfeiting” and “intentional adulteration.” Examples of EMA include:

- Milk diluted with water
- Milk extended with melamine
- Wheat extended with urea
- Turmeric extended with lead chromate, and
- Olive oil diluted with hazelnut oil.

Dilution with water goes back many years to when milk was purchased on the basis of weight; it was easy to add the cheapest possible liquid, water, to artificially increase the value of that material. Of course, standards were developed many years ago to deal with that. Milk extended with melamine is a more modern example, resulting from the use of nonspecific technologies—Kjeldahl and other methods—that assay total nitrogen as an indicator of protein content instead of more specific methods. Wheat extended with urea hits close to home. It happened in the 1980s in Minnesota (FDA Consumer, 1990), and again resulted from using nitrogen as a surrogate for protein content. Several cases of lead-chromate extension of turmeric have been reported in India, where a lot of turmeric comes from. Recently, turmeric was recalled from US stores because of lead contamination (Terry, 2011), the possible culprit being lead chromate which has a yellow color similar to that of turmeric. This example provides a global perspective; what happens halfway around the world can impact us here. The olive-oil industry has had authenticity problems due to dilution with other vegetable oils. Hazelnut oil—commonly used because its fatty acid composition is similar—contains allergens and thus raises potentially serious public-health concerns.

## FRAUD OPPORTUNITY

Factors underpinning EMA include rising prices of agricultural raw materials, complex supply chains, and complex and variable compositions. Many of the new ingredients that we try to define and characterize are not simple food additives, but rather are complex, botanically derived ingredients that are difficult to characterize chemically and can vary season to season and with geographic origin.

Sophisticated fraudsters play into this. Some of them attend conferences on EMA, staying abreast of new technologies and one step ahead of quality-assurance (QA) systems. At USP, we feel that tools are lacking to prevent this sort of activity and, accordingly, it is a focus of our effort. Sociocultural aspects, as they affect ethics and what constitutes fraud, are important. Adherence to driving-speed limits provides a useful parallel. Do you drive right at the speed limit, five miles an hour over, or 10 miles an hour over? Sociocultural norms influence what is viewed as acceptable, irrespective of public-health considerations.

These factors together create an environment conducive to food fraud. No one knows its economic impact, but EMA most definitely is a multibillion-dollar industry.

## PUBLIC-HEALTH CONSEQUENCES

As already indicated, fraudsters understand QA systems and constantly are designing adulterants and new food products to circumvent those systems. The QA system then evolves with development of new detection methods, and the end result is the creation of an endless list of new adulterants.

A good example is provided by cassia oil, an essential oil extracted from the bark of *Cinnamomum cassia* used in foods and other consumer products. For hundreds of years, rosin has been used as an adulterant, but specific gravity and optical rotation provided easy ways to quickly pick this up. Those methods were countered by fraudsters mixing kerosene and rosin together, which turned into a test for rosin specifically and is still described in testing-standard monographs today. As we moved into the twentieth century and the chemical compositions of essential oils became understood, it was discovered that cinnamaldehyde is a dominant constituent, which led to the addition of synthetic cinnamaldehyde to cassia oil to extend it. In due course, radiocarbon analysis was used to reveal the presence of synthetic cinnamaldehyde versus the biobased counterpart. In turn, fraudsters went back to the drawing board and came up with <sup>14</sup>C-enriched synthetic cinnamaldehyde, which can be analyzed only with site-specific natural isotope fractionation-nuclear magnetic resonance (SNIF-NMR), not an inexpensive tool for this purpose.

Food safety presumes knowledge of composition and, when the next adulterant is unknown, from our perspective, food safety collapses to a singularity, and that is the fraudster. The ethics and the knowledge of the fraudster define the safety of a food product throughout the whole supply chain. Melamine provides a good example. With an LD<sub>50</sub> of 3.16 g/kg body weight (rat), it isn't particularly toxic. On the other hand, it caused the deaths of infants and pets. In the case of the pet-food scandal, some fraudsters used inexpensive, scrap-grade melamine that was contaminated with cyanuric acid, which hydrogen-bonds with melamine and creates a toxic co-crystalline complex that precipitates in renal tubules (Dobson *et al.*, 2008). In the case of infant formula, a similar situation prevailed. The melamine complexed with uric acid to form, again, a toxic co-crystalline complex, causing renal failure in infants.

The melamine example demonstrates that the fraudsters' ethics and, in this case, lack of knowledge—they didn't understand the toxicity of melamine and related compounds—defined food safety throughout the supply chain.

## REDUCING THE RISK

A multi-pronged approach is needed to reduce the risk of EMA. Industry resources are being invested to manage their supply chains, know their suppliers and do trace-back, to implement good QA systems and management practices, to introduce HACCP<sup>2</sup> systems in their suppliers, audits, *etc.* Testing is an important component. It “anchors” the food-

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<sup>2</sup>Hazard analysis and critical control points is a management system in which food safety is addressed through the analysis and control of biological, chemical, and physical hazards from raw-material production, procurement and handling, to manufacturing, distribution and consumption of the finished product.

safety system in reality by guaranteeing ingredient authenticity. All QA systems are built on the assumption that ingredients brought into the plant are genuine. For example: it's milk, not milk contaminated with melamine.

In terms of analytical approaches to help verify ingredient integrity, testing for a known adulterant is the easiest thing to do. Liquid chromatography triple quadrupole tandem mass spectrometry (LC-MS/MS) and gas chromatography/mass spectrometry (GC-MS)—relatively simple methods—have been developed to test for presence of melamine. The downside of this approach is that just because an adulterant is known does not guarantee that it will be detected. Melamine is good example. Pet-food adulteration occurred in 2007 and again in 2008, but people were obviously not testing for melamine when the milk-contamination scandal occurred in 2008. The other factor to consider here is that it isn't economical or even feasible to ensure safety by testing for all known adulterants, the list of which keeps growing. And, lastly, unknown adulterants cannot be tested for. It's impossible to anticipate what the fraudster will come up with next, to take preventative action.

The analytical method predominantly used at USP to develop standards is the compendial approach, *i.e.* using identity and purity tests to verify the integrity, the authenticity of an ingredient. The concept is to detect EMA by looking for a decrease in the purity of an ingredient and by examining a fingerprint for an ingredient to check that it matches the known fingerprint. The advantage of this approach is that it can detect both known and unknown adulterants. For example, if melamine is present at a significant level, the specific assay for protein will reveal a decrease in purity, and the melamine will be detected in an ID test. It's a powerful approach, although its development is challenging.

USP's FCC is a compendium of testing standards. The FAO/WHO's Joint Expert Committee on Food Additives has produced a similar book, known as the "JECFA standards." Figure 1 shows the monograph developed at USP for rebaudioside A, a new stevia-based ingredient.

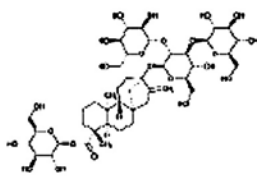
## COMPENDIAL TESTING STANDARDS

It is important to note that compendial methods powerful enough to detect and deter EMA of many widely used food ingredients—*e.g.* wheat gluten, whey—are virtually nonexistent. Identification tests that work in compendial and rapid industrial settings remain to be developed. Many tests that do exist even for simple, single-constituent food additives, are outdated. They are nonspecific, often based on wet chemistry methods like solubility and flame tests. For example, gums, galactomannans, are discriminated by solubility tests that only poorly detect and deter EMA. Easy ways are available to the fraudster to circumvent these.

Regarding purity tests—"assay tests" in FCC—many nonspecific, outdated, again wet-chemistry tests go into these compendial standards that are not sufficient to detect and deter EMA. For example, the use of the Kjeldahl method as a way to measure protein. Many standards use titrimetric methods. Calcium-salt additives are determined by titration against EDTA, which fails to take account of anions that often are the more important constituent.

**Rebaudioside A**

First Published: Second Supplement, FCC 6

**Reb A****Rebiana**Kaur-16-en-18-oic acid, 13-[(2- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 2)-O- $\beta$ -D-glucopyranosyl-(1 $\rightarrow$ 3))- $\beta$ -D-glucopyranosyl]oxy]- $\beta$ -D-glucopyranosyl ester, (4 $\alpha$ )13-[(2-O- $\beta$ -D-glucopyranosyl-3-O- $\beta$ -D-glucopyranosyl- $\beta$ -D-glucopyranosyl]oxy] kaur-16-en-18-oic acid  $\beta$ -D-glucopyranosyl esterC<sub>41</sub>H<sub>72</sub>O<sub>22</sub>

Formula wt 967.01

CAS: [58543-16-1]

**DESCRIPTION**

Rebaudioside A is a white to off-white, hygroscopic fine crystal, granule, or powder having a sweet taste. It is freely soluble in ethanol:water 50/50 (v/v), sparingly soluble in water and sparingly soluble in ethanol. It is obtained from the leaves of the *Stevia rebaudiana* (Bertoni) plant in a multi-step separation and purification process. Principle steps include extraction of steviol glycosides from the leaves using an aqueous or aqueous alcoholic (ethanol or methanol) solvent, and purification of rebaudioside A from the resulting mixture of steviol glycosides by resin adsorption followed by recrystallization from an aqueous or aqueous alcoholic (ethanol or methanol) solvent. It is composed predominantly of rebaudioside A, a glycoside of the ent-kaurenediol diterpenoid aglycone known as steviol.

**Function:** Nonnutritive sweetener; sugar substitute**Change to read:****Packaging and Storage:** Keep dry, and store in tight containers at ambient temperature. <sup>(USP 11)</sup>**IDENTIFICATION****A. INFRARED ABSORPTION, Spectrophotometric Identification**

Tests, Appendix III C

Reference standard: USP Rebaudioside A RS

Sample and standard preparation: A

Acceptance criteria: The spectrum of the sample exhibits maxima at the same wavelengths as those in the spectrum of the Reference standard.

**B. PROCEDURE**

Acceptance criteria: The retention time of the major peak (excluding the solvent peak) in the chromatogram

of the Sample solution is the same as that of the 4750 mg/L Rebaudioside A standard solution in the Assay.

**ASSAY****Change to read:****PROCEDURE**

[NOTE—Rebaudioside A is hygroscopic, and accurate quantitative analysis requires moisture equilibration before analysis. Equilibrate sample and rebaudioside A standard specimens in the lab NLT 24 h before weighing. Intermittent stirring will ensure uniform moisture absorption. The Water content used in the calculation should be determined at the time of weighing and after equilibration.] <sup>(USP 11)</sup>

**Acetate buffer:** Dissolve 0.125 g of ammonium acetate in 900 mL of water, adjust to a pH of 4.3 with glacial acetic acid solution, and dilute to 1 L. [NOTE—It may be necessary to adjust the ratio of ammonium acetate to acetic acid. Changing the pH adjusts the retention time of rebaudioside A and related glycosides. Decreasing the pH of the buffer will decrease the retention time of rebaudioside A.]

**Mobile phase:** <sup>(USP 11)</sup> 13% (v/v) Acetate buffer in acetonitrile <sup>(USP 11)</sup>**Diluent:** 25% (v/v) Acetate buffer in acetonitrile. [NOTE—Allow Diluent to come to room temperature before use.]**Rebaudioside A standard solutions:** <sup>(USP 11)</sup> 250, 1000, 2500, and 5000 mg/L of USP Rebaudioside A RS in Diluent**Stevioside standard stock solution:** 250 mg/L of USP Stevioside RS in Diluent**Stevioside standard solutions:** <sup>(USP 11)</sup> 0.5, 5.0, 25, and 250 mg/L of USP Stevioside RS in Diluent; from Stevioside standard stock solution**Sample solution:** 5000 mg/L in Diluent**Chromatographic system, Appendix 1A****Mode:** High-performance liquid chromatography**Detector:** UV 210 nm**Column:** 15-cm  $\times$  4.6-mm, packed with a propylamino silane phase bonded to silica gel (5- $\mu$ m particle diameter)<sup>(1)</sup>**Column temperature:** 30 $^{\circ}$ **Flow rate:** 1.5 mL/min**Injection size:** <sup>(USP 11)</sup> 15  $\mu$ L**System suitability****Samples:** <sup>(USP 11)</sup> 5000 mg/L Rebaudioside A standard solution and <sup>(USP 11)</sup> 0.5 mg/L Stevioside standard solution <sup>(USP 11)</sup>**Suitability requirements**

**Detector response:** Peak-to-noise ratio (peak height/baseline noise) is NLT 3 for the stevioside peak from the <sup>(USP 11)</sup> 0.5 mg/L Stevioside standard solution, where peak height is expressed in mAU, and baseline noise is the maximum deflection of the baseline (mAU) in a blank at the retention time of stevioside over the same baseline peak width in min.

<sup>(1)</sup>Cosmosil Sugar-D (Nacal Tesque) <sup>(USP 11)</sup> or equivalent.

Figure 1. USP-developed example of a food-ingredient compendial standard: rebaudioside A.

We are looking for ways to bring compendial testing technology into the twenty-first century. Although the technologies exist for many compounds, adapting them for real-time, accurate, and precise use as valuable compendial tools by industry will require tremendous R&D effort.

Figure 2 shows the types of identification tests we are looking at, including non-targeted approaches for making identifications, using rapid spectral techniques combined with chemometrics or multivariate data-analysis tools. With semi-targeted approaches, such as chemical fingerprinting methods, the amino-acid profile of a protein, for example, indicates if it came from soybean or from milk or another source. Isotope-ratio fingerprinting has been used with honey, for example, to pick up the addition of high-fructose corn syrup; the carbon-isotope ratio is affected by whether the source is a C4 or C3 plant; although it's a technology of great utility, no compendial standards take advantage of it.

Other technologies of potential use include PCR, differential scanning calorimetry, rheological methods and microscopy. Although microscopy has been around for a long time, there has been little use of it for botanical identification. For assay or purity tests, simple adaptation of HPLC and GC methods has significant potential and they are the predominant technologies we use for new standards at USP. Similarly, older standards—going back decades—could benefit from the addition of LC and other separation methods.

- **Higher selectivity, instrumental methods**
  - Identification Tests
    - Non-targeted analysis using IR, Raman, or NMR + **chemometrics**
    - Semi-targeted (chemical fingerprinting) using LC-UV/Vis, GC-FID, LC-HRMS, GC-MS, CE + **chemometrics**
    - Isotope ratio fingerprinting: IRMS, SNIF-NMR
    - Other: PCR; DSC; Rheological Methods; Microscopy
  - Assay (Purity Tests)
    - Instrument LC or GC methods

Figure 2. Opportunities to advance compendia testing standards.

## MOVING FORWARD

USP has formed an expert panel on EMA who have prioritized “at risk” food ingredients. Significant effort is being expended in assessing the vulnerability of existing FCC standards from an analytical perspective. We are also trying to generate a repository of historic incidents of EMA in food fraud, to create a baseline of what’s happened in the past to provide insight into how fraudsters have evaded QA systems, and thus reveal vulnerabilities. This will also help risk assessors to identify ingredients that pose the greatest threat.

The expert panel has formed collaborations with people who are working on predictive models for EMA, including Shaun Kennedy<sup>3</sup> and Frank Busta<sup>4</sup>. Also, it has recommended R&D projects to develop new and revised compendium standards on what are viewed as high-risk ingredients, including skim-milk powder, natural colors and cocoa powder.

**PROBLEMATIC INGREDIENTS: USP DATABASE**

We have scoured scholarly literature as well as media articles and collected a substantial database on food fraud for the period 1980–2010, which will be published in 2012. Figure 3, from the database, shows the fifteen most problematic ingredients *vis-à-vis* EMA. Olive oil is no surprise; it garners media attention regularly. Milk was a little surprising for some people. Honey also is the subject of many media reports. Some were surprising to me, such as star anise, which we actually picked up on a couple of years ago and are working

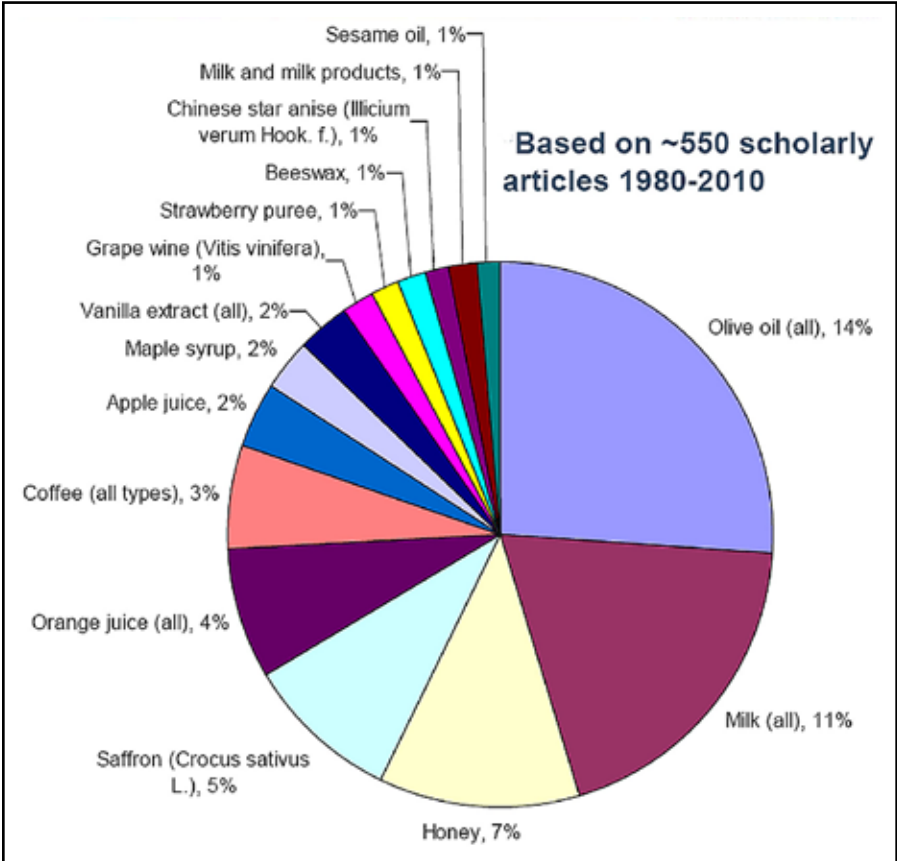


Figure 3. The fifteen most problematic ingredients for EMA.

<sup>3</sup>Pages 191–207.

<sup>4</sup>Pages 15–23, 221–224.

on better standards for Chinese star anise. I didn't expect the inclusion of beeswax, but reports stemming from China indicate that its adulteration is a significant problem.

Skim milk is a vulnerable, high-volume ingredient. In 2008, 8 billion pounds went into food products that impact infants, children and adults. Its nutritional value is based on protein content, with attendant problems mentioned above. No test is available to identify skim-milk powder, and EMA of milk ingredients includes urea in fake milk in India, melamine in China and hydrolyzed leather meal in China. The objective of our project is to develop and validate new compendial testing standards for skim-milk powder that will exclude known and unknown EMA materials. Ten organizations are involved in this collaborative effort comprising more than thirty scientists. We determined early on that there is no magic bullet—no one test solves all of our problems. Each company has unique risk-management approaches and analytical capabilities, indicating that a toolbox of standards is needed.

### RAPID SCREENING

Rapid screening methods are particularly important to industry, where an answer is needed within 20 seconds on whether something looks normal. Also required are rapid confirmatory methods; verification of abnormality is crucial, before removal of an ingredient from the supply chain. Methods for checking purity—*e.g.* for protein as mentioned above—are essential. And, of course, supporting reference materials and spectral libraries are indispensable. Therefore, our skim-milk-powder project has two analytical strategies. One is to create methods that are capable of detecting abnormalities or aberrations in what may be thought of as the fingerprint for a food ingredient caused by a significant level of a known or unknown adulterant. We have some interesting data already for skim-milk powder. Figure 4 shows data from Fourier transform near-infrared (FT-NIR) spectral analysis, a rapid technique that picks up almost every organic compound and

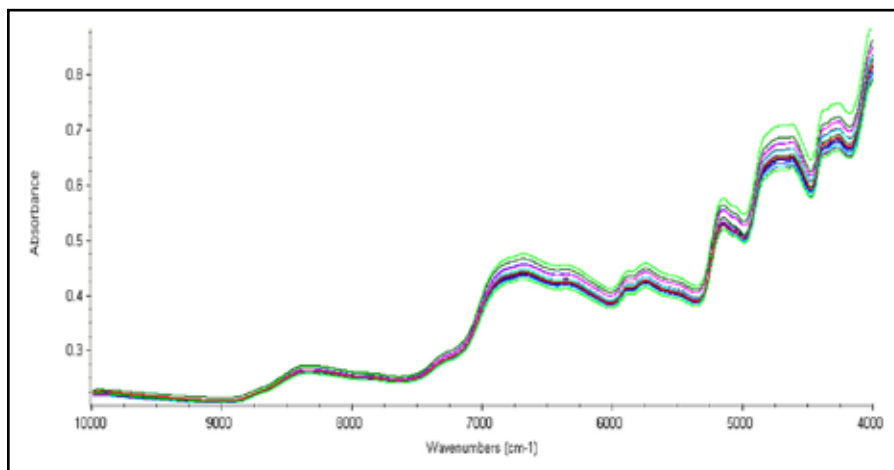


Figure 4. FT-NIR of skim-milk powder, pure and adulterated with 500 ppp to 1% melamine, cyanuric acid, and/or urea.



some inorganic compounds. These are data from a number of authentic skim-milk-powder samples as well as samples that have been spiked with adulterants, melamine, cyanuric acid, urea, or combinations, between 500 ppm and 1%. A spectrometrists may be disappointed that stronger differences are not seen in these data. However, chemometrics teases out subtle differences in the spectral fingerprints; Figure 5 shows these data analyzed by principle component analysis (PCA), successfully differentiating authentic from adulterated materials down, again, to 500 ppm, much lower than we thought would be possible using this approach.

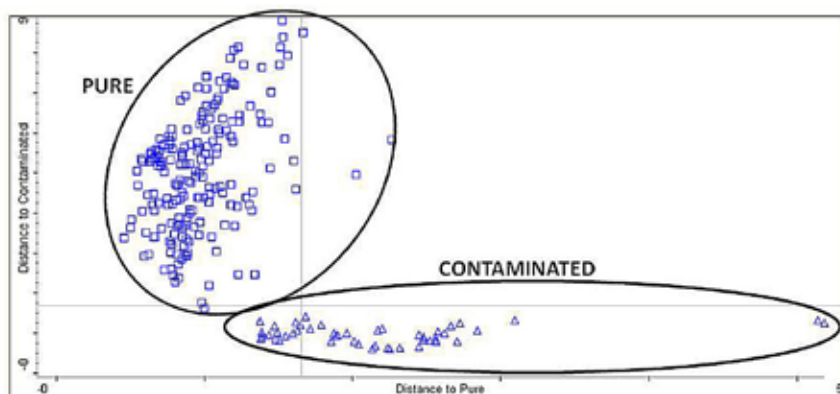


Figure 5. Principle component analysis of the data in Figure 4.

We are looking at other non-targeted analytical methods (Figure 6), including Raman spectroscopy, matrix-assisted laser desorption/ionization mass spectrometry, NMR and LC-high-resolution mass spectrometry. Also semi-targeted approaches are being appraised, including amino acid fingerprinting, intact protein analysis using ultra-performance liquid chromatography and capillary electrophoresis. We envision perhaps a hand-held instrument to scan incoming ingredients with automatic comparisons with a library of authentic data linked with chemometric analysis, providing, say, a green or red light to indicate a normal milk powder or to flag something that looks abnormal for immediate removal from the supply chain for investigation. The interface could look something like Figure 7. The protocol for skim-milk powder might provides a measurement of 85%, below a preset threshold and judged as a failure. With enough data, not only for authentic but adulterated materials, the problem may be rapidly determined and, in this case, a non-authentic protein indicated as being present.

The fusion of more than one orthogonal measurement—termed “data fusion”—provides another opportunity for improved authentication. Biometrics offers a relevant example: combination of fingerprinting with retinal scans and facial recognition provides an infinitely more powerful tool to authenticate a human than fingerprinting alone. Similarly, to authenticate a food ingredient, bringing several technologies to bear simultaneously would create an extremely powerful tool.

- Technologies under investigation
  1. Non-targeted analysis of entire matrix coupled with chemometrics
    - NIR, Raman, MALDI-MS, NMR, LC-HRMS
  2. Amino acids fingerprinting coupled with chemometrics
    - Microwave digestion + UPLC
  3. Proteins fingerprinting coupled with chemometrics
    - UPLC and CE

Figure 6. Skim-milk-powder project: authentication.

**Protocol:** Skim Milk Powder Authentication

**Measurement:** 85%

**Result:** **FAIL**

**Potential Issue:** Non-authentic protein

Figure 7. A possible interface for real-time authentication.

As mentioned, we are re-examining total-protein methods. One of the more promising approaches—albeit not a novel idea—is to define total protein on the basis of amino acid content. We are addressing many challenges, including the use of rapid microwave hydrolysis to decrease the traditional 24-hour hydrolysis to less than 20 minutes in preparation for identifying individual amino acids

Milk powder provides an example of the need for multidisciplinary approaches to make progress. Milk is complex and variable, requiring food and dairy-scientist expertise, as well as chemists to develop analytical tools. We also need chemometric and food-informatic experts to deal with the overwhelming amount of data that will result from many of these approaches. Of course, skim-milk powder is just one ingredient, many others are also at risk. Scientists from many disciplines must combine forces to meaningfully address the problem of EMA.

## IN CONCLUSION

The unknown nature of EMA and the paucity of analytical detection methods means that the safety of counterfeit foods is in the hands of fraudsters—a frightening scenario. A significant gap needs to be filled to develop analytical technologies to detect and deter EMA. Since food and agricultural scientists know the ingredients, they should lead these efforts in collaboration with scientists in other relevant disciplines.

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Dr. Moore has more than eight years experience in food science with an emphasis in functional food chemistry, analytical methods development and validation, and frozen-food research and development. He has authored more than fifteen manuscripts in peer-reviewed food-science journals. Prior to USP, Moore worked for Nestlé. He holds a PhD in food science from the University of Maryland.