

Perspiration Tests Of Consumer Products

By Michael Pickering, Ph.D., Pickering Laboratories

Testing laboratories are essential to economic growth. A rapidly developing global economy requires reproducibility. Eccrine perspiration can react with consumer products to cause health problem and reduce service life. There are many product tests that require artificial perspiration mixtures, but these mixtures don't always approximate natural perspiration and none contain amino acids. Artificial perspiration is used to test bankcards, textiles, jewelry, leather, coating, fingerprint identification chemistry and many others. Analysis of natural perspiration can be used to produce an accurate artificial perspiration. Automating perspiration tests using an accurate perspiration mixture gives reproducibly.

I. Scientific Testing Methodology

The Emergence Of Consumer Product Testing Laboratories

While product testing is probably as old as tool making, scientific testing labs did not appear until the end of the nineteenth century. Railroad companies ushered in the rapid industrialization of the United States, and these companies became the focus of political and fanatical scandal. By the end of the ninetieth century, railroad tracks were crumbling and passenger rail was unsafe. Standards became necessary to insure that steel could stand up to the stress of increasing traffic.

In 1898 scientist and engineers founded the American Society for Testing and Materials (ASTM) to set standards and design scientific tests for products. Their first goal was to set standards for rail steel.

“Scientific testing” means that tests performed by these labs are designed using the scientific method. For example, the first test performed by the ASTM on steel was a scientific experiment. Samples of steel were subjected to “environmental stress” that mimicked those experienced by steel in service. Since this stress was kept constant as the samples were varied, the stress was a control. The testing procedure was described precisely. Physical quantities such as force and time were reported. The goal was to make the test **reproducible**. This also encouraged the manufacturers to use these tests as part of their own **quality assurance** program.

A rail steel standard was an immediate success and a failing rail system was fixed. Independent testing laboratories quickly grew and became successful. Independent labs became a third-party that guaranteed flexibility in markets. The logos of these labs have often transcended recognition of logos of large corporations whose products they test.

Tests set standards, and standards are defined by tests. Today, standards are defined by the ISO (International Organization for Standards) and the ASTM International organizes testing. The ISO represents 155 countries, with its headquarters in Geneva¹.

ASTM International is composed of voluntary members. As of 2007, ASTM had more than 30,000 members. Some members represent industry while others are consultants and academics. Research committees formed of members examine present tests and suggest new tests².

In the U.S., the American National Standards Institute accredits standards and testing procedures. ANSI accreditation signifies that the testing procedure used meets the Institute's standard. Approximately 10,500 American National Standards carry the ANSI designation³.

Testing Labs In The Marketplace

Independent laboratories inspire flexibility in markets; new trends in markets push the need for independent testing. We live in a time when new suppliers and consumers are growing rapidly in emerging economies such as India, China and the Middle East.

In 2007 the American public was shocked by reports of lead in Chinese produced toys, but such reports are testimonies to the efficacy of existing labs and the need for more testing performed at every step of production and distribution. Supply chains change rapidly.

II. Perspiration Testing Procedures

The Need for Reproducible Perspiration Tests

Perspiration is on everything we touch or comes in contact with our bodies. It can react with certain materials and trigger allergies or shorten product service life. While the mechanics of perspirations tests

have been specified since 1947, there is no consensus for an artificial perspiration mixture that will successfully mimic natural human eccrine perspiration.

An artificial perspiration mixture used by the EU for nickel release from jewelry is defined by *EN 1811* comprising: 0.5% NaCl, 0.1% urea, 0.1% lactic acid, and pH adjusted to 6.6 by NH₄OH.

Another mixture for nickel release is defined by ISO 3160-2 comprising: 20g/L NaCl, 17.5g/L NH₄Cl, 5g/L acetic acid, 15g/L lactic acid, and pH adjusted to 4.7 by NaOH.

Denmark uses two *ad hoc* artificial perspiration mixtures for nickel release, one comprising: 4.5g/L NaCl, 0.3g/L KCl, 0.3g/L Na₂SO₄, 0.4g/L NH₄Cl, 0.2g/L urea. The other comprising: 0.3% NaCl, 0.1% NO₂ SO₄, 0.2% urea, 0.2% lactic acid, and pH adjusted to 4.5.

The Japanese also have two *ad hoc* mixtures for nickel release, one comprising: 19.9g/L NaCl, 1.7g/L urea, 1.7g/L lactic acid, 0.8g/L Na₂Cl, 0.2g/L NH₄Cl. The other comprising: 17g NaCl, 1500mL CH₃OH, 1g urea, 4g lactic acid, 1L water.

These conflicting “standards” certainly explain why perspiration test vary from lab to lab, and why testing should be done with an artificial perspiration mixture that is as close to the composition of natural human perspiration as possible.

As it will be shown, real human perspiration contains amino acids in the form of proteins and peptides, yet none are included in the above mixtures. The assumption may be that amino acids have little or no effect, but the history of science shows that disregarded factors often produce surprises.

Perspiration Tests Of Bankcards

Bankcards must be able to endure harsh environments. More than 10 ISO standards address the mechanical, electromagnetic, and chemical tests that successful cards must pass. Many of these tests relate to the magstripe⁴.

The magstripe is a plastic tape containing small particles of a magnetic alloy. This tape is thermally bonded to the card and coated. These particles are magnetically polarized to encode bits of information.

Many tests measure the attenuation of the magnetic signal strength. If this strength gets too low then the polarity of the bits are no longer discernable and are lost. While the magstripe code contains some redundancy, eventually an environment that removes bits can render the card inoperative.

The magnetic alloy must have a high coercivity (requiring strong magnetic fields to erase) and must resist corrosion. While the particles are sealed in plastic tape that is covered by a coating, these coated plastics are permeable to chlorine – the most corrosive ingredient of perspiration. The particles must be small so that the tape is smooth. Their area to volume is thus great and presents a large chemical interface. Corrosion can reduce coercivity and the magnetic particles size. Smaller particles present a reduced magnetic strength.

Barium Ferrite (BaFe_2O_4) has become the bankcard magstripe of choice. Its coercivity is greater than 4000 Oersteds. Purse top magnets, motors, metal detectors or point-of-sales devices designed to erase Electronic Article Surveillance tags do not easily erase it. Barium Ferrite also resists corrosion.

The fact that some chemical tests can affect the magnetic alloy shows that the tape and coating are permeable. Interestingly, some magstripes retain 100% of their bits in perspiration tests, but become inoperative when exposed to concentrated ascectic acid. Optically encoded smart cards pass perspirations test, but show the same wipeout with ascectic acid⁵. In both tests, cards are immersed for 24-hours.

In a recent publication ANSI advocated a review of the immersion time for the artificial perspiration tests, suggesting that 24-hours is unrealistically long. Recent research on the effects of perspiration on money, however, may indicate that bankcards are exposed to the corrosive effects of perspiration for longer periods.

Andrea Dietrich and others researchers at Virginia Tech discovered that the “mushroom-metallic” odor associated with coins was caused by the compound 1-octen-3-one. This compound can be produced by the metabolism of organic compounds in perspiration. Apparently, the amino acids in perspiration form a film around the coins where this reaction can take place⁶. Bankcards are often handled in the same way as coins. This can only argue for a more exact replica of natural perspiration to be used in bankcard tests.

Perspiration Controls To Test Latent Fingerprints

Fingerprint identification is over a hundred years old, but the technology continues to grow.

Latent fingerprints are left on surfaces by perspiration secreted by the eccrine glands on the fingertip ridges. Depending on the porosity of a surface, the perspiration is absorbed. Once absorbed, the latent print is well preserved.

Latent prints are made visible by reagents that attach to amino acids found in perspiration. DFO (1,8-diazafluore-9-one) is most effective on porous surfaces. It attaches to the amino acids in the perspiration and fluoresces red-orange when exposed to a special light. Ninhydrin is most effective on semiporous surfaces. It dyes the amines purple. Cyanoacrylate ester (Superglue) is most effective on nonporous surfaces. When heated the ester vaporizes and forms a white polymer with the amino acids.

To test that a null result is actually the absence of prints and not the results of the detection chemistry interaction with the surface or surface contaminants, Crime Scene Investigation technicians make a control print of their own finger on a similar surface. To standardize this control print, Crime Science, Inc. offers Swetcheck™ artificial perspiration manufactured by Pickering Laboratories and dispensed in single-use sterile swabs⁷.

According to Paul Couture, president of Crime Science, Inc., "Before SwetCheck, technicians applied their own fingerprints onto surfaces to use as controls. However, the results were inconsistent, as individuals do not always sweat. An alternative product is based on a sponge soaked with an amino acid solution. This product does not have all of the same components as real sweat, and has a risk of disease transmission from one individual to another. SwetCheck produces consistent results that more closely mimics real prints without the risk of disease transmission."

Perspiration Tests Of Textiles And Dye

Textiles are a trillion dollar industry. One of oldest technologies, it has initiated industrial revolutions from the first in England to those in emerging countries. Asian textile exports alone are a multi-billion dollar industry.

Natural textile dyes have been used for over 5000 years. The first synthetic dyes were prepared in 1834 from coal tar. Synthetic dyes have replaced natural dyes since they cost less and offer a wider range of colors. Dyes react differently to different types of fabrics. Their reaction is also very dependent on the pH of the dye solution. Proteins in fibers such as wool have side chains. A dye with an acidic group can form salts with the amino groups in these chains. Fabrics like cotton without such chains must be treated with a metallic salt. The dyes then form a chelate with the metal ion.

Metallic salts containing chromium provide strong colorfastness, but can create a health problem. Perspiration can leach chromium from the dye and cause a *contact dermatitis* allergic reaction.

Acid dyes are anionic and attach to cationic groups in the fibers. Basic dyes are cationic and attach to anionic groups and are often used on acrylic fibers. Direct or substantive dyes are water-soluble compounds that have an affinity for fiber, such as benzidine derivatives. They are cheap, easy to apply, and often sold in packages for home use. Since their washfastness is poor, they are no longer used commercially.

The ions in perspiration react with the ionic bonds of dyes and affect colorfastness. Some effects are more pronounced with acidic perspiration while others are more affected by alkaline perspiration. Tests are usually performed with artificial perspiration mixtures having a pH of about 3 and 8.

Reactive dyes attach to fibers by covalent bonds and generally are more colorfast. These dyes show the greatest fading to perspiration when simultaneously exposed to light⁸. Cu-complex azo reactive dyes appear to be the most sensitive, whereas anthraquinone dyes show the best stability. Colorfastness is highly sensitive to pH. Low pH usually increases sensitivity. Inorganic salts usually decelerate fading of reactive dyes⁹.

While it is well known that amino acids in natural perspiration form peptides attached to side chains of fabrics to produce "protein stains," none of the artificial perspiration mixes contain amino acids. Proteases are the most widely used enzyme in detergents to remove such stains since proteases break these peptides into amino acids¹⁰.

Colorfast perspiration tests specify that the fabrics are placed between other undyed fabrics with a given heat and pressure. To test for fading a like fabric is used. To test for washing fastness a different fabric is used. Artificial perspirations with different pH are poured on different places on the fabrics.

An artificial perspirations mixture is prepared and separated into two containers. One is made acidic and the other basic. For example, in one test, an artificial perspiration mixture is made according to (BS 1006 E04: 1978) by dissolving in one liter of distilled water 0.5g 1-histidine monohydrochloride monohydrate ($C_6H_9O_2N_3HCl \cdot H_2O$), 5.0g sodium chloride, 2.5g disodium orthophosphate ($Na_2HPO_4 \cdot H_2O$). One mixture pH is adjusted to 8 and the other mixture adjusted to 5.5 by adding a solution of 0.1N NaOH and 0.1N acetic acid. AATCC Test Method 15-1994 specifies another mixture. This mixture contains 0.25g/L 1-histidine monohydrochloride monohydrate, 1g/L disodium orthophosphate, 10g/L and sodium chloride. The pH are set to 4.3 ± 0.2 and 8.0 by adding a solution composed of 1g/L lactic acid (85%) and 4g/L ammonium carbonate.

Perspiration Tests Of Metal Alloys Used In Jewelry

The growing popularity of jewelry containing nickel has revealed that 12% of the female population and about 6% of the male population are susceptible to *contact dermatitis* nickel allergy. While some countries have banned body jewelry containing any nickel, others allow some, and others have no regulations regarding nickel content.

One of the most contentious issues is the alloy “white gold.” This is an alloy of gold and palladium that may contain nickel. Both nickel and palladium are whitening agents. Increasing the amount of palladium in the alloy helps prevent the release of nickel by perspiration, but palladium is very expensive relative to nickel.

Several manufacturers in the U.S. claim that they have succeeded in producing safe white gold alloys containing nickel. W.R. Cobb in Rhode Island introduced a nickel-gold-palladium alloy called “Prince White Gold,” which is reported to have no skin problem complaints. Also, Stuller in Louisiana launched a white gold alloy containing nickel called “X1”. They claim complete customer satisfaction.

In 1990s, the European Union formed a task force to set nickel content standards. The “Nickel Directive” was proposed in 1994 to set nickel release standards, Perspiration tests varied from lab to lab. Denmark,

Germany and Sweden banned nickel in body jewelry¹¹.

Three European standards were developed that apply to nickel allergies:

EN 1810 references a test method to determine the nickel content in body piercing. The alloy part that comes in contact with the body must not exceed a content of 0.05% by weight.

EN 1811 references a test for nickel products that are intended to remain in prolonged contact with the skin. The product must not release more than 0.5 micrograms of nickel per cm² (surface of the piece) per week.

EN 12'472 references a test to simulate wear and corrosion to determine the nickel released in 2 years of normal use of coated objects.

Ironically, attempts to market palladium-nickel equal-blends have been completely abandoned in the U.S. If you want white gold then the choice is between nickel or palladium alloy, but not any combination of the two, despite claims by the Nickel Institute, "The metal that will determines whether nickel will be released from nickel-containing gold alloys is palladium: the higher the palladium content, the less nickel will be released." Since nickel alloys are 20% cheaper, they are the best sellers.

White gold is a classic example of confusion and conflicting global trade laws resulting from non-uniformity of standards. The lack of a reproducible and more exact artificial perspiration is certainly one of the culprits.

Perspiration Tests Of Leather

Like textiles, leather is tested for colorfastness and strength. Vegetable agents can be used to tan leather, but agents with chromium salts, provides a wider variety of colors, better protection against decay and produces stretchable leather most suitable for garments. Perspiration is the major cause of deteriorating of leather in use. Sodium lactate formed under moist conditions causes the release of chromium, which can trigger a *contact dermatitis* allergy and reduce the shrinkage temperature. The main effect of perspiration on vegetable tanned leather is darkening caused by released phenols due to the increase in pH¹².

Colorfastness tests require cycles of exposure to artificial perspiration and drying and rubbing to-and –fro while being exposed to an artificial perspiration mixture, according to EN ISO 11640-11641. Gray chips compare the end color.

Need For Accurate Reproducible Artificial Perspiration

Perspiration tests have been proscribed since 1947, but little importance has been given to an accurate artificial perspiration mix. Often these mixtures were little more than saline solution with urea and an acid or base to adjust pH. Eventually standards organizations specified mixes for particular tests.

Science literature is abundant with contentious theories resulting from a lack of adequate experimental controls. The lack of rigorous controls often becomes apparent when others try to reproduce experiments.

While it's possible to speculate on the results that inclusion or exclusion of an ingredient will have on testing results, tests are experiments, and by their very nature are empirical. Unexpected consequences often result from ignored reagents.

The mineral and metabolite contents of natural eccrine perspiration were long known by conventional analytic chemistry. The mineral proportions were later refined by mass spectrometry. In 1984 Marshall published the analysis of human sweat proteins by two-dimensional electrophoresis and found more than 400 peptides containing over 20 amino acids¹³. In 2002 Flad *et al* published their analysis using ProteinChip™ technology¹⁴. They were able to investigate samples as small as a µL from many donors and determine differences between slight or copious perspirations. They did not report any significant difference.

These analysis have shown that perspiration contain:

Metabolites: Uric Acid, Lactic Acid and Urea

Minerals: Sodium, Calcium, Magnesium, Zinc, Iron, Copper, Potassium, Chloride, and Phosphate

Amino Acids: Ammonia, Glycine, L-alanine, L-arginine, L-asparagine, L-aspartic acid, L-citrulline, L-glutamic acid, L-histidine, L-isoleucine, L-leucine, L-lysine, L-methionine, L-phenylalanine, L-serine, L-threonine, L-tyrosine, L-valine, and Taurine.

Producing Accurate Artificial Perspiration

Remarkably, none of the many mixtures of artificial perspiration specify any given purity to their constituent reagents. Many of the reagents used could have even small amounts of impurity, and that can explain why many testing results are not reproducible.

Pickering Laboratories artificial perspiration is a product of instrumentation analysis and control. Pickering Laboratories artificial perspiration is mixed accurately to reproduce the above analysis. Furthermore, to insure that there are no impurities, only reagents that are chromatographic pure are used. Impurities are thus on the order of a femtomole.

Regular Pickering Lab's artificial perspiration has a pH of 4.5, but it can be ordered with a pH between 3 and 8. Regular orders are prepared fresh with a preservative and have a 1-year shelf life. The amount of the preservative is orders of magnitude below the other constituents.

Pickering Lab's artificial perspiration can be ordered sterilized without a preservative. Sterilized artificial perspiration is delivered frozen. This is the best choice if the test is to replicate the effects of increasing metabolites as a result of natural flora.

Designing A Perspiration Test

A procedure for developing a perspiration test of coatings that prevent corrosion to metal was published by Marsh¹⁵. Existing tests were examined and a systematic approach was developed to analyze the intermediate results of an essentially pass/fail test. That is, Marsh devised methods for examining the action of the artificial perspiration reaction on the coating during the exposure until the final pass/fail. He developed a general procedure to design tests as well as a specific test for the perspiration corrosion of coated handles of shopping carts.

Marsh examined two tests for perspiration on coated metal – an ANSI test for effectiveness of coating to protect metal from corrosion, and a Volvo test to check leaching of chrome through coatings. The ANSI test was chosen with its mixture for artificial perspiration containing by weight: Sodium Chloride 5%, Acetic Acid 5%, Butyric Acid 3%, Valeric Acid 3% and Deionized Water 84%.

This ANSI test requires that the metal be exposed to the artificial perspiration and periodically rubbed with a #2B pencil to simulated service abrasion. According to Marsh, the pass/fail point is too subjective since it requires that the tester determine when the zinc-plated steel is beginning to degrade. Marsh designed a test using electrical impedance spectroscopy (EIS).

The coated metal is one of the capacitor plates while the other is a probe. A $\pm 10\text{mV}$ signal was sweep from 0.1Hz to 30KHz by a single channel ACM autoAC DSP (1996 model). Samples were abraded using a #2B pencil after each 15-minute exposure period, before EIS measurements were taken. This test was conducted for an hour.

Since a capacitor with an ideal dielectric (approximated by the coating) exhibits only the reactance component of impedance, resistance indicates that some of the ingredients of the artificial perspiration are penetrating the coating. An end point of this test can be determined objectively by setting a resistance that corresponds to field service failure experience. Marsh chose a resistance of $100\Omega/\text{cm}^2$ as the failure point for the shopping cart handles.

This was not a simple pass/fail test, but it produced a graph that documented the degree of failure. Coating manufacturer can use such a graph to develop coatings by examining the time points as the coating failed. Also, this graph can be used to monitor the testing procedure. By doing several tests differing only in the manner that the #2B pencil is used to simulate service, differing results might emerge from different technician performing the test. Also, the end point is fixed by an instrument reading. This might suggest that whenever possible procedures and endpoints should be determined by instrumentation. For example, the abrasion test should be replaced with a more reproducible electromechanical computer-controlled device.

The artificial perspiration mixture used in this test, as every other, lacks amino acids. The coating was exposed to artificial perspiration for an hour. The assumption is that this period replicates service, but if the cart handles hold a film of amino acid like coins do, then these handles are exposed to captured perspiration for long periods. Similar EIS tests could be well suited to make tests of dielectric surfaces since they can quickly determine the magnitude of any activity that is taking place. If it's determined that a culture increased the metabolites during the test, then a sterilized artificial perspiration mixture should be used.

This test could not be applied directly to bankcards since EIS require electrodes on both sides of the dielectric, but it could be used to develop and manufacture coatings. This would also answer many questions regarding exposure time and the efficacy of using an accurate artificial perspiration mixture. Experimentation has become more reproducible by instrumental analysis and control; the same should be applied to product testing.

Dr. Michael Pickering is the President of Pickering Laboratories, Inc.
800-654-3330
support@pickering.com

References:

1. www.iso.org
2. www.atsm.org
3. www.ansi.org
4. ISO/IEC JEC 1/SC 116, 2001-10-08, Identification Cards
5. Wayne Tompkin, "Enhanced Physical Logic Security," <http://csrc.nist.gov/publications/nistir/IR-7056/Security-Privacy/Tompkin-enhanced.pdf> p22.
6. Philip Ball, "A metallic smell is just body odour," BioEdOnline. www.bioedonline.com October 25, 2006.
7. www.crimesciences.com
8. Asim Kumar, Roy Choudhury, Textile Preparation and Dyeing (Barns & Noble ISBN-13: 9781578084043, 2006) p.369
9. Dehua Zhuang, Liyuan Zhang, Dawei Pan, Jinxin He (2007) "Fading of reactive dyes on cellulose under light and perspiration," Coloration Technology 123 (2), (2007) 80–85.
10. Guy Broze, Handbook of Detergent, Part A: Properties. (CRC Press ISBN 9780824714178, 1999). p472.
11. Modern Jeweler, July 2006, [www.modernjeweler.com/print/Modern-Jeweler/White-Knights/1\\$109](http://www.modernjeweler.com/print/Modern-Jeweler/White-Knights/1$109)
12. Monon Kite, Roy Thomson, Conservation of Leather and Related Materials, (Elsevier. ISBN 0750648813 2006) p.52
13. T. Marshall, "Analysis of human sweat proteins by two-dimensional electrophoresis and ultrasensitive silver," Analytical Biochemistry. 139, 2, 506-509 (1984)
14. T. Flad, R. Bogumil, J. Tolson, B. Schitteck, C. Garbe, "Detection of dervcidin-derived peptides in sweat by ProteinChip™ Technology," J. Immunological Methods (2002).
15. J. Marsh. Using Electrical Impedance Spectroscopy (EIS) to Support Conventional Artificial Perspiration Testing. The Journal of Corrosion Science and Engineering, V2 Submitted August 1999

-end-