GMP
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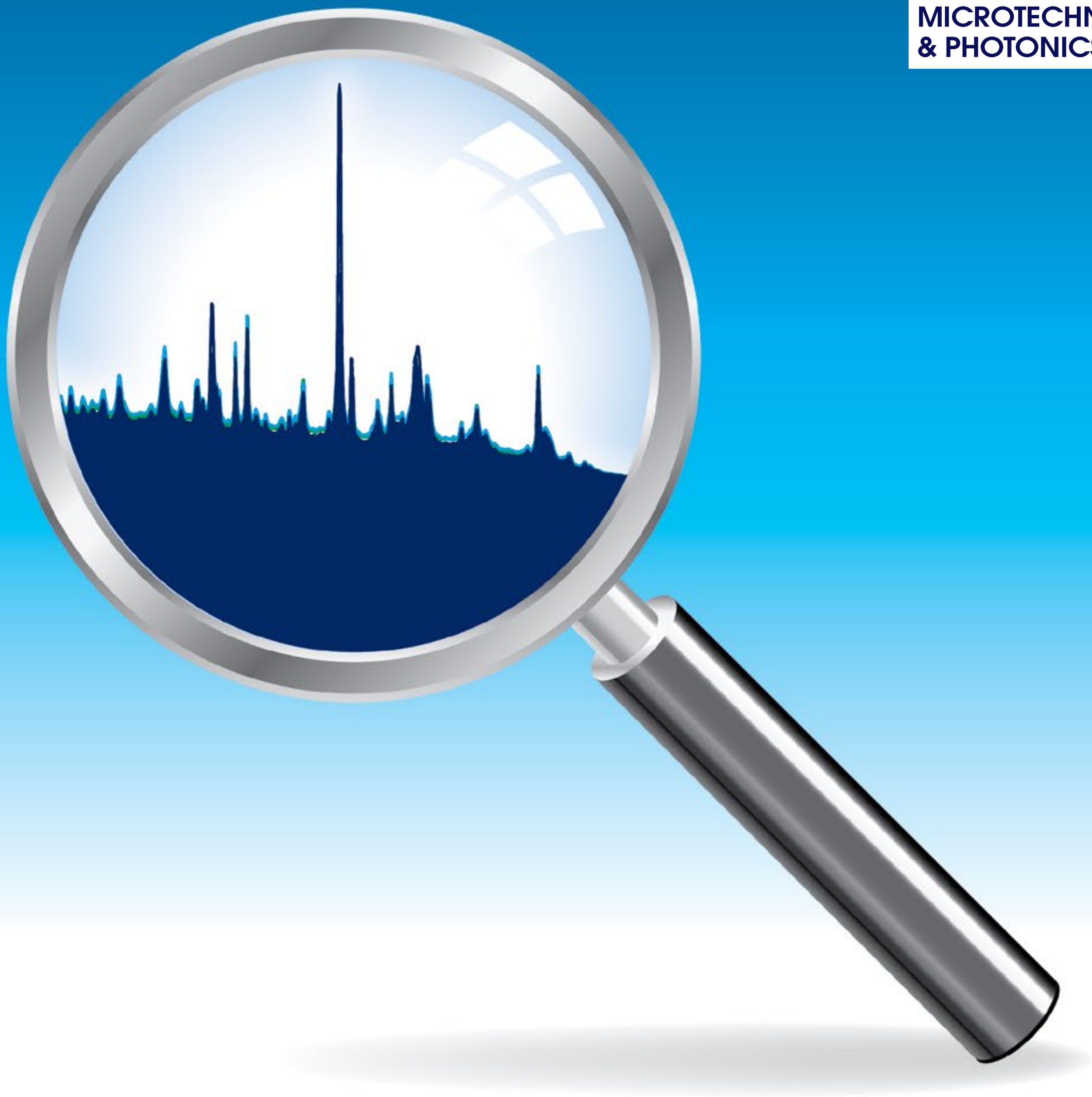


Ocean Optics

AUTHENTICATION & ANTI-COUNTERFEIT

SPECTROMETERS | ACCESSORIES | SUBSYSTEMS | COMPLETE SOLUTIONS

Table of Contents

Our new James Clerk Maxwell T-shirts have arrived! Turn to the back cover to find out how to win one of your very own.

Introduction

Is it real? Is it safe? Is it worth the price I'm about to pay? These are questions Ocean Optics has been helping customers answer for years using spectroscopy. Our modular spectroscopy systems offer the flexibility to look at materials using more than one method, switching between reflectance and transmission, or from identifying optically tagged objects to measuring powders and liquids. We've worked with OEMs to convert laboratory test setups into compact, field-ready systems yielding a clear yes/no answer. Through the following pages, you'll learn how, and equally importantly – why.

Why Authenticate?

According to the International Chamber of Commerce, counterfeiting is one of the fastest growing economic crimes, with an estimated annual cost of more than $1 trillion worldwide. The globalization of trade gives consumers access to a far wider range of goods, but with far less information about where and how those goods were produced. Growing populations are driving demand, while resources to meet that growing demand become increasingly scarce.

The vast majority of counterfeiting is economically motivated – not only by companies and individuals seeking to increase their own wealth, but also by organized crime and military groups aiming to fund illegal activities. Counterfeiting affects us all, from the quality of the food we eat to the impact on our economies of forged currency and laundering of subsidized fuel. It costs us as consumers, and devalues the brands on which we depend.

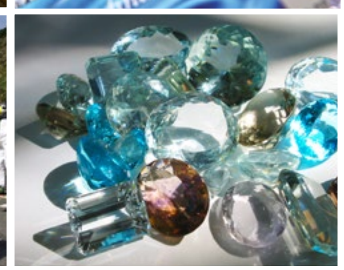
Ocean Optics modular spectroscopy systems offer many ways to counter fraud, from measuring novel optical materials and features to bank note validation to Raman detection systems for explosives and illegal narcotics. Optical authentication has the potential to save lives, whether from reduction in illness and death due to food fraud and counterfeit pharmaceuticals or ensuring basic safety from terrorist attacks.

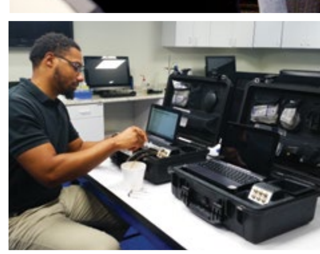
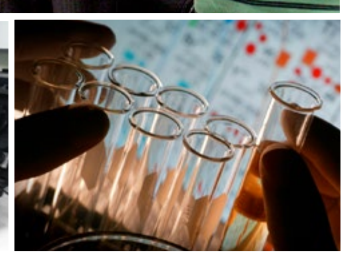
Optical Solutions

Those on the front lines responsible for identifying and authenticating the nature of goods and materials need robust equipment based on sound science. Compact spectroscopy systems fill that role well on many levels; not only can chemometric analysis and fingerprinting techniques be used to identify origin and quantify mixtures, but far more optically sophisticated tags and dyes can be integrated into goods for anti-counterfeiting. The power of spectroscopy exceeds all of our senses together, for it probes the very nature of materials. Like a high-definition image, it exposes every flaw in the intended artifice. Whether in the lab or in the field, Ocean Optics has the experience to help you create an optical solution for your authentication needs.

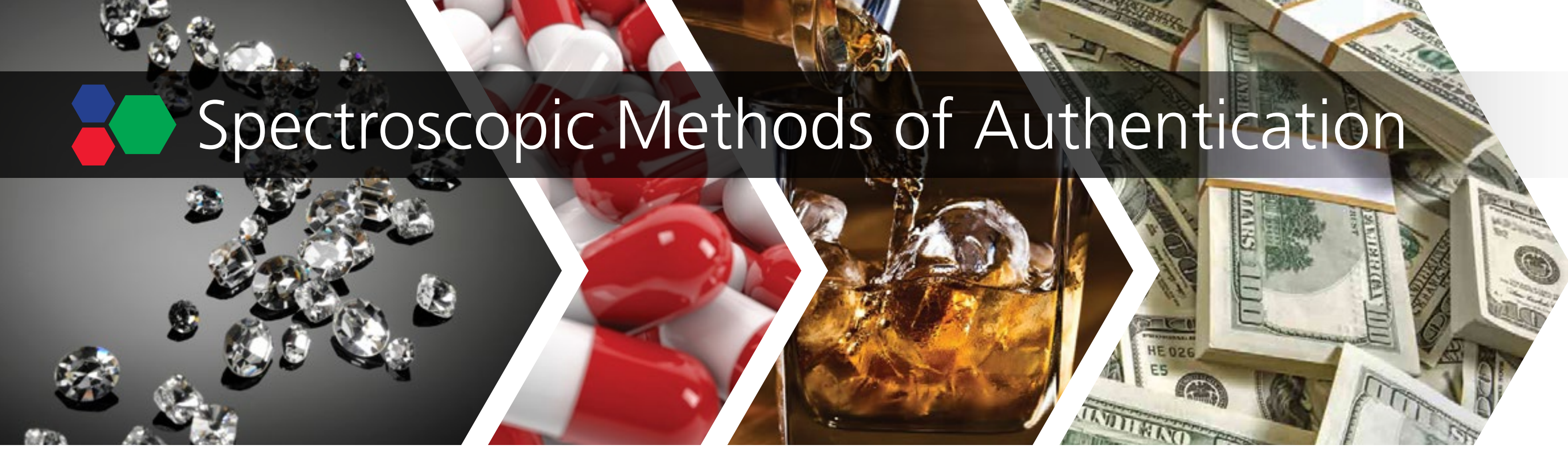






Spectroscopic Methods of Authentication



Authenticating an object or substance often begins with visual clues like color, texture and structure. Experts are trained to recognize the most subtle deviations from genuine product, even using taste and smell. Microscopic evaluation can also be helpful, as can chemical analysis like HPLC, GC-MS or FTIR. These methods, however, are not conducive to rapid field testing by non-experts, and can require that a portion of the sample be consumed or sent to a central laboratory for complete evaluation.

Spectroscopy offers several alternative and complementary techniques that allow non-destructive testing or use of very small samples to achieve identification or authentication. When performed with compact, modular spectrometers, the measurement can be taken to the sample, offering several advantages:

- Rapid on-site analysis of precious or historical objects
- Instant material ID in the field for defense and security
- Authentication at multiple points in a supply chain
- Spectral imaging to look for evidence of tampering

Reflectance and Absorbance

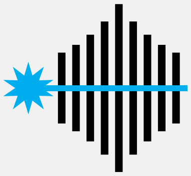
Reflectance and absorbance measurements probe the chemical composition of a material directly via the wavelengths absorbed when light is transmitted through or reflected from the sample. Absorbance is most often used for liquids, as Beer's Law simplifies quantitative analysis. Reflectance yields similar information for solids, and has the benefit of being non-contact and non-invasive.

Spectral data acquired in the visible range (380-780 nm) can be used in place of more subjective human assessment of color, as might be done to authenticate a painting. UV spectra reveal the electronic transitions in a sample, like the characteristic absorption bands for picrocrocin and safranal used to evaluate the quality of saffron. NIR spectra offer a multitude of peaks attributable to vibro-rotational transitions, offering insight into composition that can be used to distinguish grains and thereby validate gluten-free cereals.

Fluorescence and Luminescence

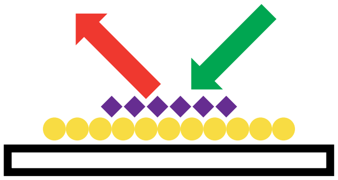
Luminescence is often used for authentication in combination with other forms of spectroscopy. It may act as a complementary technique, as in gemstone analysis, or be one layer in a suite of security features, like the fluorescent graphics used in passports. Not all compounds fluoresce, and even in similar materials, small differences in composition, size or shape can cause the fluorescence spectrum to be unique. This is useful, particularly when the fluorescent compound used for authentication has been placed there deliberately as a means of fuel marking or bank note authentication. Invisible under regular lighting, luminescent features appear only when excited by high intensity light of a certain wavelength, and can be characterized by their spectrum or their lifetime. Fluorescent pigments, inks and coatings are often used in document security.

Raman Spectroscopy

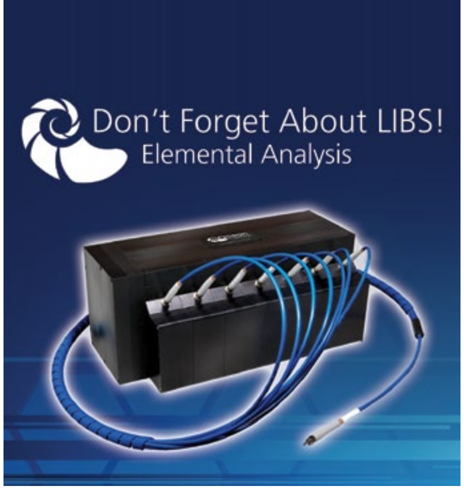


When laser light is scattered off a sample, one in every million photons returns with information about its chemical composition. Many of the same peaks seen in an NIR reflectance or absorbance spectrum can be probed equally well using Raman spectroscopy, without spectroscopic interference from water. Each compound has its own unique Raman fingerprint that can be stored in a library, then compared against unknown samples like explosives or narcotics for rapid identification. Not only is this method non-contact, but it can penetrate glass and plastic packaging. This eliminates the need to open bags or bottles, thus reducing potential contamination of evidence and the risk of exposure for personnel.

SERS (Surface Enhanced Raman Spectroscopy)



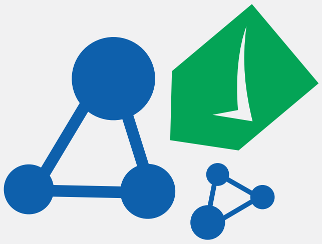
Metal colloids and nanostructures have been found to enhance the Raman effect by a factor of up to 100 trillion, spawning a new technique for trace detection of materials known as SERS. A full Raman spectrum is still acquired, allowing rapid and conclusive matching to a library of known compounds, but the options for sampling are further expanded. A fruit can be swabbed for pesticide residue and then inserted into a SERS scanner, or a surface can be swept for trace explosives. Narcotics have been detected in saliva, and pigments identified using the tiniest of samples. Measurement down to ppb concentrations can be accomplished, combining both sensitivity and specificity.



Laser-Induced Breakdown Spectroscopy (LIBS) uses a laser to create a microscopic plasma on the sample surface, followed by spectroscopic detection of the many atomic emission peaks of the constituent atoms. LIBS is used for authentication of materials as diverse as spices, pesticides, documents and art. It is even being investigated as part of a method to identify the origin of stones stolen from historic sites throughout the UK.

Read more at optics.org/news/6/7/36

Optical Tagging



Optical tags expand the detection options in authentication by deliberately adding a specific material to the item of value for the purpose of measuring it later for validation. By adding a specific concentration of a tag or marker, quantitative detection can be used to identify dilution with substandard materials, or blending of material from multiple sources, as in fuel marking. An effective tag or marker must be durable, difficult to mask, easy to detect with the right equipment, adapt to multiple media and be sufficiently complex to deter replication. Fluorescence and SERS are popular techniques for detection of optical tags and markers, though any spectroscopic method could be used.

Food Security

A century ago, most food was sourced locally, and the world's resources supported a mere ~25% of the current population. Since then, advanced processing of food and globalization of trade has reduced prices, increased selection, and made many seasonal items available year-round. With this convenience has come an increase in food fraud – substitution or dilution with lower quality ingredients to reduce cost, and/or adulteration or treatment with banned ingredients.

Food fraud is a global problem, affecting some 10% of our food supply; thousands of tons of substandard food are seized by Interpol each year. Though food fraud is often aimed at deceiving affluent food lovers, severe incidents can result in poisoning, illness or death. Improved methods are needed to validate the safety and authenticity of foods to protect both consumers and the brands they consume. Fortunately, spectroscopy is beginning to offer solutions that are robust and portable enough for deployment into the food chain, at customs, and even for consumers.

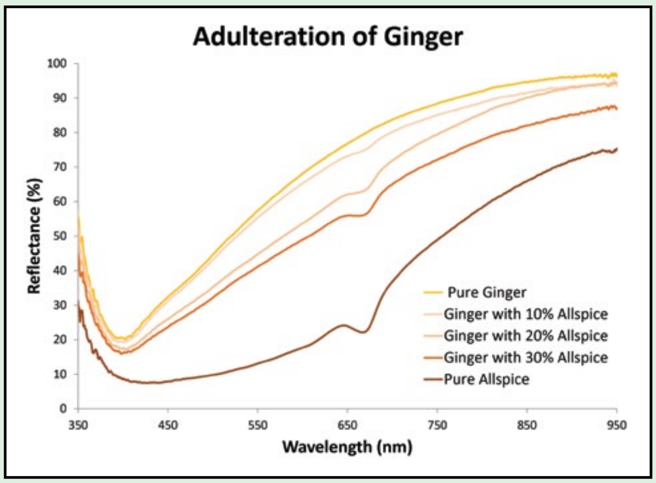
Application Note: *Adulteration of Spices*

Challenge: High value ground powders like spices are frequently adulterated, as it is often difficult for consumers and importers to evaluate spice quality based on sensory input alone

Solution: Reflectance spectra can reveal features signaling common spice adulterants, providing rapid quality assessment without the need for chemical analysis

Spices are being used more than ever as consumers seek to reduce salt intake and expand their palates. Sold most often as ground powders, spices like turmeric, paprika and ginger can easily be cut with fillers, from less expensive spices to flours, corn starch and even sawdust. In extreme cases like the large-scale 2005 recall of chili powder due to adulteration with the red dye Sudan 1, toxic or potentially carcinogenic substances are added to hide aging of a product or the presence of fillers.

Modular reflectance spectroscopy offers a rapid, cost-effective alternative to chemical analysis, and allows the ground powder to be measured directly. To demonstrate this, we looked at ginger, a spice sometimes cut with allspice to reduce cost. The two spices were mixed in various ratios. We pointed a reflection probe at 45° to the underside of a glass dish filled with spice, measuring the spectrum using a tungsten halogen lamp and FLAME-S-VIS spectrometer. Though both spices are much more reflective at longer wavelengths, allspice possesses a characteristic dip in its spectrum at ~670 nm, visible even at levels as low as 10% of the ginger-allspice mixture. This spectroscopic analysis demonstrates the speed and simplicity with which the purity and authenticity of products can be validated within the food supply chain.



Detecting Food Fraud

Processed foods like powders and liquids are most frequently adulterated; additives like colorants and flavors can be used to mimic the authentic product, and dilution or replacement can be difficult to detect. Premium liquors and spirits are a popular target (see sidebar for our solution), while lower-grade wines may be passed off as expensive vintages. Illegally produced “honey” represents 7% of all food fraud cases, from falsified origin to presence of banned antibiotics and pesticides. Even meats are at risk for adulteration, with recent scandals involving addition of horse meat and organs to ground beef. Absorbance, reflectance and Raman spectroscopy systems from Ocean Optics have proven useful for authentication and safety testing of these foods, as have fluorescence techniques sensitive to proteins, DNA, polyphenols and vitamin content.

Produce is less vulnerable, but can be difficult to test due to the need for nondestructive measurement. Reflectance and through-sample transmission techniques in the visible and NIR work well for fruit and dairy product testing. SERS, meanwhile, is gaining ground for detection of banned pesticides and fungicides on produce, as well as antibiotics and fungicides used in illegal fish farming. Ocean Optics’ highly selective SERS substrates offer the sensitivity and low cost per use to make field testing feasible (see page 15). We’ve even developed a complete fluorescence-based optical assembly for an OEM instrument to test against regulated mycotoxin limits in food and feed products (www.ToxiMet.com).

The Spirit Sampler is a fully integrated portable instrument for rapid on-site authentication of premium liquor and spirit brands. Clear, light or dark spirits can be analyzed in under 15 seconds, displaying a clear pass/fail answer. This easy-to-use instrument features a simple control screen and requires minimal training to operate. New brands can be easily added to the brand library in the lab or the field.

Read more at oceanoptics.com/spirits

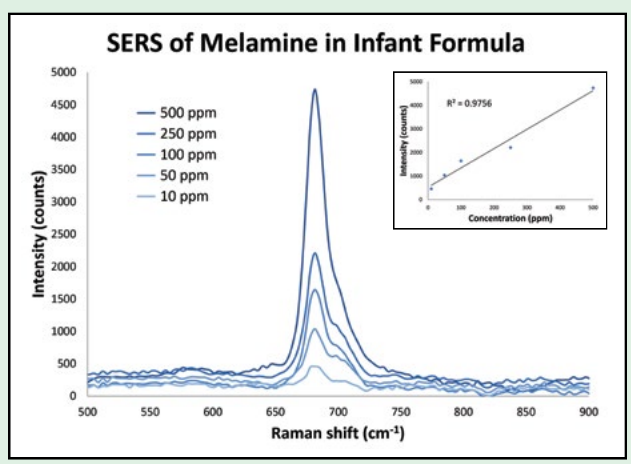
Application Note: *Melamine in Milk Products*

Challenge: In the 2008 Chinese tainted milk scandal, melamine was added to infant formula to boost the nitrogen content, fooling tests designed to ensure protein content met acceptable levels

Solution: Surface-Enhanced Raman Spectroscopy (SERS) offers a rapid, field-portable alternative to chromatographic and other screening techniques for melamine and other contaminants

An estimated 300,000 babies became ill in China after being fed milk powder adulterated with melamine, a flame-retardant plastic most often used in industrial products. Six infants died, and more than 50,000 were hospitalized with symptoms of kidney stones, kidney damage and malnutrition. Products from more than 20 companies were involved, demonstrating the prevalence of economically motivated food fraud in industry. Melamine contamination has also been discovered in eggs, possibly the result of use in animal feed, spurring industry to investigate methods for its detection.

Highly sensitive and molecule-specific, SERS is capable of detecting the ppb to ppm (trace) levels of melamine seen during the tainted milk scandal, with minimal sample preparation. We tested baby formula doped with melamine at several concentrations, applying it directly to our low-cost inkjet-printed SERS substrates. Unlike other testing methods, no separation of components was required prior to analysis. Samples were tested using a 785 nm QE *Pro* modular Raman system, with pure formula used as the dark reference. Strong SERS signals allowed melamine to be seen and quantified via a calibration curve down to 10 ppm levels, showing the power of this technique to perform sensitive, quantitative detection of melamine in milk products.



Modular Absorbance of Foods

Absorbance is a powerful tool for authentication and quality control of liquid food products, providing instant and quantitative results. Ocean Optics offers a wide range of flexible, modular products that can be mixed and matched to suit the needs of each application for wavelength range, sensitivity, sampling method, and size. See table below for spectrometer and light source models by wavelength region. Contact one of our Application Scientists to discuss your needs today.

Modular Spectroscopy System Options

Spectrometers	**UV**	**VIS**	**NIR**
Spark-Vis			
STS			
Flame			
HR			
Maya2000 Pro			
QE *Pro*			
NIRQuest			
Light Sources			
D-2000			
HL-2000			
DH-Mini			
HPX-2000			

Application Note: *Olive Oil Fraud*

Challenge: Global demand for olive oil now exceeds supply; sales of adulterated and diluted olive oil are on the rise, yet no convenient method of validating quality exists

Solution: Absorbance spectroscopy offers a quick and easy method to detect dilution with lower grade olive oil, or adulteration with other oils, flavors and colorants

The cost of raw olive oil has reached its highest levels in a decade, doubling in some areas in 2014 due to back-to-back years of production devastated by drought, pests and bacterial disease in Spain and Italy. The gap between supply and demand motivates producers to favor quantity over quality, impacting the price and integrity of extra-virgin olive oil (EVOO) in particular. By some estimates, 70% of EVOO on American store shelves has been adulterated in some way to reduce cost. It may be cut with lower grade olive oil, or with substitutes like sunflower, rapeseed, soybean and canola oil. Chlorophyll is added to imitate the dark green color of EVOO, while beta- carotene helps mimic its taste.

Absorbance spectroscopy using visible light is able to quantify even small differences in color and composition in oils and oil blends indiscernible to the human eye and palate, sounding the alarm on substandard olive oil. We assembled a modular absorbance system based on our compact Spark-VIS spectral sensor to measure various oils and mixtures in a cuvette from 380-700 nm.

Dilution of extra-virgin olive oil with lower grades is the most common type of olive oil fraud. Extra-virgin olive oil's characteristic dark green color persists even in 50:50 mixes, making it difficult to authenticate by eye. Absorbance spectra, however, show a clear progression correlating to the fraction of EVOO in the mixtures tested, from pure EVOO to pure olive oil (see graph on facing page). The absorbance peak at 670 nm is a particularly useful feature for this analysis, as it appears to be unique to EVOO. Features from 380-500 nm also vary with EVOO fraction, offering sufficient spectral differences between EVOO and low-grade olive oil to enable effective chemometric analysis for authentication purposes.

NIR Spectroscopy of Foods

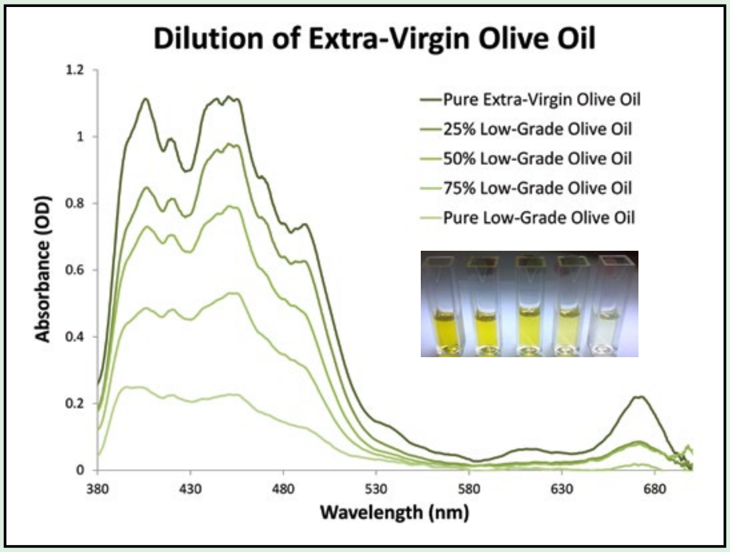
Near infrared spectroscopy is particularly well-suited to nondestructive analysis of bulk, high-moisture samples like fruit, fish, meat and grains. Light at NIR wavelengths penetrates fairly deeply without being absorbed by water, allowing internal composition to be probed via reflectance and through-sample transmission techniques. The many components of foods result in very complex spectra, necessitating the use of chemometric analysis methods like principal component analysis (PCA), linear discriminant analysis (LDA) and partial least squares (PLS), as well as machine learning algorithms like support vector machines (SVM) and artificial neural networks (ANN).

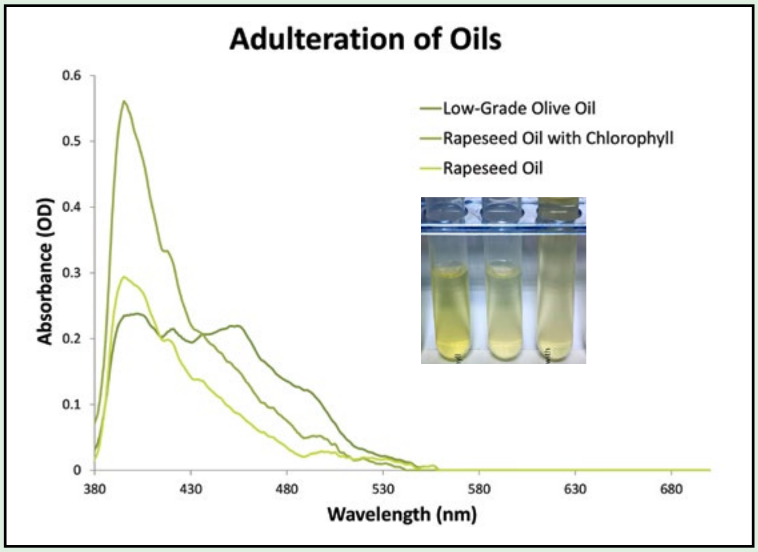
Food integrity and safety applications being tackled by NIR spectroscopy include:

- √ Fruit quality: screening for core rot, internal pests and ripeness
- √ "Gluten-free": sorting unprocessed grains with NIR and machine vision
- √ Adulterated ground beef: detecting mutton, pork, organs and fillers
- √ Fraudulent labeling of fish: identification of fish species without DNA testing
- √ Chicken quality: detecting thawed versus fresh; artificially boosted water content

The new Flame NIR spectrometer provides flexible spectral analysis from 900-1700 nm in a compact footprint. With signal to noise rivaling larger NIR spectrometers and great thermal stability, the Flame NIR delivers consistent measurement results - ideal for monitoring food identity, purity and quality at all points in the supply chain.

Read more at oceanoptics.com/flame-nir





Chlorophyll is often added to lesser-grade edible oils and sold as authentic olive oil. We simulated this adulteration with rapeseed oil, comparing it to a low-grade olive oil. While the two were difficult to distinguish by eye, the absorbance spectra are clearly different. Chlorophyll increases the absorbance of the rapeseed oil from 415-510 nm enough to alter its color, but cannot mimic the true spectrum of olive oil. Software analysis based on a simple peak height comparison would allow adulterated rapeseed oil to be easily distinguished from pure olive oil.

From validating product grade and identity to detecting the presence of artificial colorants and flavorings, absorbance spectroscopy is a powerful method for rapid quality testing of liquid food products. Compact sensors like the Spark-VIS offer a high-performance, low-cost option for deployment of food validation measurement systems throughout the supply chain.

Document Security

Many valuable documents are still printed on paper, protected only by an array of security features designed to deter counterfeiting, tampering and forgery. Ready access to advanced printers, inks and graphic design programs by counterfeiters has forced the adoption of ever more complex techniques in recent years. Novel optical materials and features are at the forefront of this field, drawing on the advantages of spectroscopy for their development – and even their detection. Well over 50 specific techniques are in use to facilitate authentication of printed documents and deter tampering, from special inks and patterns to unique physical elements. The higher the document value, the more layers of overt and covert protection are used concurrently.

Optical Inks

Inks and pigments with optically unique properties can provide quick visual verification of authenticity, and can be difficult to replicate. Iridescent or color-shifting inks cause a change in color with viewing angle, while fluorescent inks can be used to overlay special words or images that appear only when illuminated by UV light. Fluorescent fibers can even be incorporated into the paper itself. Tunable fluorescent inks have been developed to act as an optical signature, and with multiple emission peaks, the only way to authenticate in the field would be using a handheld spectrometer.

Application Note: *Looking at Fluorescent Inks*

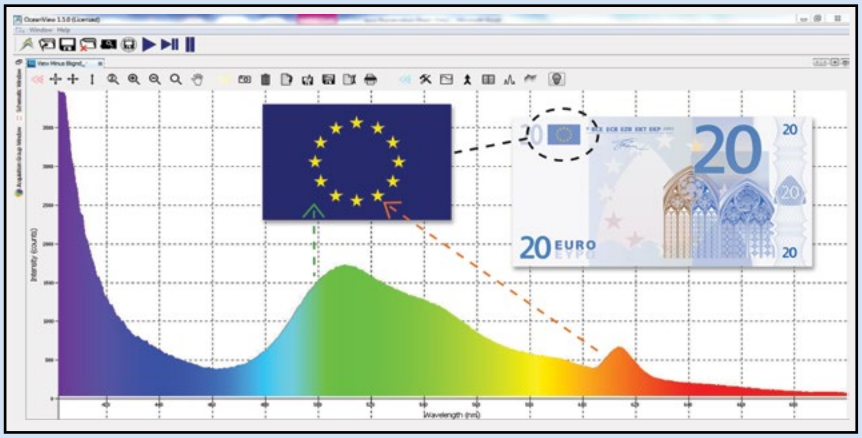
Challenge: Fluorescent inks can be used to print security features visible only under UV light, but could potentially be replicated using fluorescent inks now available on the market

Solution: A fluorescence spectroscopy system can validate authenticity more accurately than the human eye to distinguish counterfeit fluorescent features from those which are authentic

To demonstrate bank note authentication, we assembled a system to measure the European Union flag security feature on a 20 Euro note. Under UV light, the blue background on the flag should fluoresce green, while the yellow stars should emit orange light.

Our modular system consisted of a QR600-7-VIS-NIR reflection probe, an LLS-385 light source for UV excitation and a Flame-S-UV-VIS-ES spectrometer for detection. A probe pointed at the flag detected a broad peak at ~490-560 nm, corresponding to the expected green fluorescence. Fluorescence from the stars was also visible as a strong peak at 610-620 nm.

While a counterfeit bill might be able to replicate this feature accurately enough to fool the eye on first glance, a full spectral measurement enabled by analysis software could very quickly discern a fake.



Advanced Optical Security

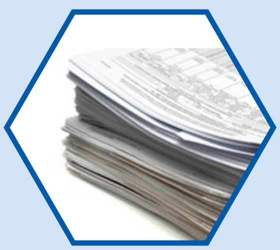
Spectroscopy plays an important role in the development of many optical security features. Upconverting nanocrystals incorporated into inks allow infrared light to be used for excitation with visible detection. Optical tags based on Raman, SERS and other micro- or nanoparticles also show promise, and require compact spectroscopic systems for detection.

Optically variable devices (OVDs) like holograms shift their appearance and color with illumination; replication is nearly impossible thanks to the use of complex diffractive elements or interference films. Even surface plasmon resonance is being used to create OVDs. As the properties of advanced tags, inks and OVDs are refined for widespread use, spectrometers are being used to evaluate their performance.

Though many security measures like the use of OVDs are designed to provide immediate visual authentication of documents, counterfeiters are never far behind. More sophisticated authentication methods will be needed. Ocean Optics can create integrated OEM spectroscopy solutions to assist in advanced authentication and forgery prevention using a wide variety of optical detection methods, tags and markers.

Spark-VIS is a revolutionary spectral sensor designed for size, scalability and value, and is ideal for a wide range of volume authentication applications. The first in a line of new, ultra-compact modular spectroscopy components, Spark covers 380-700 nm. A plug-and-play unit with micro-USB connector allows proof-of-concept in the lab, while OEM and detector-only versions can be embedded directly into handheld instrument designs.

Read more at oceanoptics.com/spark

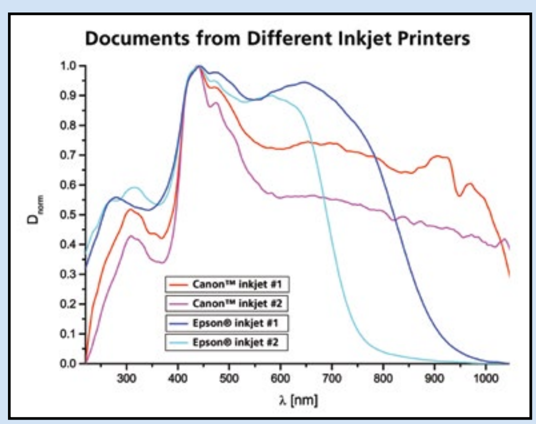


Application Note: *Forensic Document Analysis*

Challenge: Laser and inkjet-printed documents can be easily forged, copied or altered, yet validating authenticity and origin often requires complex chemical analysis

Solution: Vis-NIR reflectance spectroscopy can quickly and non-destructively discriminate among printer brands and models, even allowing a document to be mapped to spot alterations to text or signatures

Forensic analysis to determine the origin and age of a document requires microscopic evaluation and often destructive analysis of the ink's chemical composition via TLC, HPTLC, GC-MS and HPLC. Vis-NIR reflectance spectroscopy offers a nondestructive alternative for evaluating prints from different inkjet and laserjet printers. A system composed of an HR4000-CG spectrometer, DH-2000-BAL UV-Vis-NIR light source and reflection probe at 45° AOI measured samples from 450-1000 nm, referencing against blank paper to account for paper inhomogeneity.



Spectral differences were analyzed using principal component analysis (PCA), allowing ink from each printer to be uniquely characterized using a three component model. Printed documents from each brand of printer displayed similar spectra; each model of printer could also be differentiated mathematically based on the spectra. To test the model, an "unknown" inkjet document was analyzed using PCA, and was correctly identified as originating from an Epson® printer. It is thus conceivable that an entire document could be quickly and nondestructively mapped using a portable Vis-NIR spectrometer and compared to other pages and/or documents, thus providing evidence of tampering or forgery.

Fuel Authentication

Fuel theft, smuggling and fraud cost governments and private oil and gas companies an estimated $1 billion or more in lost excise taxes and revenue each year. While domestic transport fuels are taxed to generate revenue, governments often subsidize the cost of fuel used for heating and industry. When fuels of a similar grade are sold at different prices within the same country, it often leads to fuel fraud in the form of adulteration, blending and dilution. Differences in fuel taxation from one country to the next add to the problem with smuggling and theft, often by organized crime groups. The effects on oil and gas companies include reduced profits, increased liability issues and brand erosion when substandard fuels affect engine efficiency or cause engine damage.

Fuel Markers and Dyes as Deterrent

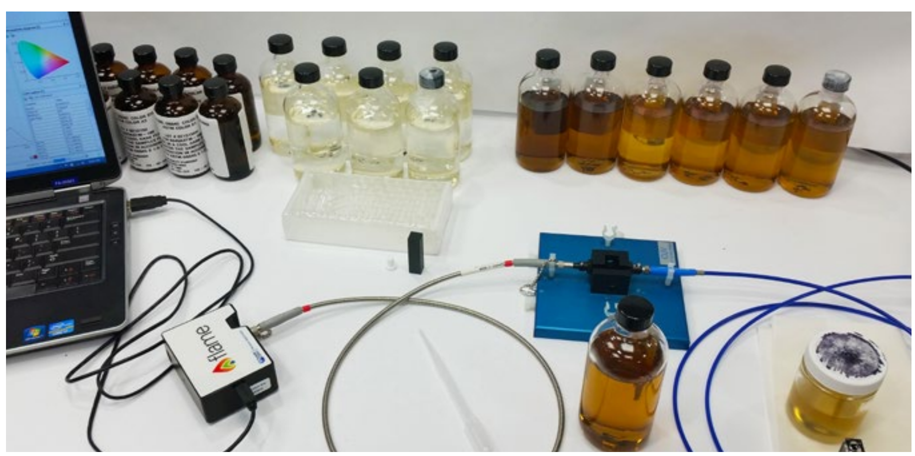
Many governments now add fuel markers and dyes to subsidized or tax-exempt fuel to deter fraud. If the markers or dyes are not visible to the naked eye, a quick color-change chemical test can often identify fuel diluted by as little as a few percent. Fluorescent dyes provide a more covert method of fuel marking, particularly when combined with a spectral detection system.

Let us create a custom OEM system for authentication to meet your needs:

- √ Easy to operate
- √ AC and/or battery powered
- √ Dependable pass/fail answers
- √ Remote data connectivity
- √ Secure onboard data logging
- √ Robust optics and mechanics
- √ Wide operating temperature range
- √ Shock and vibration damped

Download our OEM Solutions Guide at oceanoptics.com/oem-brochure

Still, fuel is sometimes "laundered" to remove the dyes via chemical processing, heating or adsorbent materials; measurement with a spectrometer may be needed to detect the residual dye. The increased sensitivity of spectroscopic detection also enables the use of lower concentrations of markers, reducing cost and likelihood of detection by criminals.

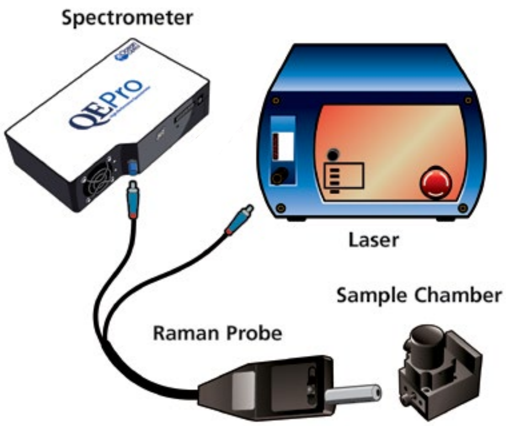


More advanced fuel markers possess a unique signature that can be sensed only by proprietary readers and traced back to a specific point of origin. Governments and fuel suppliers often work together with companies specializing in fuel authentication who establish fuel marking programs to deter fuel fraud and help pinpoint the location within the supply chain at which the fraud occurs. This holds retailers accountable for the fuel they sell, reduces the smuggling of illegal fuels across borders, and helps to identify illegal traders.

Portable Spectroscopic Detection

The latest generation of covert fuel markers involve extremely complex recipes and increasingly sophisticated detection. Ocean Optics spectrometers are up to the task, allowing identification of multiple markers at extremely low concentrations. Our spectrometer systems offer the flexibility, sensitivity and durability to take new fuel marking technology from the lab to the field, allowing fuel to be authenticated at every point within the supply chain.

Once proof-of-concept has been established using a modular system such as the one shown at right, our OEM engineering team can custom-design your fuel marking detection system to sense a wide variety of absorbing, fluorescent, Raman or SERS-active dyes and markers, or to offer concurrent detection via multiple optical methods.

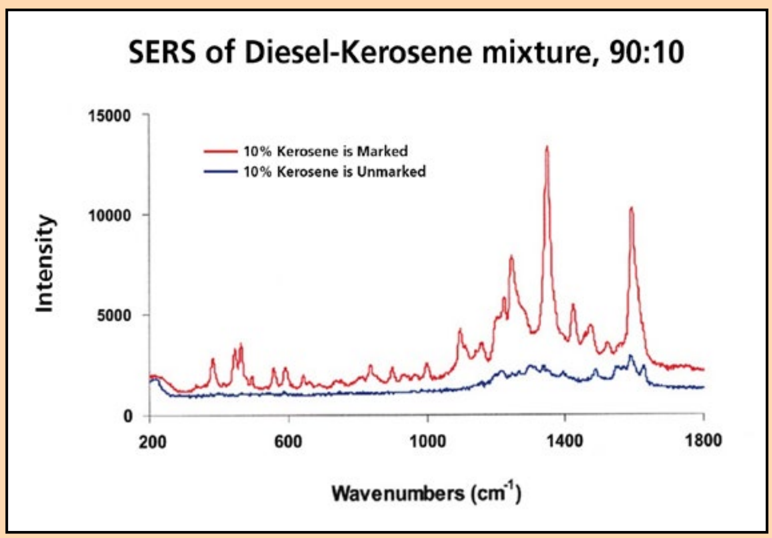


Our systems are cost-effective detection solutions that can be widely deployed throughout the fuel supply chain for protection against smuggling, adulteration and dilution of fuels, thereby protecting brand identity for oil and gas producers and assisting in excise tax recovery for governments. Fuel marking systems that deter organized criminal activity and protect the supply of subsidized fuels benefit corporations, governments and consumers alike.

Application Note: *Fuel Markers and SERS*

Challenge: SERS-based optical markers offer advanced security against fuel fraud, but require specialized detection using Raman spectroscopy

Solution: A portable spectroscopy system ruggedized for field use and sensitive enough to detect SERS-based fuel markers at ppb levels



One novel optical marker to track fuel adulteration and smuggling is based on advanced detection via SERS, surface-enhanced Raman spectroscopy. Raman spectroscopy provides a unique fingerprint for each molecule detected, an effect that can be enhanced through the use of metal colloids or patterned substrates to achieve trace level detection. A silver colloid marker suitable for SERS detection has been developed that is stable in fuel, even when subjected to sunlight exposure, chemical alteration and adsorption materials.

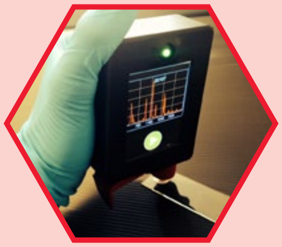
A robust, field-portable system based on an Ocean Optics spectrometer was developed to conclusively and accurately detect the silver colloid marker at extremely low levels, even when operated by non-technical personnel. The system uses a relatively low power 532 nm excitation laser, with detection over a 200-2000 cm^{-1} Raman fingerprint range. Once the sample is prepared in a glass vial, the total time to execute sampling, measurement and data processing is under five minutes.

Though the excitation laser may cause other additives within the fuel to luminesce, the strong fluorescence quenching effect of the silver colloid and selectivity of the Raman detection method prevent interference. The resulting system not only identifies the presence of a given marker, but quantifies it down to ppb levels to provide clear, dependable answers from plant to pump.

Explosives Detection

Defense and security have long relied heavily on technology. Concerns over terrorism and illegal stores of weapons have served only to increase the focus on security at local and international levels, and on explosives detection in particular. The multibillion explosives trace detection (ETD) market is expected to grow at a rate of 16% per year, driven by the needs of air/sea/land transportation, military, law enforcement, critical infrastructure protection and public safety.

Raman spectroscopy is a key technology in explosives detection, able to fingerprint pure materials and mixtures, and adapting quickly to the development of new compounds. Compact handheld systems like the IDRaman mini are routinely used in the identification of bulk unknown powders in the field, allowing law enforcement to discriminate between urea and ammonium nitrate used as fertilizers and the explosives they may be used to manufacture. Standoff Raman is used to evaluate potential threats at a distance, often using UV excitation lasers to reduce the potential for eye damage and interference from sunlight while obtaining a strong signal free of autofluorescence. The field of trace detection of explosives, in contrast, has been dominated by ion mobility spectrometry (IMS) and its variants, though with limitations on portability and field servicing due to the use of radioactive materials.



Application Note: *Trace Detection Using SERS*

Challenge: The need for lower detection limits, greater field portability and ease of use is driving the development of new techniques in trace detection of explosives

Solution: SERS offers highly sensitive and selective detection down to ppm and even ppb concentrations of explosives, and is compatible with existing handheld Raman systems

Terrorists and criminals are getting better at eliminating the residues from explosives manufacture and transport on their bodies, belongings and vehicles. To stay one step ahead, military and security personnel need trace level detection methods that are sensitive and easy to deploy at airports, borders and in the field. SERS substrates allow the analytical advantages of Raman to be applied to trace levels of explosives by enhancing the Raman signal by a factor of up to 10^{11}.

To demonstrate the effectiveness of SERS for common explosives, we tested two well-known types at low ppm and sub-ppm concentrations: RDX and PETN. Each was applied to a patent-pending sputtered SERS substrate recently developed at Ocean Optics, based on a cost-efficient gold/silver alloy. Measurements of each explosive solution were made with a QE *Pro* Raman spectrometer, 785 nm excitation laser and Raman probe, subtracting the Raman signal obtained as a background from the blank SERS substrate. Just 10 µL of each sample dissolved in acetone was applied to the substrates, drying rapidly prior to measurement.

RDX (cyclotrimethylene-trinitramine) is a common explosive that is second in strength only to nitroglycerin; it can be mixed with plasticizers to make C-4. Our measurements showed a strong primary RDX peak at 870 cm^{-1}, as well as other known peaks at 930, 1258 and 1312 cm^{-1}. PETN (pentaerythritol tetranitrate) is structurally similar to nitroglycerin, and is often used in plastic explosives for its power. We consistently observed two of its known SERS peaks at 1053 and 1295 cm^{-1} with our new sputtered SERS substrate.

Handheld Raman Detection

IDRaman mini

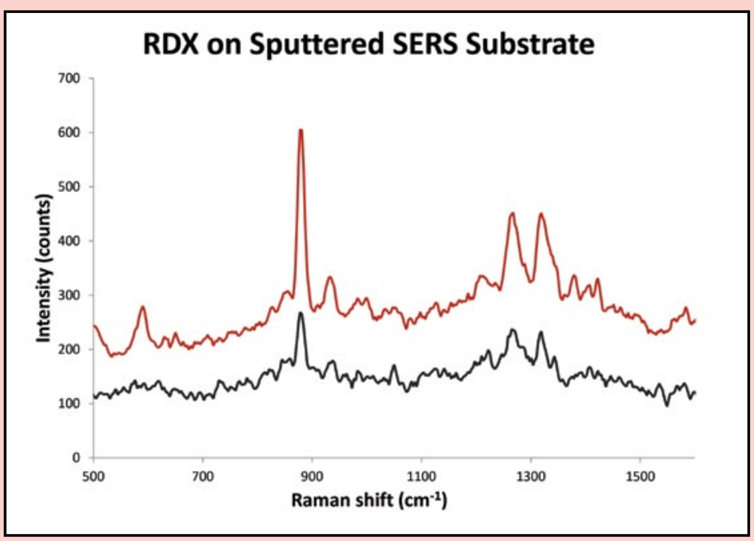
Threat detection in the field demands rapid, conclusive identification of unknown substances in a robust, easy-to-use unit. The IDRaman mini is a compact, powerful Raman analysis system with pushbutton interface for instant identification, authentication or screening of substances. Raster Orbital Scanning (ROS) probes the sample in a daisy-like pattern for improved sensitivity, lower detection limits and consistent identification of inhomogeneous and irregularly shaped samples. An optional sampling accessory enables SERS substrates to be read in the field for trace detection.

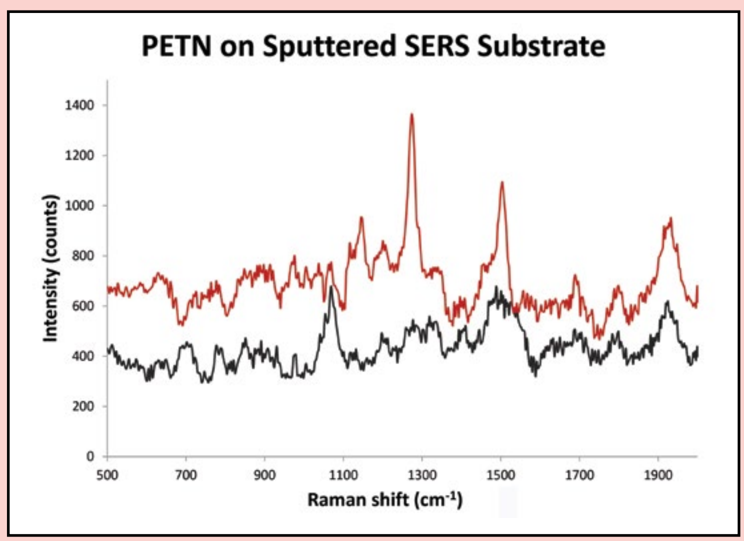
Spectral Libraries

Spectral matching to a stored library of known materials allows unknown materials to be quickly assessed using Raman spectroscopy. New materials can be characterized and added to the library, or two unknowns can be compared in real-time to establish a match prior to laboratory analysis. Our standard explosives library includes >60 known compounds and precursors. Additional libraries are available for over 10,000 compounds, including toxic substances, narcotics and industrial chemicals.

You don't need an expensive patterned substrate to get a strong SERS signal. Our proprietary inkjet-printed substrates offer better performance at a fraction of the price, conveniently immobilized on a glass slide for use with any Raman spectroscopy system. Ocean Optics SERS substrates offer ppb-level detection of chemical and biological materials in the field, as well as pharmaceuticals, explosives, and tags for anti-counterfeiting.

Read more at oceanoptics.com/sers





This proprietary new sputtered substrate has out-performed other SERS substrates in head-to-head testing at customer sites. Though details of the concentrations measured are covered under NDA, Ocean Optics sputtered SERS substrates showed a lower limit of detection (LOD) for all explosives tested. In addition to RDX and PETN, our customers have seen excellent test results for other materials like TNT and chemical warfare agents, demonstrating the versatility of our new SERS substrates for security and defense applications. Like the inkjet printing used in Ocean Optics standard SERS substrates (see top right), this patent-pending sputtering technique was developed specifically to provide a low-cost alternative to other SERS substrates on the market. Use of sputtering to create the enhancement surface further increases durability of the substrate for routine use in harsh field conditions. Sputtered SERS substrates have been tailored specifically to security applications, and thus are currently available only upon request. Please contact our Sensors group to discuss your application.

Value Validation

Art Valuation

The value of art depends not only on its beauty and the skill employed, but also on its authenticity. Who was the artist? Does it belong to a specific time period? Has it been altered or restored using newer materials? Many of these questions can be answered via spectroscopic identification of pigments and other construction materials, even penetrating into sublayers nondestructively.

Early pigments were entirely natural – derived from earth, mineral or botanical sources. Some colors were precious, like the intense blues once created using the stone lapis lazuli. Azurite, ground cobalt glass and indigo arose as substitutes, overtaken by synthetic pigments like Prussian blue and phthalocyanine blue. When combined with style and technique analysis, pigment studies can thus provide a much deeper insight into the historical origin and integrity of a piece of artwork to establish its authenticity or authorship.

Unlike chemical analysis, most spectroscopic techniques are non-destructive. Reflectance spectroscopy can be used to obtain quantitative measurements of the color of pigments as an aid in restoration, to create a color "map" of the artwork that can act as a fingerprint, or to validate authorship (as seen at right). Raman spectroscopy can very accurately identify inorganic compounds in art pigments to validate authenticity or areas of restoration, but can suffer from interference due to fluorescence from binders and varnishes.

Application Note: *Authenticating a Painting*

Challenge: Authenticate "EL 1920," a painting from a private collection credited to El Lissitzky, an important figure in the Russian avante-garde movement

Solution: Compare visible reflectance spectra of blue areas in the painting to a database of phthalocyanine blue pigments to assist in dating the period of creation

Blue phthalocyanine pigments have been used extensively in paintings and restoration since their introduction in 1935. A team at the University of Bergamo has performed a comprehensive reflectance spectroscopy study of these pigments, creating a database of commercially available pigments from a variety of producers in varnish, tempera and acrylic formulations. Their work used an HR2000-CG spectrometer and a reflection probe measuring a ~5 mm sampling area, collecting data from 200–1100 nm. By analyzing the data, they were able to identify characteristic features of each particular phthalocyanine pigment, allowing each to be uniquely identified by its spectrum.

The researchers then measured several blue and gray-blue areas of "EL 1920," finding upon comparison to their database that the spectral measurements conclusively identified the presence of blue phthalocyanines. Thus not only did the painting "EL 1920" originate after 1935, but it could not have been a creation of the Russian avant-garde movement.

Gemstone Authentication

The global market for rough diamonds in 2013 amounted to approximately 130 million carats, or a value of approximately US $14 billion. While demand is expected to continue to grow, particularly in countries like China and India, it is forecast that the gap between demand and production will begin to widen starting in 2019. As prices rise, so will the prevalence of counterfeit diamonds. Other precious gems are also prone to substitution or alteration for financial gain, including emerald, ruby, coral, jade and pearl.

Raman spectroscopy can quickly and easily be used to discriminate many natural stones from artificial, non-destructively and with no sample preparation. The spectral fingerprints provided by Raman spectroscopy contain peaks that can be tied to a gemstone's chemical structure, as well as the trace minerals and inclusions that give stones like emerald and ruby their distinctive hues.

Luminescence induced by a high power, short wavelength light source offers additional information that can be used for authentication and to detect various treatments. Natural and synthetic emeralds, for example, have the same chemical structure and therefore identical Raman spectra. Both get their deep green color from the presence of chromium and vanadium ion impurities, but slight differences in the concentrations and presence of other metal impurities affect the intensity and wavelength of the chromium photoluminescence bands, allowing synthetic emerald to be distinguished from natural types.

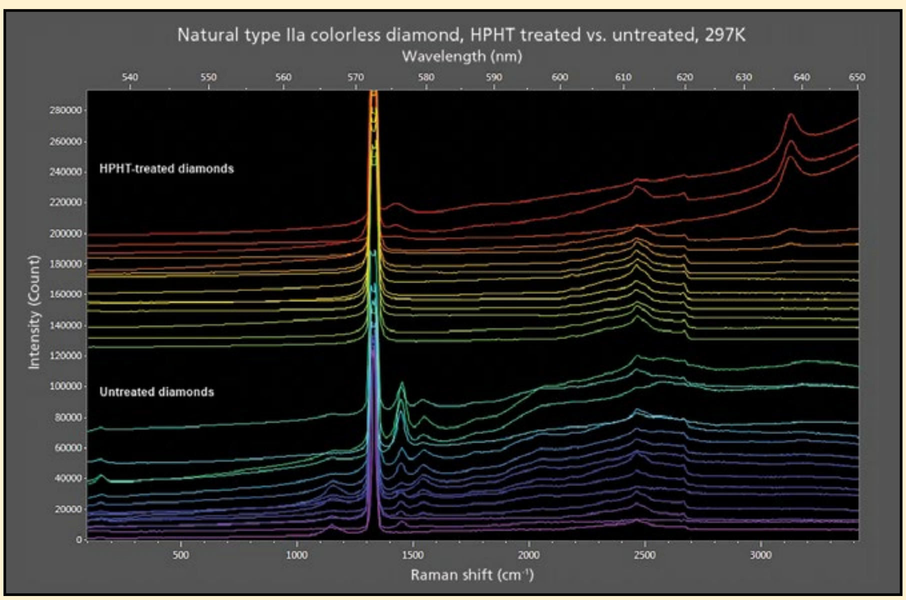
Raman and photoluminescence measurements performed concurrently using a 532 nm excitation laser can allow gemologists to determine whether coral and freshwater pearls have been dyed to enhance their natural color, thus artificially increasing their value. It is even possible to identify endangered *Stylaster* corals being sold as the more prevalent *Corallium* coral permitted for legal trade.

Application Note: *Detecting Treated Diamonds*

Challenge: High-pressure, high-temperature (HPHT) treated diamonds are often sold as untreated diamonds, driving a need for rapid authentication

Solution: A system capable of measuring both Raman signal and photoluminescence concurrently can provide analysis of both natural diamond and its simulants

Natural diamond has a strong characteristic Raman peak at 1332 cm^{-1}, while diamond simulants possess no such peak – a feature that allows near-instant authentication. It is much harder, however, to detect brown and gray diamonds that have been made near colorless using high-pressure, high-temperature (HPHT) treatment. Though they cost dramatically less, HPHT-treated diamonds are sometimes fraudulently sold as high quality, untreated diamonds. A specialized system developed using the QE *Pro* Raman facilitates identification using minor differences in the photoluminescence spectrum compared to untreated diamonds, protecting both diamond merchants and consumers.



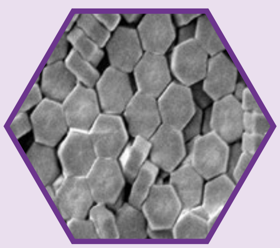
Spectra courtesy of Foral Design Ltd. See www.gemmoraman.com for instrument details.

Brand Protection in Industry

Industry's stake in authentication spans brand and consumer protection, as well as recourse against liability claims. Counterfeit packaged goods are a large and growing market – the U.S. Customs and Border Protection seized $1.7 billion in illicit goods alone in 2013, up ~40% from the previous year. While the security of imprinted barcodes, serial numbers and logos can be bolstered by working on a microscopic scale or with invisible inks, replication is still possible. Optical markers and tags make forgery exponentially more difficult, providing a much more secure method of authentication. Often the counterfeiter simply doesn't know what to look for, where or how.

Counterfeit packaged goods range from luxury items like designer handbags and cosmetics to safety equipment, automotive parts and electronics. Circuit boards and their components are frequently cloned using substandard or recycled components, compromising the integrity of critical electronic systems like communications, power grids, medical equipment and government and military networks. Counterfeit pharmaceuticals are a particularly grievous problem, resulting in up to one million deaths annually.

Many of these products are now turning to spectroscopy for authentication. Optical tags, markers and dyes can be printed on packaging and surfaces, and even integrated directly into materials during manufacture. From brand verification to asset tagging and manufacturing traceability, optical authentication protects us all.



Application Note: *Creating Unique Barcodes*

Challenge: Manufacturers need optical tags capable of authenticating individual products within a brand, and for traceability to individual manufacturing stations

Solution: An infinite number of unique barcodes can be created using intelligent materials based on up- and down-converting rare earth nanocrystals

As the number of unique products to be authenticated rises, intelligent materials offer a novel solution with multiple options for blending. Most fluorescence is downconversion – one photon is absorbed, and a longer wavelength (lower energy) is emitted. In upconversion, two or more photons are absorbed, and one photon of shorter wavelength (higher energy) is emitted. Rare-earth nanocrystals are capable of both, and their exact emission spectrum can be precisely tuned by varying either the composition or shape of the crystals during growth. Changing the excitation wavelength also affects emission. When different crystal types are blended, the number of possible combinations is endless. At just 200 nm in size, crystals can be detected at ppb levels when added to inks, fibers, plastics, metals, solvents and mixtures. These intelligent materials have been used to monitor concentrations of key ingredients in manufacturing, to uniquely identify manufacturing stations for quality control, as markers in brand-name prescription drugs and perfumes, on luxury goods labelling, and even to trace parts back to a specific 3D printing machine when liability is in question. Use of a spectrometer for detection allows full use of their multiplexing capabilities, and makes duplication impossible.

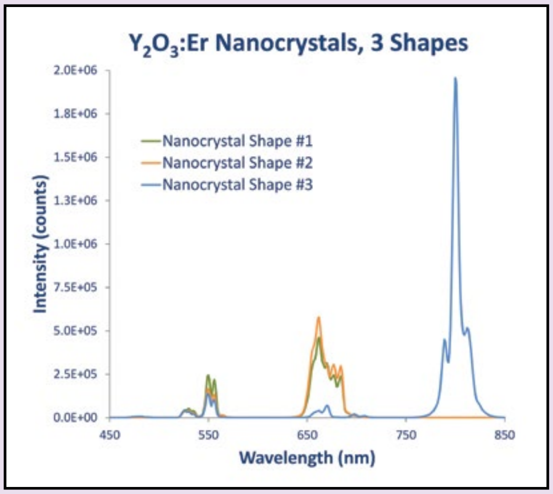
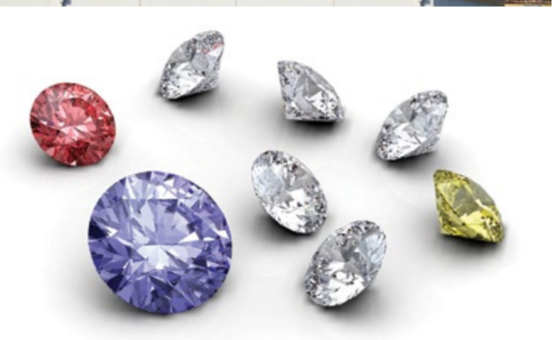


Image courtesy of Intelligent Material Solutions, www.intmatsol.com

Application Note Library

Delve deeper into authentication with these related application notes and more at oceanoptics.com.



Foods

Combating the Rise of Food Fraud
Spirit Sampling for Counterfeit Detection and Brand Authentication
Evaluating Food Safety using SERS
Counterfeit Detection in Olive Oil
Fluorescence of Edible Oils with OceanView
Detection of Harmful Food Contaminants Using SERS
ToxiMet Mycotoxin Testing System (see OEM Solutions Brochure)
Controlling the Color Consistency of Beverages Using Spectral Sensing
Measuring Beer Color with OceanView
NIR Spectroscopy for Rapid Grains Identification
Diffuse Reflectance Analysis of Seeds and Grains
Near-Infrared Spectroscopy Analysis of Powders and Grains
Dynamic Sampling for NIR Food Measurement
Ultrasensitive Detection of Mercury: Beyond FRET
Absorbance of Anti-Oxidants in a Fruit Juice Blend
Near-Infrared Diffuse Reflection Analysis of Fruit
In-line Gumball Sorter Demonstrates Range of Spectroscopy Techniques
VIDEO – From Farm to Fork – Food Safety in the Supply Chain

Documents

Spectroscopy's New Role in Document Security

Fuels

Authenticating Fuel from Plant to Pump
Characterization of Diesel Fuel Using a Modular Raman System
Biodiesel Quality: Harnessing Good Emissions

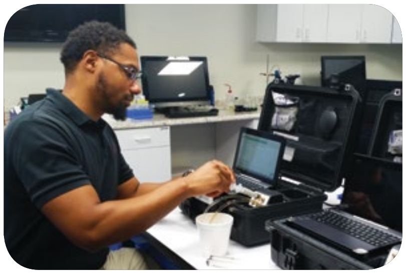
Art and Gemstones

Spotting Art Forgeries
Pigment Analysis in Paintings
HPHT Treated Diamonds (see Ocean Optics Raman Catalog)
Identifying Natural and Synthetic Gems

Industrial and Pharma

Detecting Drugs in Saliva (SERS)
ROS Probes Inhomogeneous Pharmaceuticals (see Ocean Optics Raman Catalog)
Raman Analysis of Pharmaceutical Ingredients
Accurate Wafer-Level Color Testing of LEDs for White Solid State Lighting
Miniature Spectrometers Address Challenges of LED Research and Production
Sorting Plastic Resins Using NIR Spectroscopy

Custom OEM Authentication Solutions



Are the products you buy or sell frequently counterfeited or adulterated? Do you need to assess the authenticity of gems, artwork or critical documents? Are you sure that your food products are high quality and safe for consumers? Our OEM engineering team can design a robust, spectroscopy-based solution customized for your specific application, industry and user interface needs.

Our flexible, modular systems adapt easily to the wide range of markers and detection methods used for authentication, and can be quickly translated by our engineers into drop-in modules or integrated turnkey systems for use throughout the supply chain.

Reliable solutions for valuation, safety and authentication

Learn more about our system integration capabilities at oceanoptics.com/oem

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