

Developing a Chemical-Imaging Camera

Infrared (IR) imaging, the technology for using an IR camera to generate images of hot sources, has become an important tool in the optoelectronics industry, and it is used routinely in industrial sensing, security, and

Infrared detectors use two types of materials, either photon detectors, such as indium antimonide (InSb) and mercury cadmium telluride (MCT), or thermal detectors such as deuterated triglycine sulfate (DTGS).

in the mid-IR (2–15 μm) was funded by the astronomy community and the U.S. Department of Defense. Defense spending drove the technology toward military technical specifications and applications that includ-

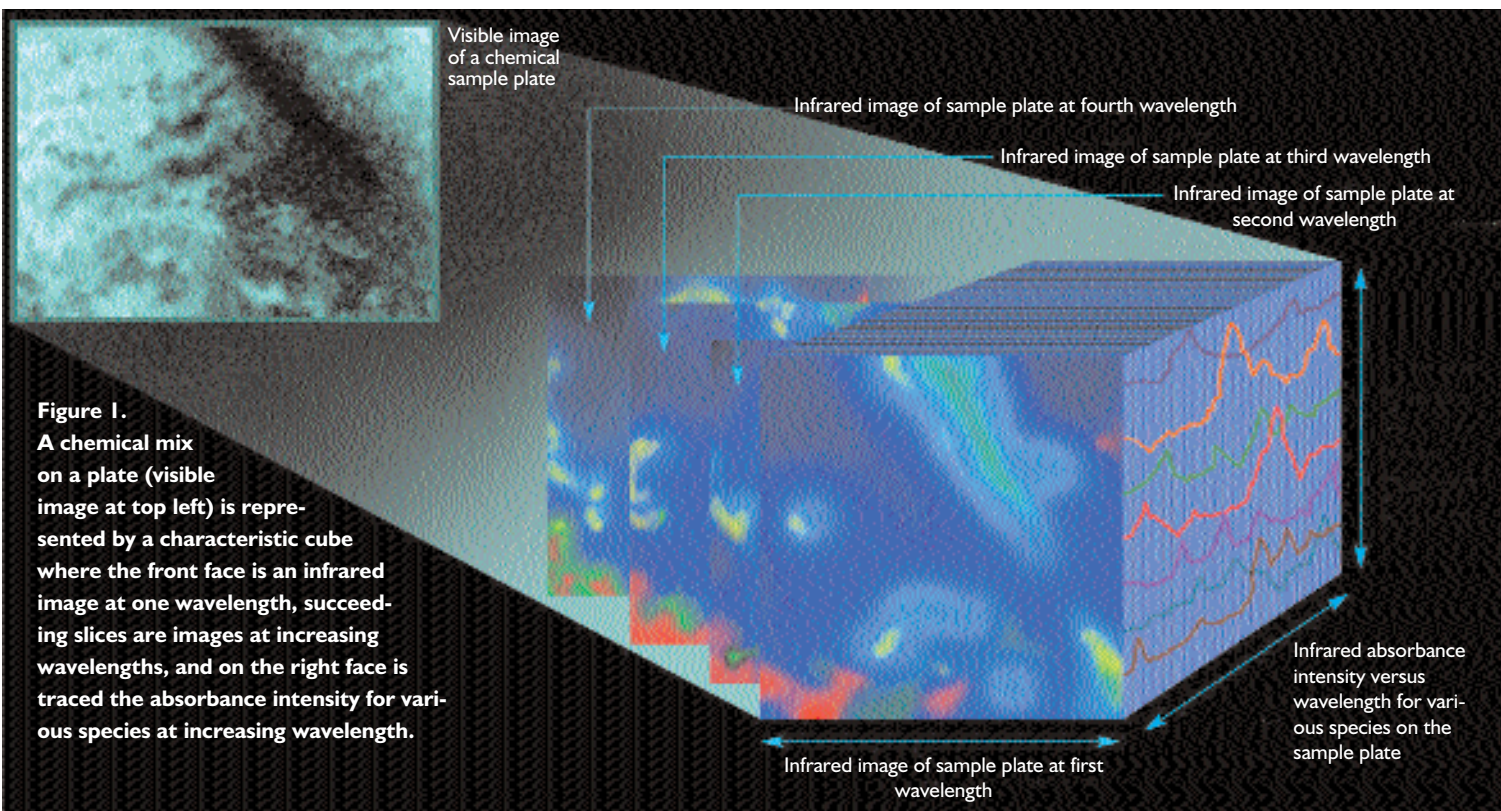


Figure 1. A chemical mix on a plate (visible image at top left) is represented by a characteristic cube where the front face is an infrared image at one wavelength, succeeding slices are images at increasing wavelengths, and on the right face is traced the absorbance intensity for various species at increasing wavelength.

firefighting. Major developments in detector technology have made IR imagers and focal-plane arrays available to industry and in technical areas such as quality control, where the cost was previously prohibitive.

These advances have also laid the foundation for developing a chemical-specific imaging camera, one dependent on IR technology and capable of capturing the chemical composition and distribution of a sample in seconds. When fully developed to the size of a camcorder with almost instantaneous imaging, this technology will have applications in research, industrial, security, military, and first-responder operations. It will, for example, enable a biohazards team to immediately determine whether a clear liquid leaking from a truck is water or a toxic fluid.

Both classes of detectors have proven technologies, and they are used as single-detector elements in many applications, including IR spectrometers.

An IR imaging system takes the technology of the detector and packages it to generate images. In a mechanical scanning system, one or more mirrors scan IR radiation across a linear array of these detectors and slowly build up an image of the sample. Focal-plane systems are two-dimensional detector arrays located at the focal point of the optical system and act as the film in a conventional camera.

Definitions of various IR wavelength ranges differ, especially in detector technology, between chemists and physicists (Table 1).

Initial development of focal-plane arrays

ed heat-seeking missiles and night-vision heads-up displays for aircraft and ground vehicles. Recently, however, emphasis has shifted from military uses to the development of commercial applications by private companies.

The technology for using focal-plane array detectors to sense IR radiation and generate thermal pictures has developed and matured over the past 15 years. Today, the technology is divided into two technical areas, uncooled and cooled. Table 2 lists some materials used for array detectors, each of which has parameters that make it appropriate for some applications and not others.

Uncooled technologies currently receive the most development funding. Often, however, either their wavelength response is inad-

equate to determine chemical spectral signatures, or the optical requirements of the detector material are too stringent for a spectrophotometer application. Nonetheless, uncooled focal-plane arrays are used in some commercial applications, including security systems and industrial inspection, so prices should fall as the technology matures. The most consumer-oriented application is called Night Vision, which General Motors' Cadillac Division began incorporating into its DeVille models in 2000. Night Vision relies on an uncooled

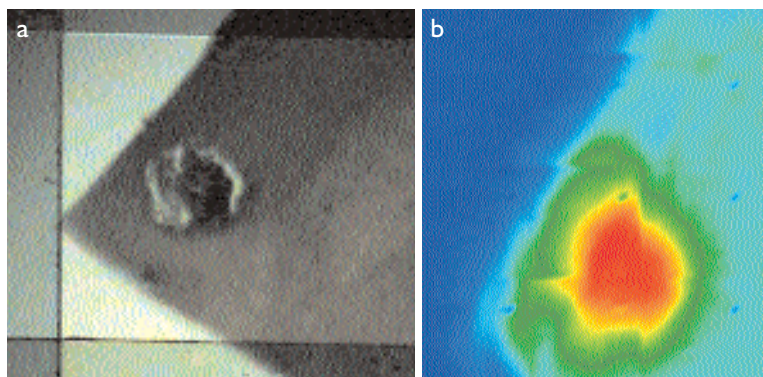


Figure 2. A visible image of a styrene acrylonitrile copolymer sample with a defect (a) does not show nearly as much information as an infrared image at a wavelength of 1735 cm^{-1} (b).

camera, which projects an image of the road ahead onto the windshield and allows the driver to see objects before the headlights illuminate them.

Chemical information

Chemical information derived from the fundamental vibrations of molecules is available in the 2- to $20\text{-}\mu\text{m}$ region of the spectrum. A subset of that region, called the fingerprint region, lies between 5 and $10\text{ }\mu\text{m}$ and is the richest in chemical data. Chemists have used the fingerprint region since the 1950s to determine the chemical identity of a compound by measuring frequency-dependent absorbances. Initially, the instruments used gratings or prisms and scanned across the wavelengths of interest.

In the late 1960s, chemists took a cue from physicists and began using Fourier transform IR (FTIR) instruments for chemical analyses. The first commercial FTIR unit entered the marketplace in 1969, and by the

mid-1980s, almost all laboratory-based general-purpose IR instruments were FTIRs. Today, FTIRs can capture the entire IR spectrum in a single scan of the interferometer and obtain a high-quality spectrum in less than 1 s, but without spatial information. Coupling an FTIR to a focal-plane-array detector with a broad-range linear response gives both a spectral and spatial picture.

This coupling idea dates back to 1972,

when A. E. Potter of the National Aeronautics and Space Administration patented a concept for a multispectral imaging system using a Michelson interferometer. Practical execution of this system took until 1979, when Potter and R. J. Huppi of the Stewart Radiance Laboratory (Bedford, MA) independently implemented the idea for atmospheric and astronomical measurements. Again, chemists were slow to notice the

technology, and it took twenty-five years for them to use it in a laboratory setting.

The first commercial spectrochemical imaging instrument used in a chemical laboratory was introduced in 1995. It incorporated an InSb detector, which gave chemists some chemical information. But because of the detector's long-wavelength IR cutoff at about $5\text{ }\mu\text{m}$, it had limited uses. To overcome this problem, Digilab introduced a commercial MCT-based spectrochemical imaging system in 1997. MCT focal-plane arrays available at that time typically had large formats (256×256 pixels or larger) and were custom-designed for military or astronomical applications. The new analytical instruments used a smaller-format device (64×64 pixels), the only cost-effective MCT array readily available at the time, which was developed for the U.S. Army's heat-seeking Javelin missile. Most of the early spectroscopy studies of chemical systems published in the chemical literature since 1995 have used a 64×64 -pixel MCT array, commonly called the Javelin detector.

The Javelin detector's essential technology did not change much between 1997 and 2000 because of the limited number of low-cost MCT focal-plane arrays commercially available. The Javelin detector has several design parameters that limit its application in laboratory spectroscopy. First, the device's rolling-mode readout, in which it reads one column of data as it integrates the next, is slow and requires

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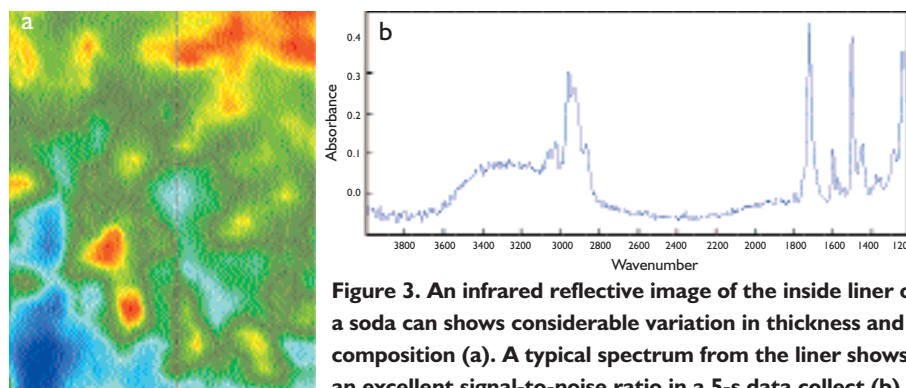


Figure 3. An infrared reflective image of the inside liner of a soda can shows considerable variation in thickness and composition (a). A typical spectrum from the liner shows an excellent signal-to-noise ratio in a 5-s data collect (b).

the interferometer to scan at slow speeds. As a result, the amount of data gathered is only about 3% of that possible, because the pixels are sampled sequentially and large amounts of usable information are lost.

Matching the flux levels from the spectrometers is another serious

issue with Javelin detectors. In a spectroscopic experiment, the spectrometer typically provides high flux levels. To use all the energy provided to the detector most efficiently, the focal-plane array must be capable of dealing with the high flux levels and remain linear, which the Javelin cannot do because its design does not allow independent adjustment of the integration time regardless of frame rate. To couple efficiently to the interferometer, the Javelin detector's limitations in a spectroscopic application can be overcome by using a snapshot readout, which increases the detector's efficiency from about 3% to more than 30%.

Chemical camera

The potential for instruments with wavelength specificity and spatial resolution to deliver images in the IR opened the door for a camera that could quickly pick up a specific chemical signature and generate a three-dimensional data cube of spectral, spatial, and intensity information (Figure 1).

With the experience gained with the Javelin detector, Digilab developed a second generation of focal-plane array systems for use with FTIR spectroscopy. This family of mid-IR focal-plane arrays is available in formats from 16×16 to 128×128 pixels. Arrays of 64×64 pixels can be read out rapidly, allowing their use with a conventional rapid-scan FTIR spectrometer and providing fast data-acquisition times. Even the 128×128 format array can read out

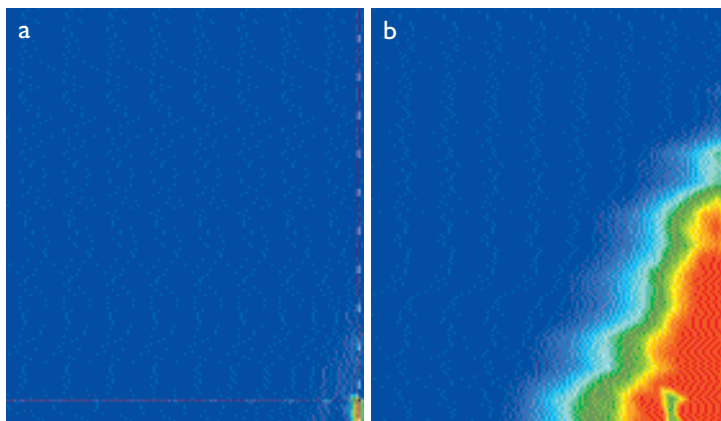
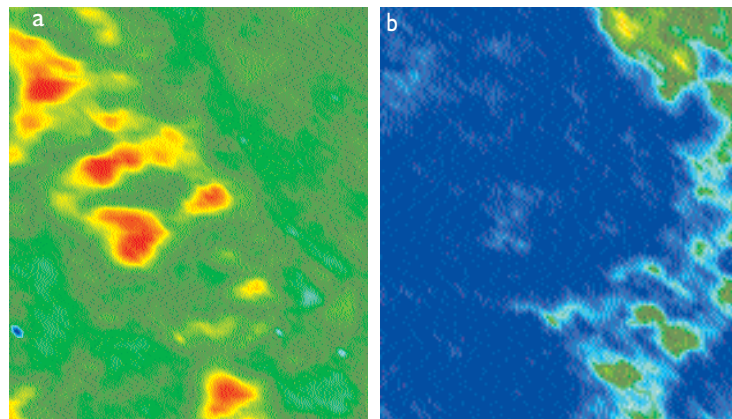


Figure 4. An infrared image at $1,675 \text{ cm}^{-1}$ of a metal surface that was contaminated with methyl salicylate and then cleaned still shows hot spots (red) where the contaminant was not removed (a). An image at another characteristic frequency ($1,090 \text{ cm}^{-1}$) confirms the contamination (b).

faster than the older technology using a scan-data collect rate of 800 Hz. These two advantages led to the ability to create a chemical-specific imaging camera, which in

Figure 5. Infrared images of an eggshell contaminated with salmonella show lower concentrations of calcium carbonate, the major component of eggshell, where the salmonella attenuates the $1,460\text{-cm}^{-1}$ carbonate absorbance (top right in a) and high concentrations of salmonella at the characteristic $1,630 \text{ cm}^{-1}$ frequency (b).



the laboratory can produce a spectral and spatial image in 2 s.

The new camera system consists of a commercial FTIR instrument, the newly designed MCT array, and a PC with a frame-grabber card, and it runs Windows 2000. In some applications described here, the camera was put on a microscope optical system designed to work in the IR to obtain approximately a $15\times$ magnification of the sample. The measurement of chemical heterogeneity, which drove the initial development and applications of this system, typically happens at the microscale level. Coupling the focal-plane array to a microscope that can view in the visible and collect in the IR gives a system with a spatial resolution of approximately $5 \mu\text{m}$. This resolution, for example, can reveal whether a time-release drug coated on an implantable polymeric device has been heterogeneously

distributed so that it will deliver the correct dose.

Combining an FTIR spectrometer with an array detector enables the collection of all data and spatial information at once. Using FTIR technology enables collecting the full range of IR spectra ($4,000$ to 950 cm^{-1}) from each pixel in the detector when the system is used for spectrochemical imaging. This technology can deliver a picture of the chemicals that make up a sample and their distribution in it.

Figure 2a shows a visible image of a styrene acrylonitrile copolymer with a defect, and Figure 2b, obtained in the IR, illuminates the defect. Data on this sample

were collected with 32 scans of the interferometer at 5 kHz and 8-cm^{-1} resolution in about 30 s. Acrylonitrile has a functional group that contains a carbon with a triple bond to a nitrogen, which has an IR absorbance at 2238 cm^{-1} . Other species in the sample had absorbances in the spectral regions characteristic of styrene. The defect area showed up strongly at 1735 cm^{-1} . IR absorbance at this wavelength is due to a carbonyl species, which has a carbon double-bonded to an oxygen atom. Further examination of the spectra showed a speck of stearate material.

In a spectroscopic experiment, it is important to determine the signal-to-noise ratio in order to differentiate chemistries. Figure 3a shows an image taken in reflection on the inside of a soda can. At the spatial resolution achieved by the optics ($5 \mu\text{m}/\text{pixel}$), the inside liner shows consid-

TABLE 2. PROPERTIES OF SOME MATERIALS USED IN FOCAL-PLANE ARRAYS

Material	Wavelength range	Performance	Cooling requirements	Notes
Microbolometers	8.0–15.0 μm	Very uniform	None, thermally stabilized	—
PtSi	1.0–3.5 μm	Nonflat response	—	Low quantum efficiency
InSb	0.2–5.4 μm	Best performance in mid-IR	77 K	—
HgCdTe	2.0–15.0 μm	Best performance in longwave IR	77 K	—
Quantum-well infrared photodetector	Engineered to narrow ranges between 3 and 19 μm	Not a broad-range detector	60 K	Quantum efficiency is lower than that of HgCdTe or InSb

erable variations in thickness and composition. Figure 3b shows a typical spectrum from the can liner illustrating an excellent signal-to-noise ratio in a 5-s data collect.

In a chemically contaminated system, decontamination efficiency is an important parameter to measure. As an example, we applied methyl salicylate to a metal surface. The compound has several IR absorptions in the mid-IR region, which can be used to illustrate the power of the spectrochemical-imaging technique. Figure 4a shows the metal surface after contamination with methyl salicylate and cleaning with a swab. The image—generated at $1,675\text{ cm}^{-1}$, a strong absorption in the chemical—shows hot spots (red) where the contaminant was not removed. This data set was collected in approximately 80 s. A chemist trying to confirm the identity of a chemical compound first looks for a characteristic absorbance and then looks for a confirming absorbance at a different frequency. At $1,090\text{ cm}^{-1}$, a similar image confirmed the contamination in the lower right corner (Figure 4b).

We also examined the surface of an eggshell for biological contamination. The eggshell surface was inoculated with non-pathogenic salmonella. Figure 5a shows an image constructed at the absorption for calcium carbonate, the major component in eggshell. In it, the area of salmonella contamination shows up as a lower concentration of carbonate because the overlaid salmonella attenuates the absorbance from the carbonate species. The image in Figure 5b clearly shows the location of the salmonella on the right-hand side of the image.

Preliminary data demonstrates the feasi-

bility of developing a chemical-specific camera with important applications in industry, research, and national security. As the new technology matures, the speed and ruggedness of the equipment will improve. The ultimate goal is to develop a camera that provides images and chemical identification in real time.


Further reading

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B I O G R A P H Y

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