Future Technologies | 5

R esearch currently under way is developing new technologies that could improve significantly the effectiveness of environmental monitoring. This chapter first discusses how monitoring effectiveness might be improved, next summarizes the general directions of laboratory research, and then describes some specific approaches.

STRATEGIC DIRECTIONS

One significant improvement expected in future environmental monitoring is **remote sensing,** the ability to collect information without physically collecting samples. Remote sensing could be valuable for rapid screening of many sites, especially if that must be done without the cooperation of the state. (Note that this is not an IAEA function.) Two approaches are possible: aerial and ground-based, remote surveillance. Spacecraft already have unrestricted overflight rights, and flights for aircraft at altitudes above 10 kilometers could become acceptable under an Open Skies Treaty.[1] Sensors that operate at these ranges could be used routinely to monitor areas

of concern without on-site inspection. The other approach is for shorter-range technologies that could sample a stack plume from a convenient nearby ground location.

The schemes for remote environmental monitoring discussed here are optical in nature, using ultraviolet or infrared light. There are active schemes that supply the light they need, and passive schemes that use existing sunlight or thermal radiation. In either case, the monitoring instrument views the area under investigation and analyzes light received from it.

As discussed in the section *Improving Technology,* such techniques can identify airborne molecules, but with only moderate accuracy and specificity. They are much less sensitive to solid material, and—in most cases—they cannot differentiate among isotopes of the same element. However, they are naturally adapted to surveying a large area for suspicious occurrences, and can select and focus on a small spot within that area.

Another direction of significant improvement will be instruments of **greater sensitivity and/or selectivity**. This would allow future investigations to use smaller samples (possibly down to

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[1] U.S. Congress, Office of Technology Assessment, *Verification Technologies: Cooperative Aerial Surveillance in International Agreements*, OTA-ISC-480 (Washington, DC: U.S. Government Printing Office, July 1991).

single dust particles), process samples that are more dilute, measure additional contaminants, or provide higher-quality answers. The most dramatic improvement comes from combining two different technologies so that the substance being measured passes two independent selection screens. **Greater speed** would allow the processing of more samples for greater statistical accuracy.

Portability is also desired. Some new technologies are intrinsically small-scale, and other technologies are being miniaturized. An instrument that can be hand-carried at an inspection site can provide immediate results to guide the inspection strategy. At present, an instrument weighing 61 pounds can be called portable;[2] standards will change with further miniaturization.

Features of remote sensing and portability could be combined by mounting instruments on an aircraft and flying it to the inspection site. There it can fly through an exhaust plume, collect samples, and analyze them immediately.

IMPROVING TECHNOLOGY

Two kinds of technologies are under development for environmental monitoring to detect a clandestine weapon program. One kind looks for suspicious isotopes, such as uranium-235 or technetium-99 (as does most current technology as discussed in chapter 3). The other kind looks for suspicious molecules, such as HF (hydrogen fluoride) or TBP (tributyl phosphate). (See the end of this chapter for another possibility: looking for waste heat from a concealed nuclear reactor.)

❚ Identifying Molecules

The chemist has many analytical tools to identify molecules of interest: infrared spectroscopy, mass spectrometry, chromatography, and benchtop chemical analysis. Finding specific molecules in the environment is useful for many missions, from detecting a chemical weapon program to measuring pollution; new technologies may be truly dual-use, with application both to national security and to civilian needs. On the other hand, a specific molecule may have many legitimate sources, and its presence only indicates an anomaly worth further investigation; also, some signature molecules will not be found in the environment for reasons such as low vapor pressure or because they react with atmospheric gases to form other species.

Infrared Spectroscopy

Infrared "fingerprints" observed by infrared or Raman spectroscopy (box 5-1) can be used to identify particular molecular species. Chemists usually record the entire fingerprint spectrum using a laboratory infrared source, and laser Raman spectroscopy[3] naturally gives the entire spectrum. Another technique under development that will cover a broad spectral region is a passive airborne infrared spectrometer.[4] Alternatively, it may be possible to look at individual spectral features using DIAL (differential absorption LIDAR), in which a laser alternates between the frequency of a characteristic molecular absorption line and a different nearby frequency, and the receiver looks for a corresponding change in return signal due to the presence of the absorbing molecule.[5]

Infrared or Raman spectroscopy is able to detect molecules as vapor in air, and in solution.[6] For the lighter elements (hydrogen to oxygen), different isotopes of the same element are distinguishable because their vibration frequencies, which depend on mass, can be differentiated. It is less suited for analyzing solid material, or for

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[2] Brian Andresen et al., "A Small, Portable Gas Chromatograph-Quadrupole Mass Spectrometer for On-Site Analysis," Lawrence Livermore National Laboratory, UCRL-ID-116939, April 1994.

[3] Briefing by C. Chen, Brookhaven National Laboratory, Jan. 10, 1995.

[4] Briefing by A. J. Ramponi, Lawrence Livermore National Laboratory, Mar. 1, 1995.

[5] Briefing by Lyn Pleasance, Lawrence Livermore National Laboratory, Mar. 1, 1995.

[6] Briefing by C. Chen, Brookhaven National Laboratory, Jan. 10, 1995.

BOX 5-1: Infrared Spectroscopy

Different colors of light are waves with different oscillation frequency and correspondingly different wavelength (which is the speed of light divided by the frequency). The characteristic vibration frequencies of molecules are in the infrared (IR) spectrum; the much higher frequencies to which atoms respond are in the ultraviolet (UV). Visible light occupies the intermediate region between UV and IR, to which many substances do not respond. These substances are therefore transparent.

Light frequencies are so large that the numbers are hardly meaningful. For example, water vapor makes air essentially opaque to a broad band of infrared radiation near a wavelength of 6.2 micrometers. This corresponds to a frequency of 5×10^{13} Hertz (cycles per second). It is more usual to specify this frequency as 1600 waves per cm, or a wave number of 1600 cm^{-1}.

Most molecular species have a number of infrared absorption lines, or characteristic frequencies that they absorb strongly. The spectrum of light that has passed through air containing these molecules will show narrow dark bands (spectral lines) due to that absorption. The pattern of lines forms a "fingerprint" that identifies that molecular species.

Raman spectroscopy is another way to measure a molecule's infrared fingerprint. Here light of high frequency (visible or UV) interacts with the molecule, and re-emitted (scattered) light is analyzed. Due to the Raman effect, some of the scattered light will be shifted in frequency by an amount equal to a characteristic frequency of the molecule. With a single-frequency laser source, the returning light will display a spectrum with bright lines corresponding to molecular frequencies—also a fingerprint.

SOURCE: Office of Technology Assessment, 1995.

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distinguishing among isotopes of heavy elements, for which the relative changes in vibration frequency due to mass differences are much smaller.

In a mixture of many different molecular species the fingerprints are likely to overlap, obscuring some of the lines and complicating identification. Also, large and interesting molecules tend to have poorly defined spectral features with broader absorption lines than smaller simple molecules. As a result, infrared or Raman spectroscopy can be expected to identify and characterize simple molecules but may not be very sensitive to the large complex molecules important to environmental monitoring. Remote sensing by infrared spectroscopy does offer the possibility of rapidly screening large areas to locate any regions of suspicious activity.

Mass Spectrometry

Chemists use mass spectrometry to identify molecules based on their masses, and are therefore concerned with measuring a wide range of masses. The heaviest atoms weigh about 250 atomic mass units (amu—approximately equivalent to the mass of a hydrogen atom). Interesting organic molecules range up to 10 times this value, and biological molecules can reach several hundred thousand amu. Molecules are broken up by the ionization necessary for mass spectrometry. Thus a single molecular species can give rise to a spectrum of different fragment masses, which define the mass spectral fingerprint for that molecule.

Conventional mass spectrometers (see chapter 3) separate and identify atoms or molecules according to their response to magnetic forces. Ionized molecules are accelerated electrically and follow a narrow path through a magnet, which bends their trajectories: the larger the mass, the smaller the deflection angle. These systems need relatively large samples because the ionizer and molecular throughput are not very efficient.

Improvements in magnetic spectrometer efficiency are discussed below in connection with identifying particular nuclei. In addition, more

sensitive technologies using electric forces have been demonstrated. Ion trap[7] and time-of-flight[8] mass spectrometers do not need a narrow path, and the latter can measure molecules of biological size. These technologies can be combined with laser ionization, which causes less damage to molecules and further increases the efficiency, compared to other types of ionization.

Future mass spectrometers will have greatly improved sensitivity, making this already useful technique much more useful.

Other Tools

Molecules can also be identified by their chemical properties. Liquid and gas chromatography are techniques where the sample is mixed with a carrier that flows through a column to separate mixtures of chemicals; different substances are carried through the column at different rates, depending on how they interact with the surface coating of the column. Thus chromatography separates the sample into fractions that come out of the system at different times. The molecule of interest comes out at a time established by previous tests, and that fraction can be analyzed further. Electrophoresis is a similar technique, where substances are mobilized by an electric current instead of a flow of material across a surface.

These analysis techniques are considered destructive in that they use up the sample, precluding further tests. However, it is possible to construct a surface which selectively attracts some molecules and holds onto them without destroying them. A micromechanical surface-acoustic-wave sensor[9] can compare the density of molecules held by different surfaces, providing still another "fingerprint" that can be used to identify the molecular species (see *Specific Approaches*).

Tools that use chemical interactions require the development of a "cookbook" of recipes, specifying reactants and procedures, before they can be used in practice. Chromatography is an established technique that is already in use for environmental monitoring.

▊ Identifying Isotopes

The nuclear scientist also has a number of tools with which to find nuclides of specific interest. Most of the key nuclides are radioactive, and the radiations they emit can be detected and analyzed (see chapter 3). Mass spectroscopy can determine the relative abundance of different isotopes. Other techniques involve inducing the atoms to emit characteristic radiations. Activation analysis (neutron bombardment resulting in new radioactive isotopes due to transmutation or fission) was covered in chapter 3. There are also optical resonance (scattering of characteristic light frequencies) and induced radiation (emission of characteristic x-rays or gamma rays).

These tools are more specific than those used to identify molecules, and the nuclei they detect are much less ambiguous indicators of a clandestine weapons program. The tools are also less suitable for dual-use. However, some of them have been applied to studying the fossil record of the earth's history by measuring elemental and isotopic abundance ratios, yielding information on various geological and meteorological processes.

Measuring Radioactivity

Counting atomic disintegrations is a mature discipline (see chapter 3), and this chapter is concerned only with advanced state-of-the-art means of doing so. Radioactivity provides a highly sensitive means of detecting atoms or molecules that have previously been selected and concentrated. Its application to capillary electrophoresis and tritium measurement will be mentioned later (see *Specific Approaches*).

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[7] Briefing by Aaron Garrett, Los Alamos National Laboratory, Feb. 27, 1995.
[8] Briefing by Charles Wilkerson, Los Alamos National Laboratory, Feb. 27, 1995.
[9] Briefing by Tony Ricco, Sandia National Laboratories, Feb. 28, 1995.

Mass Spectrometry

As already mentioned, the weak point of conventional mass spectrometers is collection efficiency. An instrument with greatly improved efficiency has been developed by combining state-of-the-art technology in isotope separation and ion optics.[10] It has a better ionizer and a broader beam path.

Optical Resonance

Individual atoms can respond strongly to light that is tuned to an atomic transition frequency. For example, extremely small quantities of sodium can be measured by resonant excitation and re-emission of yellow light at 589 nanometers wavelength. This method is very selective for atomic species (nuclear charge); combining it with mass spectrometry to select for nuclear mass provides an absolutely unambiguous identification of a particular isotope. Unfortunately, the strongest responses come from the alkali metals (sodium, potassium, rubidium, and cesium), and the application of this technique to other elements is not obvious.

Induced Radiation

When a solid sample is bombarded by a particle beam (of electrons or ions), or by gamma rays, the atoms and nuclei in it can be stimulated to emit radiations. All except the lightest atoms will produce x-rays characteristic of the atomic species. X-ray tubes use electron bombardment; use of ions or low-energy gamma rays to irradiate samples can give a cleaner signal. In addition, ion bombardment of many of the heavier nuclei causes Coulomb excitation, in which the nucleus is stimulated to rotate and to emit gamma rays characteristic of the nuclear species. These methods are sensitive and selective for most nuclei of interest, and will be applied more often in future instruments.

SPECIFIC APPROACHES

▌ Laser Remote Sensing

The U.S. Department of Energy (DOE) has a program called CALIOPE (Chemical Analysis by Laser Interrogation of Proliferation Effluents). This is a collaborative effort involving five national labs, which are pursuing various ideas for laser remote sensing. It is intended to culminate with an airborne field demonstration of the most promising ideas. Current research efforts include:

- **Enhanced UV Raman Spectroscopy:** A characteristic of the Raman effect is that the return signal is weak. Using ultraviolet instead of visible light can increase the signal by a factor of 1000, and changing (modulating) the laser output and looking for changes in the return can result in suppressing the noise by a similar factor.[11] Ultraviolet light does not travel well through the atmosphere, limiting this technique to distances less than 1 kilometer. Its best application may be on-site characterization (of stack plumes, for example) instead of airborne use.

- **MWIR (Mid-Wave Infrared) DIAL (Differential Absorption LIDAR):** Recent advances in tunable infrared laser technology have made it possible to probe the spectral fingerprint lines of many molecules with a single instrument covering the spectral range from 2.5 to 4.5 micrometers.[12] This instrument could be used at airborne ranges of many kilometers.

Early tests are encouraging, but much development work remains before any of these concepts could be used routinely in the field. The ultimate sensitivity and specificity of these technologies are still to be determined; it is not easy to detect the fingerprints of molecules in trace concentrations, and most molecules, even if detected, are uncertain indicators of clandestine activity.

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[10] Briefing by Jane Poths, Los Alamos Scientific Laboratory, Feb. 27, 1995.

[11] Briefing by C. Chen, Brookhaven National Laboratory, Jan. 10, 1995.

[12] Briefing by Lyn Pleasance, Lawrence Livermore National Laboratory, Mar. 1, 1995.

∎ Airborne Measurements

The Department of Energy also has a program called AMPS (Airborne Multisensor Pod System). Three different sensor pods have been built and are being tested on a P-3A aircraft:[13]

1. Synthetic aperture radar;
2. Optical imaging sensors
3. Effluent species identification.

While all three pods are intended to gather information on clandestine activity, only pod 3 will demonstrate technologies for environmental sampling and analysis. Three instruments will sample the air through which the plane flies (which can include an exhaust plume of a suspected facility), with high sensitivity due to the large volume of air sampled, and two additional instruments will view the area within several kilometers of the plane:

- **Real-time radionuclide analyzer:** Collects particles and some vapors on filter cartridges and promptly records their high-resolution gamma-ray spectra. With a cycle time of 1 minute, it can detect short-lived radionuclides with a sensitivity that can reach 5000 atoms per cubic meter of air (for substances with a 4-hour half-life).
- **Ion trap mass spectrometer:** Collects chemical vapors and analyzes them, with a sensitivity that can reach parts per trillion.
- **Whole air sampler:** Collects air components for later analysis.
- **Echelle grating spectrometer:** Analyzes sunlight reflected off the ground to determine the molecular absorption in an exhaust plume.[14] It covers a wide spectral range, from 2.0 to 4.2 micrometers, records continuously over the entire range with very high spectral resolution, and is sensitive to parts per million in a 1-meter-wide plume.

- **IR tracking system:** Correlates an IR signature with the other sensor data.

This program will reduce to practice several technologies already available in the laboratory. A pod carrying multiple instruments is an excellent way to collect airborne data. Experience will tell whether the instruments chosen are the right ones—for example, whether the molecule detectors (ion trap and echelle grating) see any useful signals.

∎ Chemical Identification

Several different advanced ideas for identifying molecules are being developed and improved. They include:

- **Ion trap mass spectrometry:** Catches ionized atoms or molecules in an electrostatic trap where they can be held and measured precisely. Sensitive to parts per billion or less (see above).[15]
- **Time-of-flight mass spectrometry (TOFMS):** Electrically accelerates molecules and measures how rapidly they move, with heavier molecules moving more slowly than lighter ones for a given accelerating voltage. TOFMS can measure the weight of molecules up to several hundred thousand amu in mass.[16]
- **Microsensor arrays:** A micromechanical surface-acoustic-wave sensor is built with a coated chemical reagent that selectively attracts some molecules and holds onto them without destroying them. Since the propagation of sound waves along the surface depends on the density of adsorbed molecules, such a sensor can measure the concentration of the substance that binds to it. An array of these with different chemical surfaces will show different densities of attracted molecules, and

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[13] Briefing by Bruce Roberts, Pacific Northwest Laboratory, Mar. 3, 1995.
[14] Briefing by A. J. Ramponi, Lawrence Livermore National Laboratory, Mar. 1, 1995.
[15] Briefing by Aaron Garrett, Los Alamos National Laboratory, Feb. 27, 1995.
[16] Briefing by Charles Wilkerson, Los Alamos National Laboratory, Feb. 27, 1995.

thus offers some hope of identifying the molecular species.[17]

The two electrostatic mass spectrometers have been demonstrated in the laboratory, and they offer significant performance benefits. They also may offer easier portability, because they do not contain magnets. The microsensor array is in the research stage; it seems better suited for monitoring changes in abundant molecules (that is, process control) than for identifying rare ones.

▌ Nuclear Mass Spectrometry

Various improvements to ordinary magnetic mass spectrometry (chapter 3) are under development. They include:

- **Laser ablation source:** Laser light is focused on a single dust particle or a small region, vaporizing only the selected material for input to the mass spectrometer.[18]
- **Improved design:** A mass spectrometer several thousand times more efficient and more sensitive was constructed using modern advances in isotope separator and ion optics technology. It can measure the isotopic composition of atmospheric Kr and Xe from 10-cc air samples, and it can do so accurately enough not only to detect reactor emissions (natural and fission-product Kr and Xe have different isotopic ratios), but to distinguish between uranium and plutonium reactor sources.[19]
- **Accelerator mass spectrometry:** This extremely sensitive technique (chapter 3) is being extended to a large part of the periodic table.[20]
- **Projectile x-ray detection:** The accelerator mass spectrometer can be modified to select for atomic species as well as nuclear mass, by observing the x-rays that result when the selected atoms hit a target at the end of the

machine. The result is an unambiguous identification of the nuclide.[21] (Ordinary mass spectrometers do not produce x-rays because the atoms have too low a speed.)

Mass spectrometer designs of the future will draw on these technologies, as well as electrostatic mass spectrometer (see above) and optical detection (see below) technologies, to produce the best instrument for each application. Greater sensitivity and selectivity is the major benefit.

▌ Optical Resonance Spectrometry

Different isotopes of the same atomic species absorb and scatter light at slightly different characteristic frequencies. With extremely precise frequency control, a laser can be tuned to interact selectively with one isotope and detect it. Practical applications include:

- **Photon burst detection:** The atoms pass through a series of detectors while being illuminated with light at the desired isotope's characteristic frequency. The correct isotope will scatter light into each detector as it passes by. The wrong isotope may occasionally scatter light, but will not trigger all of the detectors. This method has demonstrated the ability to detect a rare isotope at a dilution of 10 parts per billion in ordinary krypton, and the current goal is 10 parts per trillion (the natural abundance of radioactive krypton-85). The method may apply to 40 or 50 atomic species, including many important fission products.[22]
- **Optical trap detection:** The atoms are caught and held in a magneto-optical trap, due to the combined effects of resonance light and a magnetic field. Their presence is measured by

[17] Briefing by Tony Ricco, Sandia National Laboratories, Feb. 28, 1995.
[18] Briefing by Brian Andresen, Lawrence Livermore Laboratory, Mar. 1, 1995.
[19] Briefing by Jane Poths, Los Alamos National Laboratory, Feb. 27, 1995.
[20] Briefing by Ivan Proctor, Lawrence Livermore Laboratory, Mar. 1, 1995.
[21] Ibid.
[22] Briefing by H. Oona et al., Los Alamos National Laboratory, Feb. 27, 1995.

the intensity of scattered light. This technique may be limited to the alkali metals.[23]

In the laboratory, both of these methods have been applied to atoms coming out of a mass spectrometer, with the promise of much greater sensitivity and selectivity.

▌ Nuclear Identification

Several miscellaneous ideas for identifying nuclei are being researched. These include:

- **Capillary electrophoresis:** A small instrument that analyzes nanoliter quantities of liquid in minutes; it has been used to separate fission products. In this application, a counter detects the radioactivity of different fractions; other detection schemes are possible. The system offers small size and speed; may be more adapted to process control than to trace element detection.[24]
- **Particle-induced x-rays:** Bombards a filter or swipe containing particles of interest with ions from a high-voltage accelerator. The system can locate a particle and then focus on it. The resulting x-rays and gamma-rays give a nondestructive simultaneous measurement of all atomic species from sodium to the high end of the periodic table, and can also provide some indication of isotope ratios in heavy nuclei.[25] Relatively costly.
- **Laser ionization mass spectrometry of iodine-129:** Improves the efficiency of a mass spectrometer to detect I^{129} by a factor of 1,000 over conventional techniques, by using a laser to selectively ionize the iodine atoms.[26] A special-purpose tool.
- **Automated hydrogen isotope system:** Automated system to extract tritium from air and count it. One measurement every three hours,

expected to be sensitive to tritium at background levels (the abundance at which it is found in the absence of a local source: two disintegrations per minute per cubic meter of air).[27] Not yet built.

In addition to technology development, new methods of data analysis are being pursued. "Nuclear Archeology" analyzes the isotopic ratios of impurities which have been irradiated in reactor components. Given a sample of graphite moderator taken from a nuclear reactor (i.e., a research reactor or a gas-cooled power reactor), the method measures the isotopic ratios of impurities such as barium and titanium. This determines how many neutrons were generated over the reactor's lifetime, and therefore its power history. Discrepancies with reported use can indicate that the reactor was used for undeclared purposes, possibly including the production of plutonium.[28] This is a new application of relatively conventional technology.

▌ Thermal Imaging

DOE is also building an experimental satellite that will view the earth in 15 different spectral bands covering the visible and infrared.[29] It will measure local ground and water temperatures to an absolute accuracy of 1 degree K (Kelvin). This should be sufficient to detect the waste heat from a clandestine plutonium production reactor. For example, the flow of cooling water from such a reactor into a river or lake has been modeled and would appear as an easily detected plume of higher water temperature. This is a demonstration program, not a monitoring program, and the satellite is expected to operate for only one to three years.

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[23] Briefing by Dave Vieira, Los Alamos National Laboratory, Feb. 27, 1995.

[24] Briefing by Brian Andresen, Lawrence Livermore Laboratory, Mar. 1, 1995.

[25] Briefing by Arlyn Antolak, Sandia National Laboratories, Feb. 28, 1995.

[26] Briefing by Bret Cannon, Pacific Northwest Laboratory, Mar. 3, 1995.

[27] Briefing by Paul Reeder, Pacific Northwest Laboratory, Mar. 3, 1995.

[28] Briefing by Bruce Reid, Pacific Northwest Laboratory, Mar. 3, 1995.

[29] Personal communication with Bob Courtney, Sandia National Laboratories, Apr. 6, 1995.