

Detecting one molecule of explosive in one thousand billion

Whether it be to counter terrorist threats, to provide against accidents, or to monitor or regenerate polluted sites, the requirement for detection, and even quantification techniques to deal with traces of explosives is becoming increasingly pressing, in the laboratory as on the ground. Research workers at CEA are contributing to the development – among a range of solutions – of “electronic noses,” exhibiting ever higher performance.



Testing, under a fume hood, a detector of the quartz microbalance type, at CEA's Le Ripault Center.

Explosives detection is an issue of burning immediacy, and raises a major challenge in terms of research and development, for the coming years. Whether for applications relating to civilian security (the growing use of explosives by terrorists, and the dissemination of mines around the world), or for environmental monitoring (regeneration of polluted industrial sites, for instance), there is indeed a huge requirement for detection, and in some cases quantification, of traces of explosives, be it in the atmosphere, soil, or water.

A few teams around the world are endeavoring to meet this demand, though the development, and validation of analytical techniques, or the design of wholly artificial, highly sophisticated devices, known as “artificial noses.” After a rehearsal of the technological and scientific

challenges raised by this issue, the following pages will present the various explosives detection techniques developed by CEA, at its Le Ripault (Indre-et-Loire *département*, central France) Center. The fight against terrorism, indeed, is one of the major remits now entrusted to the organization's Defense nexus.

An arduous problem

Explosives detection is an arduous problem, since this requires both taking on board all families of explosives (see Box), and having the capability to detect them, or even to quantify their concentration, whatever environment is encountered. The issue, obviously, is not the same, according to whether the explosive occurs in the atmosphere, in water, or in the soil.

Among the chemical identification techniques currently employed may be included conventional structural chemical analysis techniques, such as **nuclear magnetic resonance**, **infrared** and **ultraviolet (UV) spectroscopy**, **mass spectrometry (MS)**, or structural techniques coupled with separation units, such as **gas chromatography (GC)**, or **liquid chromatography (LC)**, coupled to detection by mass spectrometry, better suited to detect such low concentrations (see Box D, *Spectroscopy and spectrometry*; and Box E, *What is chromatography?*). These allow highly precise identification, and quantification, of the explosive, be it in the atmosphere, water, or soil. These techniques are peculiarly suitable for the assessment of site pollution levels, in any one of these environments. On the other hand, owing to their large footprint, cost, and operation requiring a trained specialist, they do not, as yet, meet the requirement for the detection of explosives being used for malicious purposes.

The special case of detecting traces of explosives in the atmosphere is made extremely arduous by the low vapor pressure⁽¹⁾ inherent to these compounds. Thus, TNT exhibits a vapor pressure of a few **parts per billion (ppb)**: 1 ppb meaning one **molecule** TNT for 1 billion molecules of air), while that for hexogen (RDX) stands at a few **parts per trillion (ppt)**: 1 ppt corresponding to one molecule RDX in 1,000 billion molecules of air). This means that the detection system must be especially sensitive, while exhibiting rapid response, and high selectivity. Among specific, readily mobile methods stands, first and foremost, use of animals, dogs in particular, enabling very high levels of sensitivity to be achieved. Their training, however, can prove protracted, and costly. **IMS (ion mobility spectrometry)** trace

(1) Vapor pressure: the pressure exerted by the vapor phase on the surface of the liquid or solid phase of a substance, when equilibrium sets in between these various phases. It is thus equal to the maximum pressure this substance may exert, if vapor is to be released. It is directly proportional to that substance's temperature.

The four main families of explosive molecules

Explosive molecules are subdivided into four major families:

- **nitroaromatic compounds (NACs)**, such as 1,3,5-trinitrotoluene (TNT), picric acid, hexanitrostilbene (HNS), or dinitrobenzene (DNB);
- **nitramines** or **nitrosamines**, such as octogen (HMX), or hexogen (RDX);
- **nitric esters**, such as pentaerythritol tetranitrate (PETN), ethylene glycol dinitrate (EGDN), nitroglycerine, or nitroguanidine (NQ);
- **organic peroxides**, such as triacetone triperoxide (TATP), or hexamethylene triperoxide diamine (HMTD).

detectors have been miniaturized, being offered under the names IMS Ionscan 500 DT (Smiths Detection) and VaporTracer (GE Ion Track) in the United States. Another system, relying on detection of nitrogen oxides (NO₂) yielded by the breakdown of explosives, is being brought to market under the brandname EVD-3000 (Scintrex Trace). This detection is carried out by measuring the current yielded by the **reduction** of NO₂ to NO. This device allows detection of EGDN, TNT, pentaerythritol tetranitrate, or RDX, with a response time lower than one minute. Likewise, to meet the specific requirements for detection of traces of explosives at airports, novel analytical technologies are emerging: mention may thus be made of the developments due to R. Graham Cook's team at Purdue University (Indiana), in the United States, using the DESI (desorption **electrospray ionization**) technique to detect organic peroxides, and development of the new DART™ (Direct Analysis in Real Time) source, commercialized by JEOL, allowing explosives to be detected with no sample preparation required.



A number of ranges of explosives detection systems have emerged over the past few years, in the United States. Miniaturized IMS (ion mobility spectrometry) trace detectors have been brought to market under the names IMS Ionscan 500 DT (Smiths Detection) and VaporTracer (GE Ion Track). Another system, relying on detection of nitrogen oxides (NO₂) yielded by the breakdown of explosives, is being commercialized under the brandname EVD-3000 (Scintrex Trace, AutoClear Group).

The AccuTOF-DART™
(Direct Analysis
in Real Time) source,
commercialized by JEOL,
allows explosives
detection with no sample
preparation required.



In practice, the high cost (around 20,000 €), and low reliability of such equipment stand as a hindrance to their widespread deployment. Thus it is a combination of these two types of techniques – analytical

methods, and portable systems – that will meet the issue raised by explosives detection in all respects.

Laboratory analytical techniques being developed

The means of detection available for use in the laboratory exhibit, as a rule, low mobility, owing to their large footprint, and associated ancillary systems. They do afford, however, the prize advantage of having the ability to yield very precise information as to the chemical nature of the molecules being looked for, coupled, if required, with quantification. The presence of a mix of such molecules is as a rule no impediment to these techniques, featuring as they do, for the higher-performance systems, integral separation units. Recent breakthroughs concern extension of the domain of application of laboratory methods, to cover searching for compounds present, in the environments being investigated, at very low concentrations. The outcome is the development of sampling tools compatible with laboratory resources, while remaining usable in both indoor and outdoor conditions, in remote sites targeted for analysis. The main purpose of such sampling means is to enhance the ultimate sensitivity of the analytical resource. Drawing up measurement protocols relies on an analytical approach allowing the entire event chain to be controlled: sampling in the field, sample preservation and preparation, laboratory analysis, and interpretation. Optimizations seek to minimize losses during the various transfer steps, through rigorous qualification. In most cases, the sensitivity and selectivity exhibited by such a chain are, even yet, much higher than achieved with portable techniques. This consideration means laboratory techniques are safe from most detection false alarms, whether positive, or negative. The molecules being sought may be found in the three types of environmental matrix: liquid, solid, or gaseous. For each of these, a specific analytical protocol is required, as will be seen from the following examples.

Aqueous matrices

Water is the most common liquid matrix. It is a peculiar environment, which, owing to its solvation⁽²⁾ properties, has the ability to retain naturally a varying proportion of most molecules. This environment may be directly analyzed by means of **high-performance liquid chromatography (HPLC)**, coupled to an ultra-violet photodiode-array (UV-PDA) detector and a mass spectrometer. The chromatography system allows the separation of the various analytes, i.e. the various molecules subject to analysis, upstream of the detection devices. The photodiode array and mass spectrometer provide the UV and mass spectra, respectively, for the molecules present, thus yielding, respectively, their quantification, and precise chemical identification.

The presence, in this matrix, of other molecules, whether of explosives or otherwise, causes no interference, since detection is preceded by a separation step. Figure 1, indeed, illustrates this point: this shows the

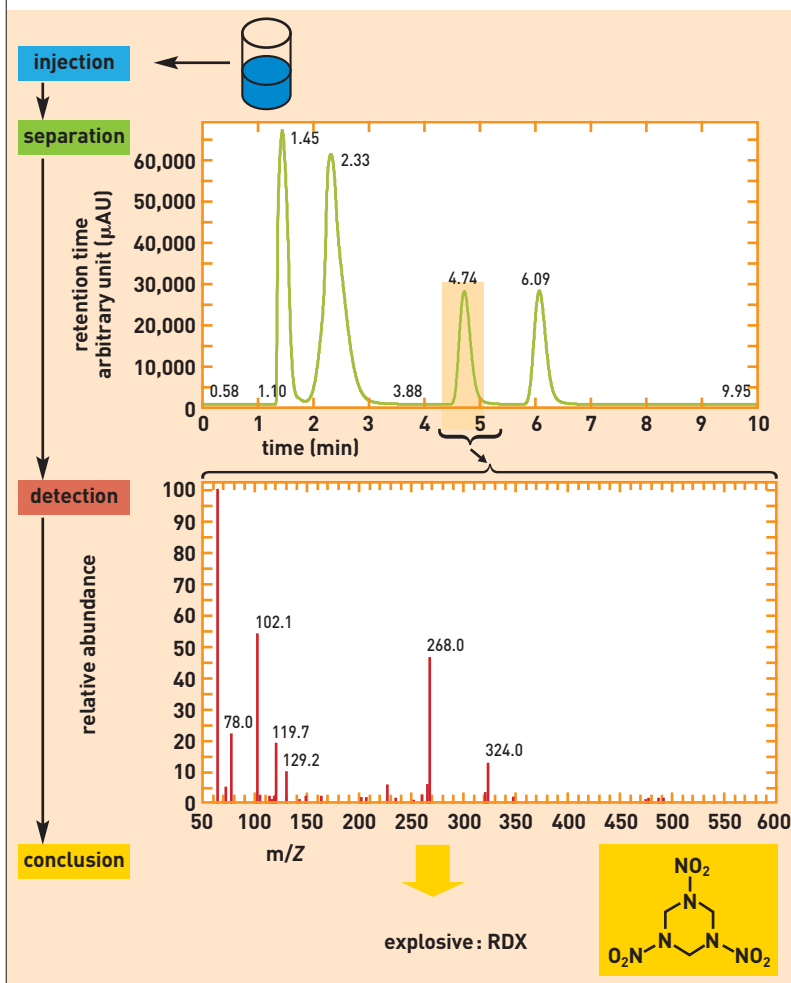


Figure 1.
Trace analyses in a liquid matrix: the example shown is the search for RDX in water. Chromatogram (top) and associated mass spectrum for an RDX-bearing aqueous solution. Detection is of the APCI (atmospheric-pressure chemical ionization) type, in negative mode.

(2) Solvation: the aggregation of molecules of one substance (the solvent), having the ability to dissolve another, with ions of the dissolved substance (solute).

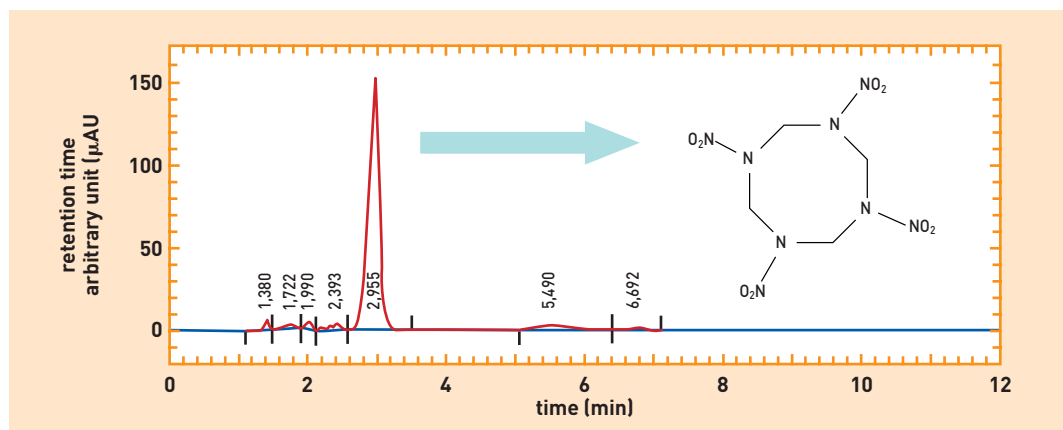


Figure 2. Trace analyses in a solid matrix: the example shown is the titration of low concentrations of octogen in soils. Subsequent to sampling, and drying, the sample is subjected to liquid-solid extraction and filtration, prior to HPLC/UV analysis.

HPLC/UV-MS analysis of an aqueous matrix bearing, in particular, traces of RDX. Searching for RDX in water, at ambient temperature, by means of HPLC readily allows detection thresholds of the order of the **part per million (ppm)** to be achieved.

Solid matrices

Solid matrices, particularly groundsoil, also allow organic products to be retained. The behavior of organic compounds with the ground environment may be attributed to three chemical properties: the structure of the molecule, its solubility in water, and its **adsorption** on soil particles. Indeed, depending on its chemical composition, the molecule will exhibit varying retention capacities, in various soils. Thus, a sandy soil exhibits a different retention capacity than a calcareous, or an argillaceous soil, owing to the setting up, or otherwise, of privileged chemical interactions, between the organic molecules, and soil grain surface chemical functions. The example shown (see Figure 2), of octogen (HMX) analysis, shows this explosive, a member of the nitramine family, tends to be retained more easily by clays than by calcareous or sandy soils. Due to this property, the analyst will have to employ appropriate sampling means, in order to ascertain the amount of octogen held in a soil. After optimization, it is not uncommon to achieve extraction efficiency rates higher than 95%. In such conditions, the detection limit for octogen in soil samples, using for instance the HPLC/UV analysis method, is close to 0.2 mg octogen per kilogram dry soil, i.e. around 200 ppb.

Gaseous matrices

Air is one of the most difficult environments to analyze, in terms of searching for traces. Due to the major stakes at hand for human communities (the environment, labor regulation, malicious activity), this area is under active scrutiny by the scientific community. CEA's Le Ripault Center has been working for a number of years on these issues, particularly on the means of sampling trace molecules dispersed in the atmosphere. Among the means employed for that purpose, *solid-phase microextraction sampling* (SPME sampling) holds a special position. This technique allows, classically, improvement, by a factor 100–1,000, of the sensitivity of such analytical techniques as gas chromatography, coupled with sensitive detectors, such as mass spectrometry, or electron-capture detectors (ECDs). Developed in the early 1950s by the Canadian team

led by Professor Pawliszyn, this extraction method affords many advantages: ease of use (being free from solvent dilution; fibers reusable after extraction), and an extensive application domain, through the large choice of adsorbent types that may be employed, according to the group of analytes being sought.⁽³⁾ The SPME sampling system takes the form of a fused-silica fiber, covered with a **polymer** coating (a few tens of microns thick). The adsorption of chemical compounds present in the atmosphere relies on the principle of a partition equilibrium, between the sample and this coating. The fiber is fitted onto a holder, allowing direct use in conventional analytical instruments. Samples are then thermally desorbed (at a temperature of about 250 °C) in the gas chromatograph's injector, and subsequently transferred to the separation column, and the detector. Various detectors may then be used, depending on the information being sought:

- a structural detector, such as the mass spectrometer, which is useful for chemical identification, as, e.g. to discriminate between isomers⁽⁴⁾ of dinitrobenzene (DNB). These laboratory tools allow the sampling, separation, and identification of sister molecules having the same molecular mass, and identical chemical functions, the sole difference being the position of these functions on the aromatic nucleus⁽⁵⁾ (see Figure, in Box E);

- specific detectors, used for an investigation requiring sensitivity, as instanced by the use of an electron-capture detector (ECD) for the detection of TNT.

The latter compound exhibits, at 20 °C, a vapor pressure of the order of one part per billion in volume (**ppbv**). In other words, when left at this temperature, TNT will disseminate its vapors in the atmosphere, attaining, at most, a concentration of about one molecule for 1 billion molecules of air. An SPME fiber, placed in this environment for a few minutes, allows, after analysis, the presence of TNT to be visualized quite clearly (see Figure 3). Even at such low concentration levels, the technique still exhibits a very strong signal-

(3) Reference: J. Pawliszyn (ed.) et al., *Applications of Solid Phase Microextraction*, Royal Society of Chemistry, RSC Chromatography Monographs, 1999.

(4) Isomer: a molecule having a structure corresponding to the same molecular formula as another molecule, but a different graphic (or semi-graphic) formula.

(5) Aromatic nucleus (or benzene nucleus): a ring formed by six carbon atoms sharing six electrons in a "collective" bond, endowing the entire ring chain with great stability.

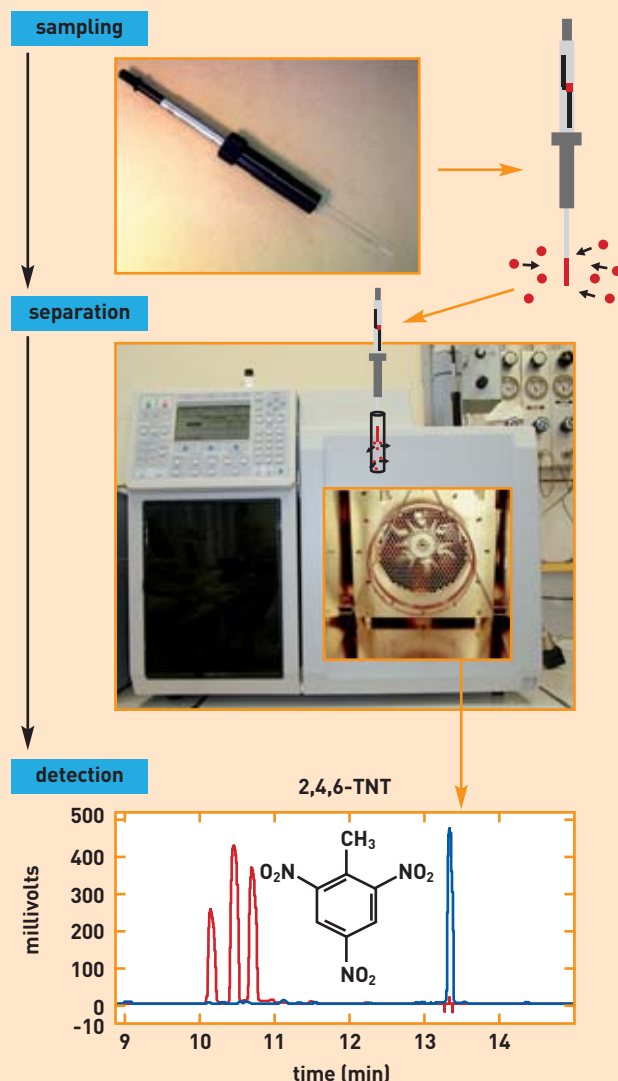


Figure 3. Trace analyses in air: the example shown is the search for TNT. The (SPME) sampling fiber is passed through an electron-capture detector (separation), then a mass spectrometer (detection).

to-noise ratio, higher than 100, which opens up prospects of reaching even more extreme detection limits, for instance for the cases where TNT vapors are diluted, or masked.

Highly sensitive chemical sensors

The principle of a chemical sensor relies on a sensitive material, endowed with a usable physical property, allowing detection of a gas (see Figure 4). This

material may be of a variety of types (organic, inorganic, metal oxide...), and exhibit one or more physical properties of interest (**conductivity, fluorescence...**). For that material to be suitable for employment, it must be deposited as a thin film onto a substrate, appropriate for the measurements to be carried out.

The development of chemical gas sensors involves a number of steps, beginning with selection, and synthesis of the sensitive material, according to its chemical and physical properties, and the gas that is to be detected. Subsequent to thin-film deposition onto a substrate, and morphological characterizations of this film, detection tests, to evaluate performance, in terms of sensitivity, selectivity, reversibility, and robustness, are carried out on various measuring rigs, ranging from quartz microbalance to fluorometer, through surface acoustic waves and conductivity.

It is with regard to miniaturization, development and industrialization that chemical sensors are proving particularly attractive, whether it be to ensure the security of public venues such as airports, to control the legality of goods, over an area of jurisdiction, to carry out disarmament operations, to locate antipersonnel mines, or to clear pollution at industrial or military sites.

The originality of the approach implemented at CEA Le Ripault lies in the use of organic compounds for the construction of sensitive devices. Many families of innovative materials are being devised in this context. Two types of sensor, in particular, are being developed for the purposes of explosives detection: quartz microbalances, and fluorescent sensors.

Transducers of the quartz microbalance type

The quantity investigated with this type of device is an oscillation frequency, related to a mass variation on the surface of the oscillating quartz. Detection is mainly gravimetric, however other parameters, such as variations in viscosity or in film density, are involved. The mass variations detected are of the order of a few nanograms. The microbalance is a tool enabling a mass variation to be converted into a frequency variation, and subsequently into an electrical signal. Materials must thus be developed, exhibiting high affinity for the compounds that are to be detected, with a very-low-cost, very-high-sensitivity sensor. As a rule, the measuring setup consists in powering an oscillator cir-

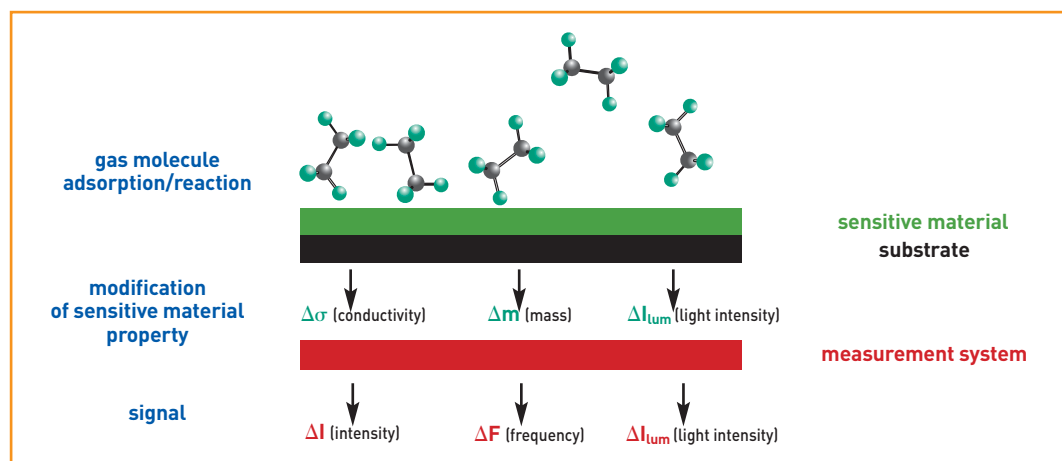


Figure 4. Principle of a chemical gas sensor.



CEA

Portable gas detector developed by CEA

cuit, allowing the quartz to be set vibrating, and plotting by means of a frequency meter the evolution of this frequency as a function of the sensor's environment.

Whether as analogons or actual explosives, such investigations are focused on detection of nitroaromatic compounds (NACs), these being close, in terms of structure, to trinitrotoluene (TNT). Various quality criteria are required, to characterize a gas sensor. The first quality criterion to be considered is *sensitivity*, characterized by the detection limit. **Polymer** materials of the polysiloxane type, allowing dinitrotoluene and trinitrotoluene to be detected at concentrations close to their vapor pressures (285 ppb, and 3 ppb respectively), have thus been tested (see Figure 5).

Selectivity is another crucial point. This determines the proportion of false alarms by the sensor. In this respect also, materials of the polysiloxane type, deposited onto a quartz microbalance, have enabled CEA research workers to achieve useful selectivity levels.

Finally, sensor robustness, or *stability*, and particularly the good aging behavior of the sensitive material, are fundamental criteria. Compounds exhibiting relatively stable performance over *more than two years* are now available. To investigate this criterion, sensor response must be tested on a regular basis (every month, for instance), and the evolution of this response must be determined.

The selection of sensitive devices, on the basis of these criteria, results in a range of materials, exhibiting different characteristics, for gas detection. A number of materials were thus selected, exhibiting very high performance with respect to detection of nitroaromatics and explosives, enabling CEA engineers to develop several prototypes, thus demonstrating that, through reliance on the quartz microbalance, portable, low-cost detectors could be offered, exhibiting quite remarkable characteristics, in terms of sensitivity, selectivity, and stability over time.

Fluorometric sensors

A second type of chemical sensor looks particularly promising: fluorometric sensors, making use of a variation in fluorescence in a sensitive material. This transduction technique allows higher sensitivity and selec-

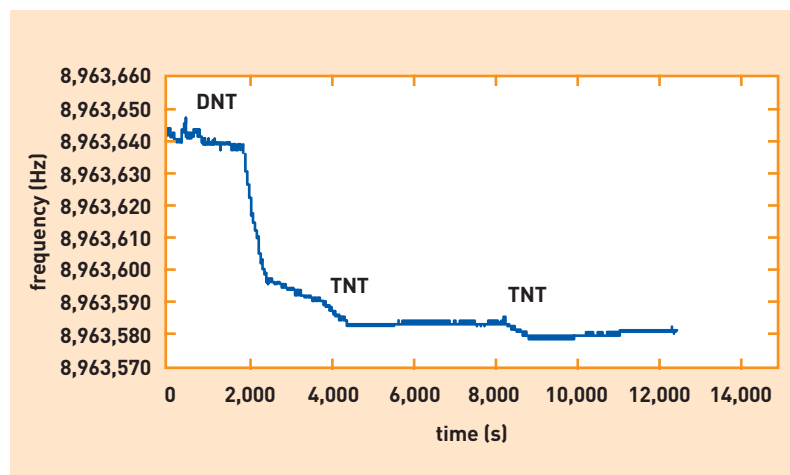


Figure 5. Detection of nitroaromatic compounds at various concentrations with a polymer film, deposited onto a quartz microbalance.

tivity levels to be achieved than with a quartz microbalance. On the other hand, miniaturization of these sensors is still at the research stage.

Fluorescent materials of interest, for explosives detection, are polymers consisting in an alternation of conjugated segments, known as **fluorophors**, and chiral units⁽⁶⁾ (see Figure 6).

These chiral units are well known to structure the material, in the solid state, increasing its porosity and facilitating access of analytes to sensitive sites, in this case the fluorophors.

The sensitivity of these fluorophors to nitroaromatics has been measured, and correlated with their electronic properties. Fluorescence inhibition in these compounds, which is due to a specific interaction (transfer of a photoinduced electron) with nitroaromatic-type compounds (NACs), has been investigated in solid-state thin films, with a view to the sensor's purpose.

Measurements of sensitivity were carried out at 20 °C on a specific fluorometer, allowing gas composition to vary from air to dilute nitroaromatic vapors in air. Figure 7 shows a variation in fluorescence intensity in a diimide film, successively exposed to air, then to 100 ppb NAC, followed by air again, then 1,000 ppb NAC, and finally air. A signi-

(6) Chirality: the property of handedness, i.e., for a molecule, having a structure that is not superposable with its own mirror image.

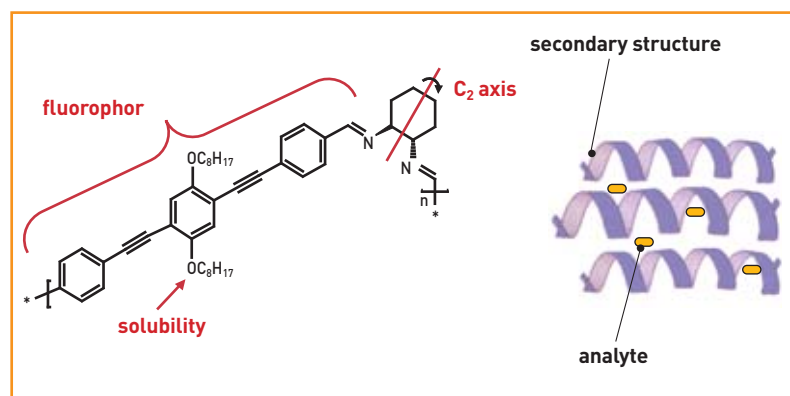
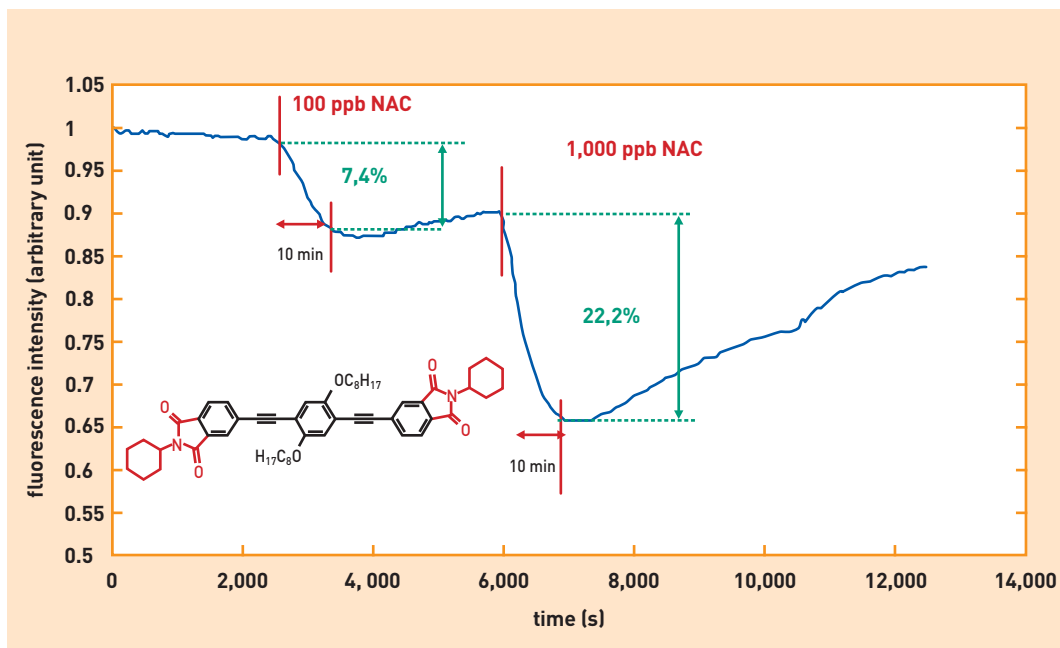


Figure 6. Fluorescent chiral polymers.

Figure 7.
Variation in fluorescence intensity of a conjugated polymer film (diimide, exposed for 10 minutes), under the effect of nitroaromatic-type compounds (NACs).



significant fall in measured fluorescence intensity is found during exposure to NAC vapors. These materials are reversible, since a gradual return to the fluorescence intensity baseline is observed, after exposure.

The two approaches detailed here demonstrate the potential of chemical gas sensors, as regards explosives detection. While microbalance-based portable devices have already been developed, fluorescent sensors look particularly promising. Future investigations will address embedding sensitive fluorescent segments into polymers, and miniaturization of measuring devices.

Avenues for optimization

There are thus a number of techniques available to detect explosives in environments as varied as soil,

water, or the atmosphere. The investigations conducted at CEA Le Ripault have allowed a range of complementary solutions to be made available, both in terms of offering systems exhibiting high performance in terms of sensitivity, selectivity, and quantification, and providing tools better suited to rapid measurements in the field.

With respect to analytical techniques, the examples presented here show the foundations on which ongoing investigations are based, with prospects of developing yet more sensitive measurement protocols, to search for traces, and ultratraces in each of the three matrices mentioned. The investigations being carried out show a concern to arrive at analytical protocols that are robust in metrological terms, but equally from one sample to the next, while seeking the best tradeoff between time required for the analysis, and measurement sensitivity. For analyses in gaseous environments, development of further polymer phases, that would be even more explosives-specific, may yet be considered, along with miniaturization of the analytical device, which could then open up further avenues, in terms of applications. The avenues for optimization of chemical sensors, for explosives detection, are many. A number of options, such as preconcentration, with regard to sensitivity, or development of multisensors, for selectivity, have been clearly identified, and are compatible with device portability.

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Prototype explosives detector, developed in CEA's Le Ripault laboratories.

Our thanks go to the team of Professor Lère-Porte, at the École nationale supérieure de chimie, in Montpellier (France).

E What is chromatography?

Chromatography, together with the various forms of spectroscopy and spectrometry (see Box D, *Spectroscopy and spectrometry*), represent the two major basic analytical techniques, the former serving for the separation, the latter for the identification of the constituents of a substance.

Chromatography (from the Greek *chrôma*, "color," and *graphein*, "to write"), allows the *separation* of the constituents of a mixture in a homogeneous liquid or gaseous phase, as blotting paper might spread out in concentric rings a liquid poured onto it.

A chromatograph comprises a sample injection device, a *column*, a detector, and a recording and analysis system. Its principle is based on the equilibrium of compound concentrations, between two phases coming into contact: the *stationary phase*, in the column, and the *mobile phase*, which moves across it. Separation relies on the differential displacement of constituents inside the column, passing through in times that are proportional to their size, or depending on their structure, or affinity for the stationary phase (polarity...). As they reach the far end of the column, a *detector* measures, on a continuous basis, the quantities of each constituent.

The most common form of chromatography is **gas chromatography**, carried out on gaseous samples, or samples that may be vaporized without incurring breakdown. The mobile phase is a gas (helium, nitrogen, argon, or hydrogen), constantly sweeping through the column, which is placed in a thermostat oven. Detectors allow the selective analysis and identification of highly complex mixtures.

If the stationary phase is a nonvolatile, or not highly volatile liquid, exhibiting solvent properties for the compounds to be separated, the process is termed **gas-liquid chromatography**, or *partition chroma-*

tography. If the stationary phase is an **adsorbent** solid (silica, alumina, zeolites, or **polymers**), this is **gas-solid chromatography**. Within this same family, of **adsorption** chromatography processes, **liquid-solid chromatography** is characterized by its stationary phase, this being a polar solid.

In **high-performance liquid chromatography (HPLC)**, the sample must be wholly soluble in the mobile phase (elution solvent). The latter must be kept at high pressure (hence the alternative name of *high-pressure liquid chromatography*), to ensure a constant flow rate inside the column, and preclude any loss of head. HPLC involves solute-mobile phase-stationary phase exchange mechanisms, based on partition or adsorption coefficients, depending on the nature of the phases in contact.⁽¹⁾

A chromatographic analysis yields a **chromatogram**, this being a graphical representation of the evolution of a parameter (intensity of the detector signal), related to instantaneous solute concentration, as function of time. This exhibits *peaks*, rising above the *baseline*, which obtains in the absence of any compounds (see Figure).

(1) There are two further types of liquid chromatography, *ion chromatography*, and *exclusion chromatography*.

N.B: This Box reproduces a number of excerpts from a presentation by Pascale Richardin, head of the Datation Group at the Research and Restoration Center of the French National Museums Administration (Musées de France), taken from the pages dealing with analytical methods, as posted on the site : <http://www.culture.gouv.fr/culture/conservation/fr/biblioth/biblioth.htm>

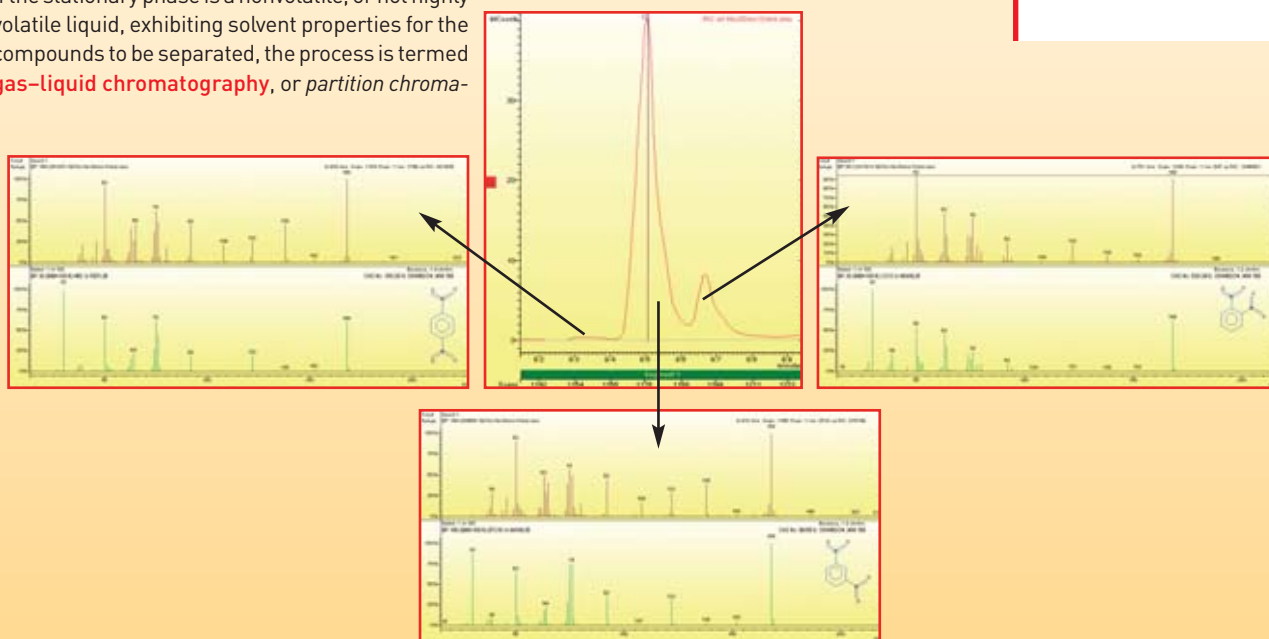


Figure.

An example of the combined use of mass spectrometry and chromatography: the separation of isomers ("sister molecules") of an explosive molecule (dinitrobenzene [DNB]), after solid-phase microextraction sampling, by gas chromatography, and their detection by mass spectrometry (SPME-GC-MS).

D Spectroscopy and spectrometry

Spectrometric methods are subdivided, as a whole, into two main categories, radiation spectrometry – itself comprising absorption spectrometry, emission spectrometry, Raman scattering spectrometry, and nuclear magnetic resonance spectrometry – and mass spectrometry.

Radiation spectroscopy and **spectrometry**⁽¹⁾ cover an ensemble of analytical methods allowing the composition and structure of matter to be ascertained, based on investigation of the spectra yielded by the interaction between **atoms** and **molecules**, and various types of **electromagnetic radiation**, emitted, **absorbed**, or **scattered** by the former.

Depending on their energy, **photons** interact selectively with the various electron shells, or levels, making up the electronic structure of the atom, or molecule. The electrons involved are **core electrons** (close to the atom's nucleus), for X-rays,⁽²⁾ **peripheral electrons** (furthest from the nucleus, and involved in chemical bonds) for light absorbed, or emitted, in the **near ultraviolet** and **visible** region. In the **infrared** radiation region, it is the leap from one **molecular vibration** level to another that is involved, the switch from one molecular **rotation** level to another for microwave radiation, and **atomic nucleus spin** for NMR.

Absorption spectrometry

Those spectroscopy methods that rely on absorption make use of the Beer–Lambert law, setting out the proportional relation between the intensity of light absorbed, and the amount of absorbing matter:

$$A = \log(I_0/I) = \epsilon \cdot l \cdot C,$$

where *A* stands for the **absorbance** of the medium traversed, *I*₀ for incident light intensity, *I* for transmitted light intensity, ϵ is the characteristic **molar** extinction coefficient, for a given wavelength, for the substance investigated – expressed in

$\text{L mol}^{-1} \text{cm}^{-1}$ – while *l* stands for the thickness passed through, expressed in centimeters, and *C* is the concentration, in moles per liter.

By measuring the medium's absorbance, for a given wavelength, the concentration of a substance, in a sample, may thus be determined.

In an **absorption spectrum**, as recorded by means of a **spectrometer**, **absorption peaks** correspond to the wavelengths the medium is able to absorb. Just as the spectrum from the Sun's light is obtained by making it pass through a prism, which breaks it up, spectrometers analyze the spectral distribution of the whole range of electromagnetic radiations, separating them out according to wavelength, by means of a reflection diffraction grating. Spectra exhibit peaks, each one corresponding to a specific wavelength.

Depending on the type of sample to be analyzed, and the performance level being sought, in the laboratory, **absorption spectrometry** is used either on molecules in liquid or gaseous phase, or on atomic vapor, obtained through thermal breakdown of liquid or solid samples.

Molecular absorption spectroscopy, in the UV–visible region, affords simplicity of use, however it is only applicable to samples of moderate complexity, since, owing to the width of **molecular absorption bands**, absorption spectra, as a rule, do not allow specific discrimination of every constituent, in a complex mixture.

In **infrared (IR) spectrometry**, absorption is the outcome of molecular vibration and rotation processes. Infrared absorption spectra thus allow the nature of chemical bonds to be determined, that make up a molecule, by ascertaining the bond's elasticity constant (influencing vibration frequency, as for a spring), thus confirming structural hypotheses.

As the number of atoms increases, the spectrum rapidly exhibits growing complexity, and interpretation becomes highly problematical, especially for organic compounds.

Atomic absorption spectrometry, in this respect, brings higher performance, since absorption by atoms yields very narrow **absorption lines**. Very precise measurements are thus feasible, even when the sample consists in a complex assembly of chemical elements. Atomic absorption is a reference technique for the ana-

lysis of trace elements in a wide variety of samples, in particular for biological samples.

Emission spectrometry

Atoms or molecules brought to an excited state may deexcite by emitting radiation, known as **emission radiation**. When the excitation is caused by selective absorption, by the atoms or molecules to be analyzed, of electromagnetic radiation, this represents a **fluorescence** emission (or a **phosphorescence** emission, depending on the electron excitation state involved).

As with absorption, fluorescence may be applied, in the UV–visible radiation region, to molecules, or atoms. **X-ray fluorescence spectrometry**, on the other hand, refers to the **X radiation** emitted by atoms excited by absorption of X-radiation. Fluorescence techniques are more complex to implement than is the case for absorption techniques, since they entail that the particle subjected to analysis be selectively excited by a monochromatic radiation. On the other hand, since the radiation emitted is likewise specific to the particle, fluorescence spectrometry involves a double selectivity, resulting in very low background noise, thus making it peculiarly well suited for the measurement of very low concentrations.

Emission of radiation may also occur when atoms are thermally excited, in an environment brought to high temperatures. Emission spectroscopy is based on the fact that atoms, or molecules excited to high energy levels deexcite to lower levels, by emitting radiation (emission, or luminescence). This differs from fluorescence spectrometry in that excitation is not applied selectively, rather it involves indiscriminately all of the particles making up the medium. **Emission lines** thus correspond to radiation directly emitted by a body brought to a high temperature, and the **emission spectrum** allows the detection, and quantification, of all atoms present in the emission source.

Raman spectrometry

Interactions between matter and electromagnetic radiation also give rise to scattering processes, such as **elastic scattering**, and **inelastic scattering**. Scattering may occur when the interface between

(1) The term “spectrometry,” initially used only to refer to recording and measurement techniques, has tended to become synonymous with “spectroscopy,” as the eye was supplanted, for observation purposes, by other receptors and instruments, while the visible region now only formed one special region, in analytical terms.

(2) It should be noted, at the same time, that X-ray crystallography is not deemed to be a spectroscopy method, in the strict sense of the term.

two media is encountered, or as a medium is passed through. This process, in most cases, is an “elastic” one, in other words it takes place with no change in frequency for the radiation forming the beam involved. Elastic scattering of solar radiation by the atmosphere is, for instance, responsible for the blueness of the sky, observed when the eye is not directed towards the Sun (*Tyndall effect*). Indeed, scattered intensity is all the greater, the shorter the radiation wavelength, which, in the case of the solar spectrum, corresponds to the color blue.

As regards spectrometry, the main use of scattering concerns *Raman spectrometry*. This involves the inelastic scattering of incident radiation by the molecules making up the sample. The difference between scattered radiation frequency, and incident radiation frequency allows the identification of the chemical bonds involved. Raman spectrometry is a technique that is widely used for structural analysis, to complement infrared spectrometry, and mass spectrometry.

Nuclear magnetic resonance spectrometry

The principle of **nuclear magnetic resonance (NMR)** is based on the fact that an atom has a *magnetic moment*, just like a spinning charge acting as a tiny magnet, governed by quantum mechanics, aligning in a magnetic field as the needle of a compass in the Earth's magnetic field. The principle of NMR consists in inducing, and detecting, the transition, for the nuclear magnetic moment, from the lowest energy level to the highest energy level, through absorption of electromagnetic radiation of a wavelength lying in the radiofrequency region: when the energy of the photon precisely matches the energy difference between the two levels, absorption occurs. Nuclei having numbers of **protons**, and **neutrons** that are both even exhibit zero spin. Carbon 12 and oxygen 16 atoms, which are very widespread in nature, thus have zero spin. On the other hand, hydrogen only has one single proton, and its nuclear magnetic moment equals 1/2: it may thus take on two possible energy states, corresponding to the two orientation states of its spin, relative to the magnetic field. Measuring the resonance frequency in the electromagnetic field allowing transition from one of these energy states to the other enables the molecu-



Spectromètre de masse d'ions secondaires utilisé au CEA pour réaliser des mesures isotopiques rapides sur un échantillon par exemple prélevé sur une installation aux activités nucléaires suspectes.

les to be analyzed. This frequency is fixed, however the various nuclei in a molecule do not all resonate at the same frequency, since their magnetic environment is modified by their chemical (electronic) environment.

Many NMR spectra exhibit more peaks than there are protons in the nucleus, owing to the interactions between protons and their neighbors. Two nuclei may interact within the molecule, though they are separated by several chemical bonds: this is known as interatomic coupling. This interaction endows the NMR spectrum with a fine structure.

Mass spectrometry

Mass spectrometry is a highly sensitive *detection and identification* technique, allowing determination of molecular structures, and thus of a sample's composition. This is not, strictly speaking, a form of spectrometry, since it is not concerned with discrete energy levels. What is its principle? A compound introduced into the device is vaporized, and subsequently **ionized** by an electron bombardment source (at 70 eV). The ion thus obtained, termed a molecular ion, allows the compound's molar mass to be determined. Breaking chemical bonds within the compound may yield charac-

teristic fragment ions. These are then sorted according to their mass/charge ratio in an *analyzer*, through application of a magnetic and/or electric field, then collected by a *detector*, which amplifies the signal associated to the ions, which arrive with varying delays. A data processing system converts the information from the detector into a **mass spectrum**, readout of which, by comparing it with reference spectra, allows the identity details of the molecule to be drawn up. Through use of a high-resolution mass spectrometer, the exact mass of the compound may be determined, together with isotope percentages for each constituent atom.

Choice of ionization method is directly related to the nature of the sample, and the type of analysis. If mass spectrometry has gradually adapted to meet the growing demands from chemists, and biologists (separation of increasingly complex, highly polarized mixtures, determination of ever higher molecular masses on samples of ever more constricted sizes), this is essentially due to advances in *ionization techniques*, these including secondary ion mass spectrometry (SIMS), chemical ionization, thermospray ionization, and fast atom bombardment (FAB) sources, further comprising, from the 1980s, matrix-assisted laser desorption ionization (MALDI), and electrospray ionization (ESI), together with advances in *detection techniques*, from time-of-flight (TOF) measurement to “ion traps” (ITs), through quadrupoles (MS or Q).

In proteomics, for instance, only MALDI, ESI and SELDI (surface-enhanced laser desorption ionization) are employed.

Ion **mobility spectrometry (IMS)** is a chemical analysis technique in the gaseous phase, which consists in subjecting a gas to an electric field. Ionized molecules acquire a velocity that is characteristic for the ion, since this depends on mass, and charge. Arrival of the ions on one of the plates generating the field results in a current, which is recorded. The length of time after which a peak occurs can be related to the nature of the ion causing it. Scientists often make use of a coupling of devices each belonging to one of the two main families of analytical techniques (see Box E, *What is chromatography?*), e.g. of a chromatograph with a mass spectrometer (or an electron-capture detector [ECD]), particularly for the investigation of trace complex mixtures.

B Fundamental interactions and elementary particles

The **standard model** of particle physics is the reference theoretical framework describing all known **elementary particles** (see Table 1) and the fundamental **interactions** these particles are involved in (see Table 2). The basic constituents of matter, known as **fermions**, are partitioned into two main categories, as determined by their participation in the fundamental interactions, or forces (the **gravitational**, **electromagnetic**, **weak**, and **strong** forces), which are mediated by **vector bosons**, the fundamental particles which carry out the transmission of the forces of nature⁽¹⁾ (see Table 2). Whether a particle belongs to the category of fermions, or to that of bosons depends on its **spin** (i.e. its intrinsic angular momentum, or internal rotation moment), depending on whether it exhibits half-integer spin (fermions) or integer spin (**bosons**).

At the same time, to every constituent of matter is associated its **antiparticle**, a particle having the same *mass*, but the opposite *charge*. The **positron** is thus the positively charged antiparticle of the **electron**, which exhibits a negative charge.

Leptons and quarks

Fermions include, on the one hand, **leptons**, which may travel freely and do not participate in the *strong interaction*, which ensures the cohesion of atomic **nuclei** (it is consequently termed a *nuclear interaction*), and, on the other hand, **quarks**, which participate in all interactions but are not individually observed, enmeshed and confined as they are within **hadrons**, the particles susceptible to strong interaction, of which they are the constituents.⁽²⁾

In the lepton category, **charged leptons** participate in the *electromagnetic interaction* (which ensures the cohesion of **atoms** and **molecules**, and in the *weak interaction* (which underlies **decay** processes, in particular **β radioactivity**). Neutral leptons, or neutrinos, for their part, participate in the weak interaction only. Exhibiting very low mass, there is one type of neutrino for each type of charged lepton.

Independently from their involvement in interactions, the basic constituents of matter are classified into three *gene-*

rations, or *families*, of particles. From one family to the next, quarks and leptons having the same charges only differ by their mass, each family being heavier than the preceding one.

The **electron**, up quark (symbolized *u*) and down quark (symbol *d*), which belong to the first generation, are the lightest massive particles, and are stable. These are the sole constituents of **normal matter**, so-called **baryonic** matter (a baryon is an assembly of quarks), which is made up of **protons** and **neutrons**, this however only accounting for 4% of the Universe's energy content! Particles in the other two families are heavier, and are unstable, except for neutrinos, which on the other hand exhibit non-zero mass, but are stable.

These latter particles may only be observed or detected in the final states resulting from collisions effected in **accelerators**, or in **cosmic radiation**, and rapidly decay into stable first-generation particles. This is why all the stable matter in the Universe is made up from constituents from the first family. According to **quantum mechanics**, for an interaction to take place between particles of normal matter, at least one elementary particle, a boson, must be emitted, absorbed, or exchanged. The **photon** is the **intermediate** (or **vector**) boson for the electromagnetic interaction, the **W⁺**, **W⁻** and **Z** are the intermediate bosons for the weak interaction, and **gluons** are those of the strong interaction, acting at quark level.

As to the **graviton**, the putative vector for the gravitational interaction, it has not so far been empirically discovered. The **gravitational force**, which acts on all fermions in proportion to their mass, is not included in the standard model, due in particular to the fact that quantum field theory, when applied to gravitation, does not yield a viable scheme, as it stands. While gravitational effects are negligible in particle physics measurements, they become predominant on astronomical scales.

Interaction ranges

Quarks and charged leptons exchange photons. The photon having no electric charge, these particles conserve their electric charge after the exchange. Since

the photon's mass is zero, the electromagnetic interaction has an infinite range. Having no electric charge, neutrinos are the only elementary fermions that are not subject to electromagnetic interaction.

In the electroweak theory (a unification of the weak and electromagnetic interactions), the weak interaction has two aspects: **charged-current weak interaction**, for which the interaction vectors are the **W⁺** and **W⁻**; and **neutral-current weak interaction**, for which the mediator is **Z⁰**. These two forms of weak interaction are active between all elementary fermions (quarks, charged leptons and neutrinos). The mass of these bosons being very large (about 80 GeV/c² for **W[±]**, 91 GeV/c² for **Z⁰**), the range of the weak interaction is tiny – of the order of 10⁻¹⁸ m. Since **W[±]** bosons have a non-zero electric charge, fermions exchanging such bosons undergo a change in electric charge, as of nature (*flavor*). Conversely, since the **Z⁰** boson has no electric charge, fermions exchanging one undergo no change in nature. In effect, neutral-current weak interaction is somewhat akin to exchanging a photon. As a general rule, if two fermions are able to exchange a photon, they can also exchange a **Z⁰**. On the other hand, a neutrino has the ability to exchange a **Z⁰** with another particle, though not a photon.

Only those quarks that have a color charge⁽¹⁾ exchange gluons, these in turn being bearers of a color charge. Thus,

(1) The participation of basic constituents in fundamental interactions is governed by their *interaction charges* (electric charge, color charge), or “conserved quantum numbers.” *Color charge*, a quantum number that determines participation in strong interactions, may take one of three values: “red,” “green,” or “blue” (these colors bearing no relation to visible colors). Every quark bears one of these color charges, every antiquark one of the three anticolor charges. Gluons are endowed with double color-anticolor charges (eight combinations being possible).

(2) To take e.g. **nucleons**: the proton holds two up quarks and one down quark, the neutron two down quarks and one up quark. A **meson** is made up of just two quarks (one quark and one antiquark).

B (cont'd)

when a gluon exchange takes place between quarks, the latter exchange their respective colors. Gluons have zero mass, however, since they do bear a color charge, they are able to interact

together, which greatly complicates theoretical treatment of this interaction. The range of the strong interaction is consequently very restricted – of the order of 10^{-15} m.

The quest for unification

The theoretical framework for the standard model is quantum field theory, which allows a quantitative description to be made of the fundamental interactions.

<div><div><div>atom</div><div>nucleus</div><div>electron</div><div>proton charge +1 mass : 938.272 MeV/c²</div><div>neutron zero charge mass : 939.565 MeV/c²</div><div>nucleon</div><div>quarks</div></div></div>						
<div><div>Fermions</div><div>Normal matter is made up of particles from this group.</div><div>Most of these particles were around just after the Big Bang. Presently only to be found in cosmic rays, and around accelerators.</div></div>	leptons able to move freely			quarks assembled into triplets, or quark-antiquark pairs, to form the many subatomic particles		
	First family	<div>electron (e)</div> <div>responsible for electricity and chemical reactions charge:- 1 mass : 0.511 MeV/c²</div>	<div>electron neutrino (ν_e)</div> <div>has no electric charge, and interacts very seldom with the ambient medium.</div>	<div>down (d)</div> <div>electric charge: - 1/3 the proton holds one, the neutron two mass : 4 – 8 MeV/c²</div>	<div>up (u)</div> <div>electric charge: + 2/3 the proton holds two, the neutron one mass : 1.5 – 4 MeV/c²</div>	
		Second family	<div>muon (μ)</div> <div>a more massive companion to the electron. mass : 105.658 MeV/c²</div>	<div>muon neutrino (ν_μ)</div> <div>properties similar to those of the electron neutrino.</div>	<div>strange (s)</div> <div>a heavier companion to “up” mass : 80 – 130 MeV/c²</div>	<div>charmé (c)</div> <div>a heavier companion to “down” mass : 1.15 – 1.35 GeV/c²</div>
			Third family	<div>tau particle (τ)</div> <div>heavier still. masse : 1,776.99 ± 0.29 MeV/c²</div>	<div>tau neutrino (ν_τ)</div> <div>properties similar to those of the electron neutrino.</div>	<div>beauty (b)</div> <div>tau particle. mass : 4.1 – 4.4 GeV/c²</div>
	Vector bosons		photon		gluon	
	Fundamental particles carrying out transmission of natural forces.		elementary grain of light, vector for the electromagnetic force		bearer of the strong force between quarks	
Higgs boson?		responsible for “electroweak symmetry breaking”		W [±] , Z ⁰ bearers of the weak force, responsible for some forms of radioactive decay		

Tableau 1.

Table showing the twelve elementary constituents for which the standard model describes the interactions involved. The three charged leptons (electron e^- , muon μ^- , tau particle τ^-) are subject to electromagnetic and weak interactions, neutrinos (ν_e, ν_μ, ν_τ) are only affected by weak interaction, and the six quarks (up, charm, top – or u, c, t – bearing a charge of $2/3$; and down, strange, bottom – d, s, b – bearing a charge of $-1/3$) are subject to all three interactions. Every elementary constituent has its antiparticle, having the same mass, and algebraic quantum numbers (such as electric charge) of the opposite sign.

tions between elementary particles, while respecting the principles of *special relativity*, as those of quantum mechanics. According to the latter theory, if one seeks to observe a microscopic structure at high temporal and spatial resolution, this entails transferring to it an amount of energy–momentum, the greater, the higher the resolution being sought. However, according to the theory of relativity, such an energy–momentum transfer is liable to undergo transformation, yielding particles not present in the initial state: fermions may be generated, or annihilated, in particle–antiparticle pairs, while bosons may be so in any arbitrary number.

All processes involving one and the same fundamental interaction are interrelated. The quantum field theory approach, in which properties of **symmetry** play a fundamental part, seeks to describe all of the processes relating to each fundamental interaction, within overarching theoretical constructions.

The strong and electromagnetic interactions are formalized, respectively, in the theories of **quantum chromodynamics**, and **quantum electrodynamics**. The weak interaction, for its part, is not subject to a separate description, being described jointly with the electromagnetic interaction, in the unified formalism of **electroweak theory**. Theories of the *grand unification* of all fundamental interactions do exist, however they remain as yet lacking any experimental validation.

All the predictions of the standard model have been corroborated by experiment, except for just one, to wit, the existence of the **Higgs boson(s)**, which particle (particles?), it is hoped, will be discovered with LHC. The **Higgs mechanism** is thought to be responsible for the mass exhibited by elementary particles, the eponymous boson making it possible for zero-mass fermions interacting with it to be endowed with mass. This would allow the unification, at high energies, of the weak and electromagnetic interactions within the electroweak theory, while effectively accounting for the **breaking** of this **electroweak symmetry** at low energies, taking the form of two interactions, which may be seen as distinct at that energy level [see *The electroweak*

interaction from one accelerator to the next: the LHC roadmap and the yardstick of LEP measurements, p. 23].

Going beyond, or completing the standard model?

The standard model features a set of parameters (such as the masses of elementary particles, or the intensities of fundamental forces) which are “anchored” in experimental findings. It is, in any event, a theory that is liable to be improved, or further elaborated, or even surpassed and left behind. It does not account in any way for the classification of the constituents of matter into three generations of particles, whereas it is precisely the existence of these three generations which makes it possible to account for **CP** (charge–parity) **invariance violation** (meaning that a physical process involving the weak interaction is not equivalent to its own mirror image), a violation that is in all likelihood the source of the matter–**antimatter** imbalance, running in favor of the former, in the primordial Universe. The model neither allows quantum treatment of gravitation, nor does it fully account for the fundamental property of *confinement*, which prevents quarks from propagating freely outside hadrons.

To go beyond, or to complete the standard model, research workers are mainly exploring two avenues:

– **supersymmetry** (widely known as

SUSY) would associate, to every particle (whether a boson or a fermion) in the standard model, a partner from the other series, respectively a fermion or a boson. Supersymmetric partners would, at first blush, be highly massive, the lightest of them being a particle interacting very weakly only. This would be an ideal candidate to account for the **hidden matter** (or **dark matter**) in the Universe, accounting as it does for some 21% of the Universe’s energy content, the remainder (close to 75%) consisting in a **dark energy**, the nature of which likewise remains to be determined. These WIMPs (acronym for “weakly interacting massive particles”) are actively being sought (see *EDELWEISS II, the quest for dark matter particles*);

– the **substructure** path assumes there could be a new level of elementarity, underlying the particles in the standard model (or some of them). This would lead to a veritable blossoming of new, composite particles, analogous to hadrons, but exhibiting masses two to three thousand times heavier.

It should be noted that, whereas supersymmetry theories yield predictions that agree with the precision measurements carried out at LEP, the theories propounding substructures (or their simpler variants, at any rate) fail to do so. As for the more complex variants, these are encountering difficulties at the theoretical level.

fundamental interaction	associated particles (messengers)	actions
gravitation	graviton?	having an infinite range responsible for the mutual attraction of any two masses and for the law of falling bodies
electromagnetic interaction	photon	having an infinite range responsible for the attraction between electrons and atomic nuclei, hence for the cohesion of atoms and molecules
weak interaction	W^+ , W^- , Z^0	responsible for β^- and β^+ radioactivity, reactions involving particles as neutrinos
strong interaction	gluons (there are 8 gluons)	ensures the cohesion of the atomic nucleus

Tableau 2.
Fundamental interactions, their vectors, and effects.