

# Chemical analysis of Martian rocks



Jean-Luc Lacour/CEA

Computer-generated imagery showing the MSL rover vehicle, which is to explore the surface of Mars for two years, from 2010. It is seen fitted with the ChemCam device, due to observe rocks by means of a high-definition camera, and carry out elemental analysis of these rocks using the LIBS technique.

**Development of a technique to provide the capability to analyze at a distance, of up to 10 meters or so, the composition of Martian rocks,** such is the challenge set by NASA to analysts and space instrumentation specialists for the coming Mars exploration mission, due to be launched at the end of 2009. The goal is to achieve a self-standing, compact, rugged instrument, allowing a large amount of information to be collected on the composition of geologic materials at the landing site, while keeping rover travel to a minimum.

Of all known analytical methods, optical emission spectroscopy of plasmas generated by **laser ablation**, or LIBS (laser-induced breakdown spectroscopy), is the only one to present characteristics compatible with the highly ambitious specifications set by the **US National Aeronautics and Space Administration (NASA)** project for the remote analysis of Martian rocks. Banking on the presence, at CEA, of a solid experience with respect to measurements in hard conditions, the **Centre d'étude spatiale des rayonnements (CESR: Radiation Space Research Center/Midi-Pyrénées Observatory)** in Toulouse (France) requested, in 2001, the participation of the engineers working on the PLANI platform (Plateforme LAser Nanoseconde pour les applications Industrielles: Nanosecond Laser Platform

for Industrial Applications) in their submission for NASA's call for tenders, regarding construction of the instrument due to be mounted on the rover vehicle for the future Mars Science Laboratory (MSL) mission.

## The French participation in the Mars Science Laboratory mission

The principle of the LIBS technique consists in focusing pulsed laser radiation onto the material subject to analysis, to vaporize it in the form of **plasma**, **spectral** analysis of which will enable the **elemental** composition to be determined, for the volume thus probed (see Box 1). The measurement being wholly based on use of optical radiation, it may be carried out at a distance,

## Principle of a LIBS measurement

The interaction of a pulsed, high-irradiance<sup>(1)</sup> – typically, several **gigawatts/cm<sup>2</sup>** – **laser** beam with a material causes fierce heating of the illuminated surface, which is vaporized in the form of **plasma** (see Figure a). The **atoms** and **ions** expelled, raised to excited energy levels, emit, as

they deexcite, a **visible and ultraviolet spectrum** formed of atomic lines, the wavelengths of which allow identification of the **elements** present, while their intensity is proportional to the density of emitting atoms (see Figure b). Provided experimental control is achieved, of all physical

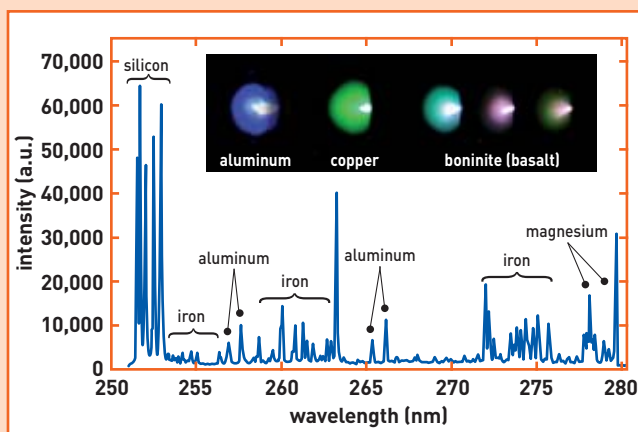
processes involved in generation of the plasma, and that a suitable calibration method is available, the material's elemental chemical composition may be derived from this.

When the material involved is a solid, laser **ablation** results in formation of a crater, the size and volume of which depend on the laser-related conditions involved (wavelength, pulse duration, illumination), on the nature and pressure of the ambient atmosphere, and on the electronic and thermal-physical properties of the material. The plasma thus generated, and hence its **emission spectrum**, depend, in a complex fashion, on the material itself, as well as on the laser parameters. On a laboratory scale, this may easily be brought under control, by freezing instrument parameters, and carrying out a calibration using materials of known composition, close to that of the material to be analyzed. Outside the laboratory, however, the position is entirely different, since the materials subject to analysis are, as a rule, unknown beforehand. Innovative signal processing methods must then be sought, allowing emission line intensity to be related to the material's composition, with no prior calibration involved. Research and development work on such methods forms one of the major research thrusts for laboratories active in LIBS development.



Figure a. Principle schematic of LIBS plasma generation.

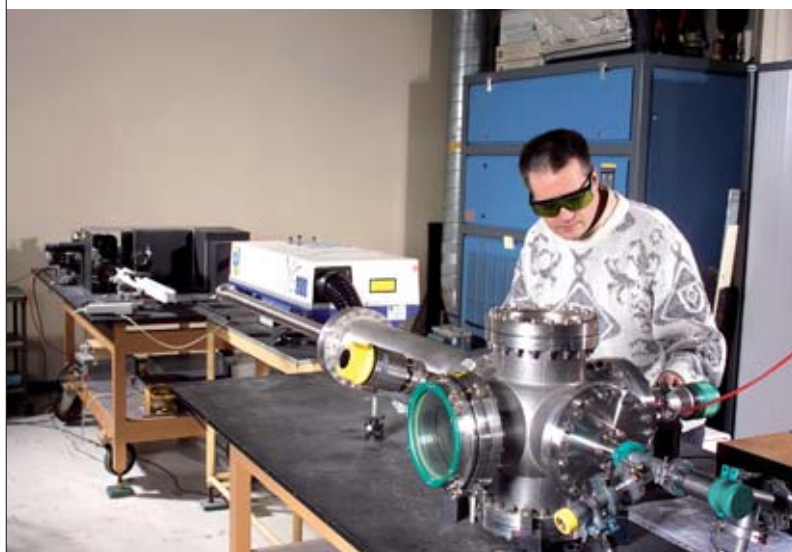
Figure b. LIBS plasmas and optical emission spectra, showing the feasibility of chemical element identification.



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(1) Irradiance (or radiant flux density): the amount of radiant power delivered per unit surface.



Laboratory instrumentation developed at CEA to investigate the LIBS technique, in the context of the ChemCam project. Rock samples are placed in the vessel seen in the foreground, which is filled with a low-pressure carbon dioxide (CO<sub>2</sub>) atmosphere, simulating the Martian atmosphere. LIBS measurements are carried out by means of the laser and spectrometer that may be seen to the rear. This setup allows LIBS measurement to be carried out at distances ranging from 2 m to 15 m, corresponding to ChemCam project specifications.

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on any type of material, be it a metallic or **dielectric** solid, a liquid, an **aerosol**, or a powder. Such flexibility is essential, for the analysis of Martian rocks, these being coated with a layer of dust particles, which must be removed prior to analysis. Thus it is the laser that will remotely carry out, by means of successive firings, that clearing operation, prior to effecting the rock analysis. An initial series of experiments, carried out in a simulated Martian atmosphere, allowed the instrument's specifications to be refined, and the anticipated analytical performance level to be set in credible fashion. On the basis of these results, NASA selected, at the end of 2004, the French team, to develop – in collaboration with the US **Los Alamos National Laboratory (LANL)** – the instrument, dubbed ChemCam, due to be mounted on the MSL rover, which will carry a total of 10 measuring instruments. The mission seeks to meet four major scientific goals, namely to gain knowledge of the geological history of Mars, of its climate and climate history, look for water and traces of life, and prepare for future exploration by humans. With the broad range of operational possibilities it offers, combined with the fact that it allows simultaneous detection of virtually all chemical **elements**, the LIBS technique is peculiarly well suited for soil analy-



sis in extreme conditions. Which is why CEA had considered this technique very early on.

### Know-how gained in the sphere of nuclear technology

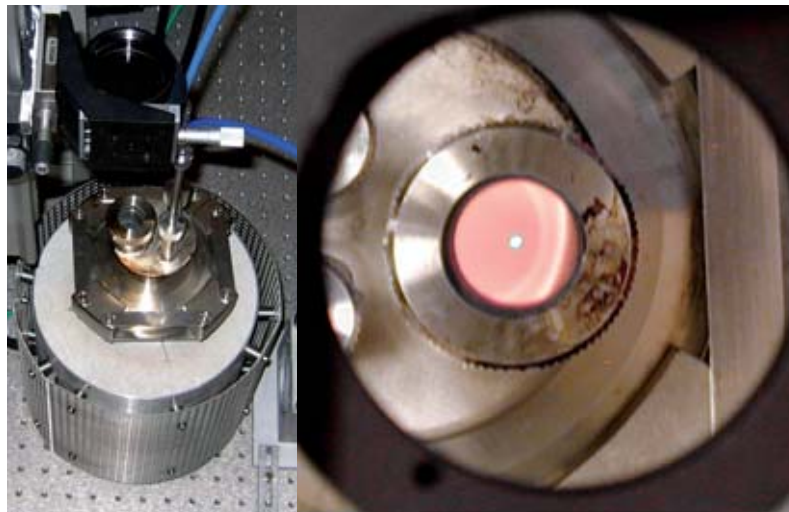
Indeed, in the context of its investigations on analysis in confined environments, such as remote analysis of materials brought to very high temperatures, or of certain **radioactive** materials, CEA has gained, with regard to LIBS measurement, an expertise that is widely acknowledged. The work carried out at Saclay, under the aegis of the PLANI platform, is concerned with various types of applications, ranging from microanalysis at the **micron** scale to remote analysis, for the investigation of materials in a hostile environment.

The advantages of LIBS, for microanalysis, lie in speed of measurement, and simplicity of use, making it particularly useful for such applications as measuring diffusion profiles in clays and cements intended for nuclear waste disposal, or measuring the homogeneity of non-metallic materials (nuclear fuel, for instance).

Remote measuring is concerned, in particular, with materials not amenable to handling, whether because they present a potential hazard, or because measurement of these materials is meaningful only if they remain in their physical-chemical environment. The applications addressed by current research work, at CEA, concern, in particular, *in situ* measurement of the composition of molten salts being investigated for nuclear fuel reprocessing by the **pyrochemical path**, and *in situ* measurement of aerosols in a high-temperature, high-pressure helium circuit, simulating the cooling circuit in a **gas-cooled nuclear reactor**.

### An advantageous method for molten salt reactors

**Molten salt reactors** represent one of the concepts selected in the investigations being carried out, on an international footing, on **4th-generation nuclear reactors**. They offer the advantage of allowing continuous extraction and recycling of the **minor actinides** and **plutonium** generated during reactor operation. In the front-end research being carried out, some investigations concern the chemical partitioning operations used in that process, such as liquid-liquid extraction using molten metal. Research on these processes entails carrying out a multiplicity of elementary chemical analyses, complicated by the fact that the temperature (around 900 °C), and chemical aggressiveness of certain materials, such as alkali halides,<sup>(1)</sup> or alkaline earths,<sup>(2)</sup> make sampling an arduous operation. LIBS is thus being investigated for the purposes of enabling *in situ* analysis, i.e. directly inside the furnace. The laser beam is focused onto the surface of the liquid being analyzed, through a window, ensuring imperviousness, and radiation emitted by the plasma is analyzed along the same axis. The advantage of this method was demonstrated in inactive laboratory conditions, with a **lanthanide** dissolved in a molten LiF-AlF<sub>3</sub> salt, at 900 °C, and subsequently on the basis of a **model** allowing performance simulation, generalized for the various elements and salts being considered. The technique is due to be deployed in the near future, in a glovebox on the ATALANTE facility, to carry out investigations in real conditions.



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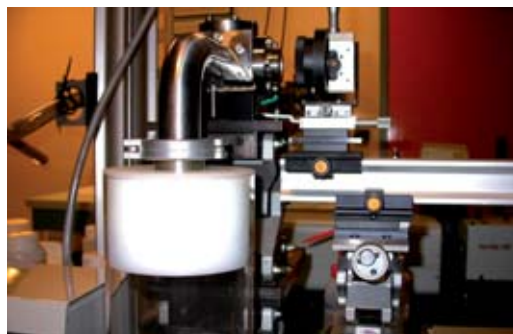
### A technique being considered for gas-cooled reactors

Use of LIBS is also being considered in the context of experimental investigations being carried out on **high-temperature, gas-cooled reactors**. In particular, research workers are planning to equip with this technique a dedicated test loop, used to investigate coolant fluid purity, to carry out *in situ* analysis of particles carried by the gas, and thus to control, in real time, the effectiveness of filtration systems, or to monitor possible component degradation during trials. Pressure and temperature conditions, namely several tens of **bars** in helium gas at temperatures ranging from 850 °C to 1,000 °C, mean taking representative samples is a highly problematic operation. LIBS will provide the means for release from this requirement, with the analysis being carried out *in situ*, directly inside the piping, through a window.

In terms of methodology, the two main issues to be dealt with are minimum density of detectable particles, and particle size. In practice, it is feasible to set up an illumination system that generates a plasma in the gas phase, for every laser firing. Particles entering this plasma are **atomized**, emitting a characteristic **spectrum**. The interaction volume to be considered is thus the volume of plasma, which typically stands at around 10<sup>-3</sup> cm<sup>3</sup>, with a lifetime of about one microsecond.

(1) Alkali halides: chemical compounds, composed of a halogen and an alkali. Halogens appear in column 17 (or VIIA) of the periodic table of chemical elements (including fluorine, chlorine, bromine, iodine, and astatine). Alkalis belong to group 1 (or IA) (**lithium**, sodium, potassium, rubidium, cesium, and francium). Lithium fluoride (LiF) is an alkali halide.

(2) Alkaline earths: these elements belong to group 2 (or IIA) in the periodic table of chemical elements (beryllium, magnesium, calcium, strontium, barium, and radium).



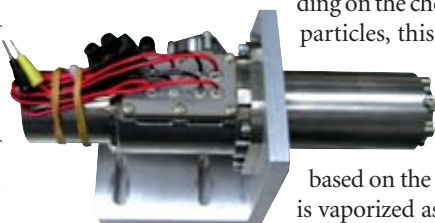
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The setup used to develop LIBS *in situ* analysis of molten salts. At left, the furnace; right, the furnace viewed from above through the window, showing the molten salt, and laser-induced plasma.

LIBS instrumentation developed for the characterization of particles carried by coolant gas in high-temperature reactors.

Laser being developed by the Thales corporation, for the ChemCam instrument. With its very small size and very low consumption, it must yet exhibit outstanding performance, generating plasma at distances of up to 10 m.

CESR/Midi-Pyrénées Observatory



With no laser synchronization whatsoever, researchers may assume that, statistically, every laser firing will result in detection of one particle, if particle density is higher than  $10^3$  particles/cm<sup>3</sup>. Below this value, the number of useful laser firings decreases proportionally with density, resulting in an increased required measuring time, to detect one particle spectrum. To avoid measurement time becoming prohibitive, at low particle densities, particles passing in the gas vein must be detected through measurement of the scattering they cause, on a laser beam probe, and synchronizing LIBS laser firing with these events. Detection efficiency, in that case, is much higher, since it is related to the number of particles passing through the volume of plasma, per unit time, i.e. to the product of particle density by the flow rate for the carrier fluid.

Minimum size, for detectable particles, is determined in turn by the minimum amount of matter required to yield a usable LIBS signal. Experience shows this amount ranges from  $10^{-15}$  grams to  $10^{-12}$  grams, depending on the chemical element. For single-element particles, this means minimum detectable size typically lies in the 0.1–1  $\mu$ m bracket. At the other end, large particles may equally be a problem. Indeed, signal processing is based on the assumption that the entire particle is vaporized as it interacts with the plasma. This

assumption does not hold true for particles that are too large (of a size greater than a few microns). Ongoing investigations are aimed, in particular, at achieving a better understanding, and control, of the experimental parameters that are of influence, in order to develop adequate instrumentation, meeting the requirement, and demonstrate it exhibits performance compatible with the goals being sought.

## The many challenges to be met for ChemCam

The ChemCam instrument, due to be mounted on the MSL rover vehicle, and currently being developed, will enable the remote analysis of Martian rocks, and their observation by means of a high-definition camera. The French team, funded by the **Centre national d'études spatiales (CNES: French National Space Research Center)**, has the remit of developing the component mounted at the top of the mast. This comprises a laser with its electronics, together with a telescope, having a threefold function: gaining high-definition images of the rocks, by means of a camera; focusing laser radiation onto regions of interest; and collecting the emission of radiation induced by laser-surface interaction. This radiation will be carried by optical fibers to the three **spectrometers** located in the lower part of the rover, development of which is entrusted to the US team.

## Quantitative LIBS signal processing

With the irradiance levels used for the LIBS technique, **plasmas** form local thermodynamic equilibrium environments, entailing that the intensity of the lines emitted is a function of two fundamental plasma quantities: the density of matter in the vapor phase, and temperature. As these two quantities are closely related to experimental conditions (**laser** wavelength, pulse duration, and illumination), and to the material's thermal-physical properties, obtaining quantitative analytical findings entails

either operating in perfectly reproducible conditions, or securing signal processing methodologies that enable signals to be compared, obtained in a variety of experimental configurations.

Of these situations, the first is well suited to the laboratory scale, in which experimental conditions are fully controlled, and the nature of the sample is known. For every **element** of interest, it is then possible to establish, by way of a calibration, the relation between the emission signal, of a given

atomic line, and concentration for the corresponding element in the material considered. This classic analytical method yields satisfactory results (see Figure a), demonstrating the LIBS technique's full potential, as regards quantitative analysis, and, in particular, demonstrating that elemental concentrations in the plasma phase are indeed representative of the material's composition.

The issue of quantification arises in a far more complex manner with field analysis. Indeed, in most cases, the nature of the material subjected to analysis is not known beforehand, and conditions for the laser-surface interaction vary widely. For the ChemCam instrument, for instance, the nature of the rocks is the very information being sought, and the spread of distances over which the device will have to operate ranges from 2 m to about 10 m. Over such a range, the size of the focal spot on the surface being analyzed varies considerably, as does emission radiation detection efficiency. Thus, variations in the emission signal will not solely be due to changes in the nature of the analyzed material, but equally to varying instrument parameters. Resorting to a conventional calibration procedure is thus ruled out, and research and development efforts are still required, to develop advanced processing methods for **emission spectra**.

The recent introduction of optical spectrometers coupled to **CCD** (charge-coupled

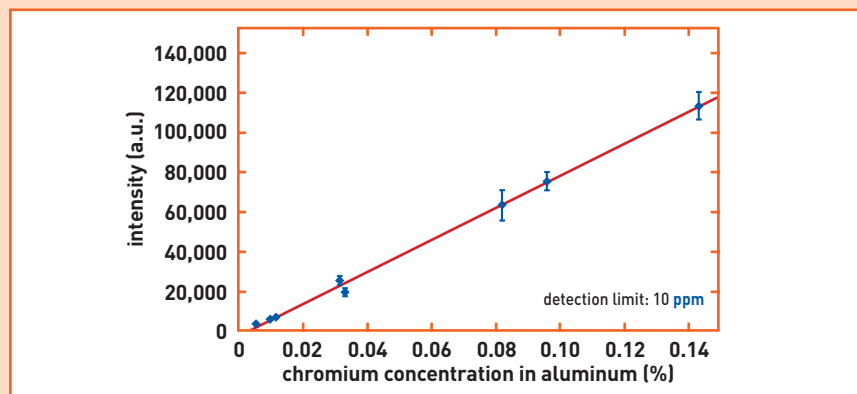
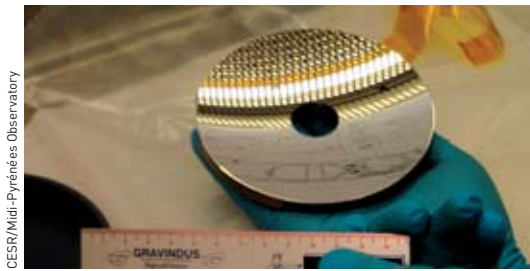


Figure a. Straight calibration line, showing the proportional relation between LIBS signal intensity, for a chromium line, and concentration for this element in materials of known compositions (aluminum alloys). Measurements were carried out at 3 m standoff distance in Martian atmosphere (under low carbon dioxide pressure), to simulate conditions for the MSL mission. These findings demonstrate that the LIBS technique allows the remote quantitative analysis of materials in a Martian atmosphere, with a satisfactory level of sensitivity.

Ambient temperatures that may range from  $-125^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$ , depending on landing latitude, and season, a planned operational lifetime of one Mars year, i.e. two Earth years, a volume equivalent to that of a 20-cm-edge cube, for a weight of 5 kg only, an energy consumption lower than 4 Wh per day, such are the stringent constraints the instrument must meet, raising many technical challenges, pushing current know-how to its limits.

Among the main hard points should be noted the construction of the laser, entrusted to the Thales Laser company. This laser, if it is to generate a plasma at a distance of up to 10 meters or so, must yield an energy of some 30 mJ, with a pulse duration of 7 ns, and high beam quality. Such performance, common as it is in laboratory lasers, involves major complications for such a very-small-size, very-low-consumption laser. Design and development of the telescope are equally encountering major difficulties, owing to its threefold function, which must remain compatible with small size, low weight, and stringent mechanical constraints. Initial integration and qualification tests, for the laser and telescope, started in June 2006, at the Midi-Pyrénées Observatory.

Concurrently with development of the instrument, laboratory investigations, carried out at the Physico-Chemistry Department, at CEA/Saclay, are seeking to determine precisely the accessible performance domain, and develop adequate signal proces-



CEISR/Midi-Pyrénées Observatory

Telescope being developed by the French ChemCam team. The threefold function assigned to it will have to remain compatible with its small size, and low weight.

sing methods, to meet the project's analytical goals (see Box 2). This research work is being carried out within a scientific team piloted by specialists from the Institut de physique du Globe de Paris (IPGP: Paris Physics of the Earth Institute), and bringing together research workers from the French Centre national de la recherche scientifique (CNRS) and academe.

At the same time, a model, allowing simulation of analytical performance as a function of experimental parameters, has been developed, and validated. As the project is now entering the instrument validation stage, this model will be used to evaluate realistic analytical scenarios, according to distance, and to plan for operational deployment of the ChemCam instrument.

> Patrick Mauchien, Jean-Luc Lacour, Béatrice Sallé and Laurent Salmon  
Nuclear Energy Division  
CEA Saclay Center

device) detectors, allowing the detection, in a single run, of the entire atomic spectrum, in the range from ultraviolet to visible light (typically, in the 200–800 nm bracket) has, in this respect, considerably expanded the field of possibilities. Of the methods being investigated, the most elaborate one seeks to determine the material's composition with no prior calibration. For every spectrum captured, the plasma's excitation temperature is determined through application of the Boltzmann equation to the measured intensities of the lines, yielded by the various atomic energy levels, for a given element. That temperature once ascertained, the plasma's electron density, determining as it does the distribution of neutral and ionized species, is then calculated. These two quantities allow the equation to be fully worked out, relating the intensity of any given emission line to atom concentration in the vapor phase. In many cases, the findings thus obtained are satisfactory, however precision levels are limited, owing to measurement error propagation, and the considerable uncertainty affecting knowledge of the spectroscopic parameters (degeneration levels, transition probabilities), for the lines being used. For the purposes of improving analytical precision, other methods are also being investigated. These are based on normalization of analytical line intensities, either by reference to the intensity of a line from a major constituent element in the mater-

ial, selected as an internal standard, or through a coefficient allowing adjustment to 100% of the sum of relative concentrations, as determined. Such an adjustment to 100% assumes that all of the major constituent elements in the material are fully detected, which is indeed the case as a rule. Figure b shows an example of findings obtained through use of these various

methods, for the case of rocks simulating Martian rocks. The good agreement found for all elements, between findings from LIBS measurements, and those from measurements made using reference methods, shows the effectiveness of the proposed approach, for field analysis in extreme conditions.

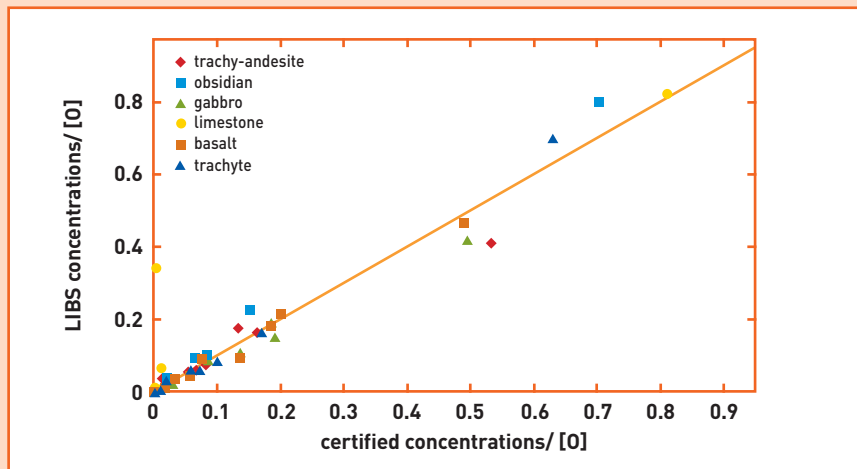


Figure b. Comparison of concentrations, as determined by LIBS in Mars conditions, and by proven laboratory techniques. The six samples used are Earth rocks, representative of Martian rocks. The findings shown bring together the measurements carried out on all of the constituent elements of these rocks. Concentrations are expressed in percent, relative to oxygen, this being the majority element in these rocks. This result shows that the signal processing method employed allows influence from the environment (matrix effects) to be discounted, and thus enables a unique analytical response to be obtained, for all the rocks concerned.



## D Spectroscopy and spectrometry

**S**pectrometric 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**<sup>(1)</sup> 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,<sup>(2)</sup> **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:

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

where A stands for the **absorbance** of the medium traversed,  $I_0$  for incident light intensity, I for transmitted light intensity,  $\epsilon$  is the characteristic **molar** extinction coefficient, for a given wavelength, for the substance investigated – expressed in

$L \text{ mol}^{-1} \text{ cm}^{-1}$  – 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 of 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 character-

istic 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<sup>(1)</sup> (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 moment, 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.<sup>(2)</sup>

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  **$\beta$  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<sup>+</sup>, W<sup>-</sup> 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<sup>+</sup> and W<sup>-</sup>; and **neutral-current weak interaction**, for which the mediator is Z<sup>0</sup>. 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/c<sup>2</sup> for W<sup>±</sup>, 91 GeV/c<sup>2</sup> for Z<sup>0</sup>), the range of the weak interaction is tiny – of the order of 10<sup>-18</sup> m. Since W<sup>±</sup> bosons have a non-zero electric charge, fermions exchanging such bosons undergo a change in electric charge, as of nature (*flavor*). Conversely, since the Z<sup>0</sup> 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 Z<sup>0</sup>. On the other hand, a neutrino has the ability to exchange a Z<sup>0</sup> with another particle, though not a photon.

Only those quarks that have a color charge<sup>(1)</sup> 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.

	leptons able to move freely		quarks assembled into triplets, or quark-antiquark pairs, to form the many subatomic particles		
<b>Fermions</b> Normal matter is made up of particles from this group.	<b>First family</b>	<b>electron (e)</b> responsible for electricity and chemical reactions charge: -1 mass: 0.511 MeV/c <sup>2</sup>	<b>electron neutrino (ν<sub>e</sub>)</b> has no electric charge, and interacts very seldom with the ambient medium.	<b>down (d)</b> electric charge: -1/3 the proton holds one, the neutron two mass: 4 – 8 MeV/c <sup>2</sup>	<b>up (u)</b> electric charge: +2/3 the proton holds two, the neutron one mass: 1.5 – 4 MeV/c <sup>2</sup>
Most of these particles were around just after the Big Bang. Presently only to be found in cosmic rays, and around accelerators.	<b>Second family</b>	<b>muon (μ)</b> a more massive companion to the electron. mass: 105.658 MeV/c <sup>2</sup>	<b>muon neutrino (ν<sub>μ</sub>)</b> properties similar to those of the electron neutrino.	<b>strange (s)</b> a heavier companion to "up" mass: 80 – 130 MeV/c <sup>2</sup>	<b>charm (c)</b> a heavier companion to "down" mass: 1.15 – 1.35 GeV/c <sup>2</sup>
	<b>Third family</b>	<b>tau particle (τ)</b> heavier still. mass: 1,776.99 ± 0.29 MeV/c <sup>2</sup>	<b>tau neutrino (ν<sub>τ</sub>)</b> properties similar to those of the electron neutrino.	<b>bottom (b)</b> tau particle. mass: 4.1 – 4.4 GeV/c <sup>2</sup>	<b>top (t)</b> heaviest in the family (observed in 1995) mass: 171.4 ± 2.1 GeV/c <sup>2</sup>
<b>Vector bosons</b> Fundamental particles carrying out transmission of natural forces.	<b>photon</b> elementary grain of light, vector for the electromagnetic force	<b>gluon</b> bearer of the strong force between quarks	<b>W<sup>±</sup>, Z<sup>0</sup></b> bearers of the weak force, responsible for some forms of radioactive decay		
<b>Higgs boson?</b>	responsible for "electroweak symmetry breaking"				

Tableau 1.

Table showing the twelve elementary constituents for which the standard model describes the interactions involved. The three charged leptons (electron e<sup>-</sup>, muon μ<sup>-</sup>, tau particle τ<sup>-</sup>) are subject to electromagnetic and weak interactions, neutrinos (ν<sub>e</sub>, ν<sub>μ</sub>, ν<sub>τ</sub>) 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.

## B (cont'd)

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 (particle?), 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 $\beta^-$ and $\beta^+$ 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.

# E What is chromatography?

**C**hromatography, 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-*

*tophagy*. 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.<sup>(1)</sup>

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>

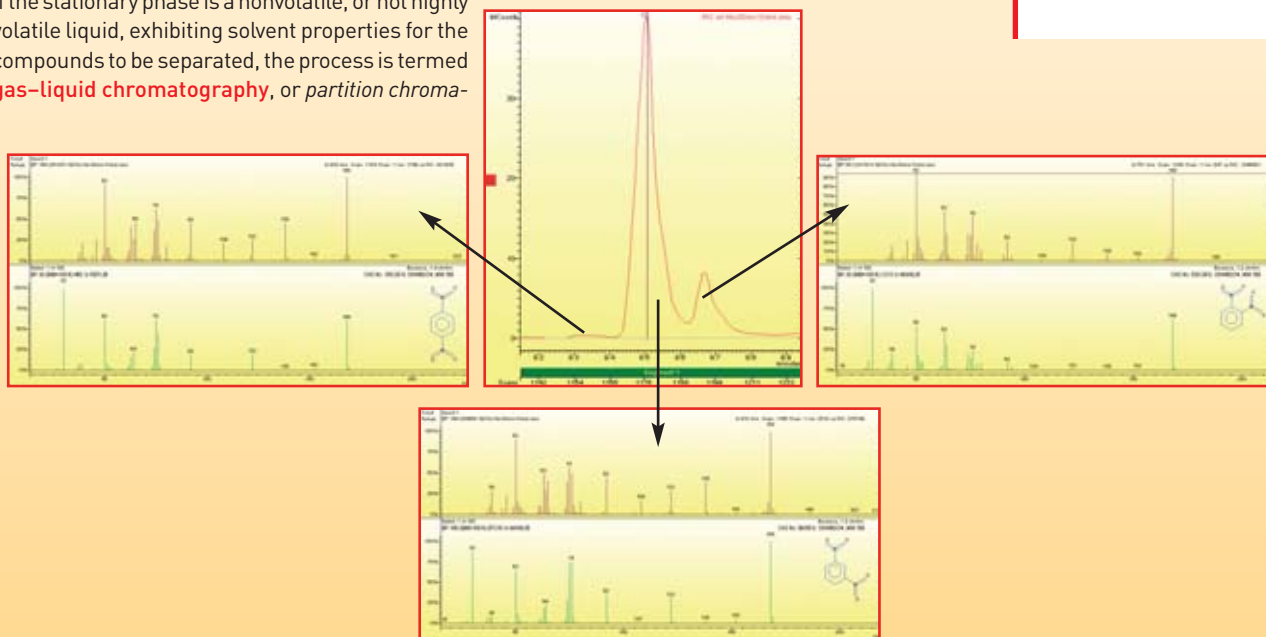


Figure.

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).