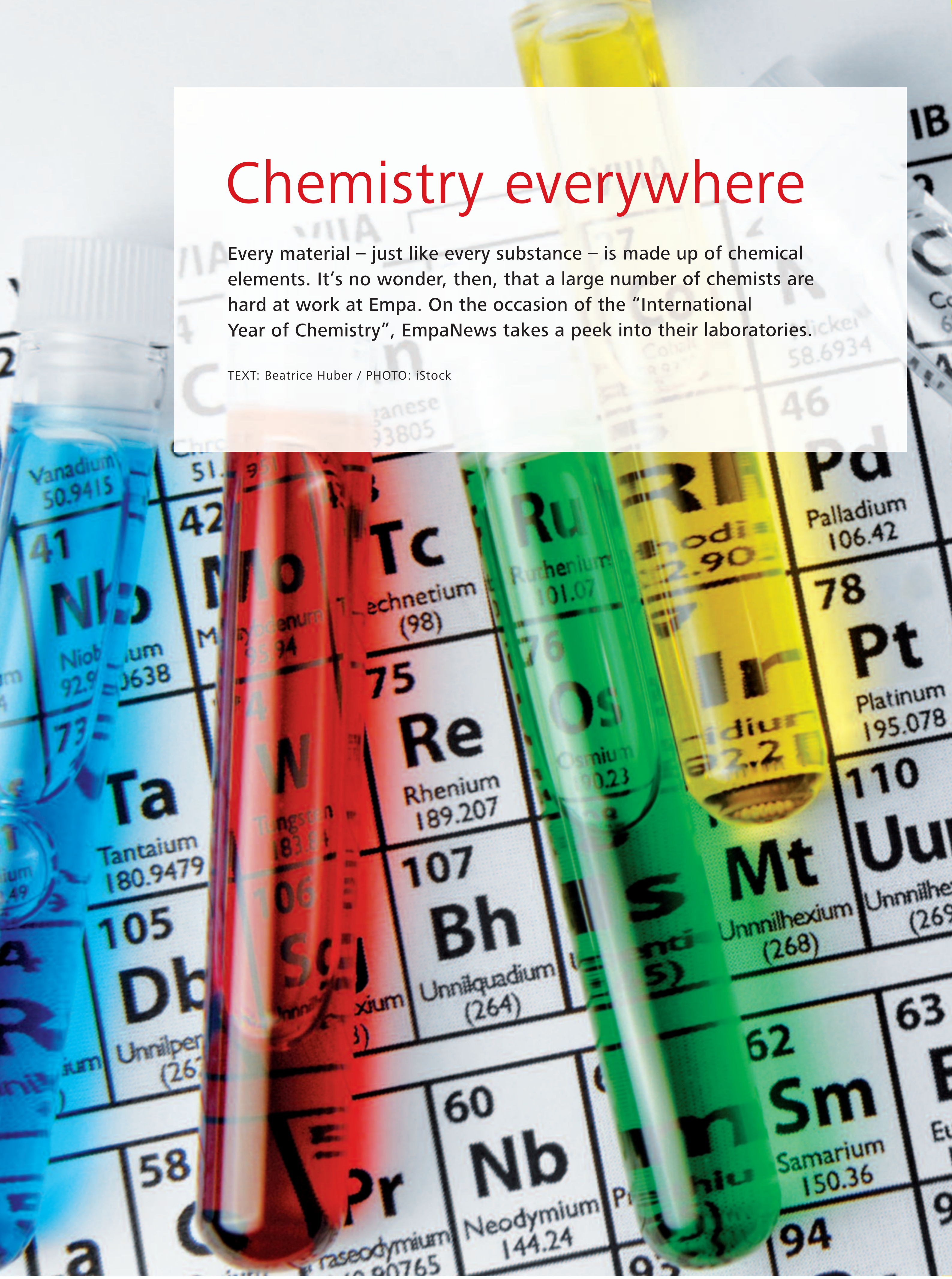

Chemistry everywhere

Every material – just like every substance – is made up of chemical elements. It's no wonder, then, that a large number of chemists are hard at work at Empa. On the occasion of the "International Year of Chemistry", EmpaNews takes a peek into their laboratories.

TEXT: Beatrice Huber / PHOTO: iStock

The chemical elements are listed in the periodic table according to their atomic number. This figure corresponds to the number of protons in the nucleus. Modern technologies, such as are applied in telecommunications or transportation, use a large number of still rather rare elements including gold (Au), platinum (Pt), indium (In), and gallium (Ga).

UNESCO along with IUPAC (International Union of Pure and Applied Chemistry) have designated 2011 the Year of Chemistry. Under the unifying theme "Chemistry – our life, our future", the achievements of chemistry and its contributions to the well-being of humankind are being highlighted. Materials science is likewise tightly woven with chemistry. After all, every material ultimately consists of elements from the periodic table. And modern technologies use more and more of them, as is exemplified by the mobile phone: in its case there's mostly carbon (in the form of a plastic) or aluminium; in the chip, silicon; in the circuit board, gold; in the touchscreen, indium; and in the battery, lithium. And that's just the start of the list – overall your average cell phone contains 40 elements, give or take.

Chemists at Empa are looking into, among other things, new materials which are expected to be more effective, less expensive and environmentally friendlier than those being used today (also see the article on page 15). For this, they are synthesising countless as yet unknown materials and studying their properties. A further important area for chemistry is analytics. Empa researchers can, for example, follow how long-lasting pollutants, some of which have been banned for decades, can accumulate in various ecosystems (also see the article on the following page).

An appreciation for Marie Curie

During the Year of Chemistry, the work of Maria Sklodowska Curie is also being honoured. This Polish-born scientist spent time in Paris investigating the phenomenon of radioactivity. Exactly 100 years ago, Marie Curie received the Nobel Prize for Chemistry for her discovery of the chemical elements radium and polonium, which are both radioactive. She was not only the first woman to be awarded the Nobel Prize; she was also one of only four people to receive the Nobel Prize twice. In 1903, she had already received the Nobel Prize for Physics together with Henri Becquerel and her husband, Pierre Curie. //

Useful in the short-term, troublesome long-term

Many substances used in industry persist in the environment, have a tendency to bioaccumulate and even decades later endanger the health of people and animals. In order to show how and in which amounts poly- and perfluorinated compounds (PFC) as well as polychlorinated biphenyls (PCB) are present, chemists at Empa are developing custom-tailored, extremely sensitive analysis methods.

TEXT: Martina Peter / PHOTOS & GRAPHICS: Empa

Many chemical "refiners", used by industry to furnish materials with desirable properties have a severe drawback. Only very poorly do these compounds decompose in the environment – if at all. They continue to show up in waterways, air and soil even decades after their production has been ceased, they accumulate to an undesirable extent in nature and present a serious threat for people and animals alike.

Persistent and surface active

Consider the example of perfluorinated compounds (PFC), which are organic hydrocarbon compounds in which all the hydrogen atoms are replaced by fluorine atoms. PFC are extremely temperature resistant and chemically virtually indestructible. Standard water-treatment plants fail to handle them because PFCs cannot be decomposed or filtered out.

Because they are simultaneously grease- and water-repellent, the textile and paper industries use long-chain PFC to produce dirt, grease and water-repellent materials and packaging, for example, raincoats and food wrappers, say, for hamburgers. PFC can also be contained in lubricants, impregnating agents and ski waxes.

PFC with hydrophilic end groups, known as perfluorinated tensides (PFT), reduce the surface tension of extinguishing foams. By almost completely covering a kerosene fire, they build up a gas-tight fluid film between the combustible substance and the foam and thus cut off the oxygen supply. Some of these PFT are also very popular in the electroplating industry. They prevent the formation of toxic mists during hard chrome plating in open metal baths.

Until now, PFC have been "in service" without any restrictions. Only one of the most important PFT, perfluorooctane sulfonate (PFOS), has had limited approval for industrial use since 2010, and there is some suspicion that it might be carcinogenic. Once taken up in the body, PFC bind to proteins and can be detected in the blood and especially in the liver, where they have been shown to cause cancer in animal studies.

Verified in mountain lakes and polar bear livers

"We're actually finding PFC everywhere in the environment, even in polar bear livers", notes Claudia Müller. She's a PhD student in Empa's Analytical Chemistry Laboratory, writing her dissertation about these problematic compounds under the supervision of Konrad Hungerbühler, Professor for Safety and Environmental Technology at ETH Zurich. "That wasn't predictable in the 1950s when we started to use them commercially." It was only about ten years ago that the problem came into focus. In 2006 in Germany, groundwater and drinking water was for the first time contaminated with PFT. Farmers used a "bio fertiliser" which was incorrectly labelled – it actually was industrial waste containing PFT – and which was washed out into rivers by rainfalls. The clean-up costs are running into the multiple millions of euros, and local residents have since been examined regularly for toxic residues. Even years after the scandal, negative effects are still being detected.

"But what's the situation like in Switzerland?" was a question posed by the Federal Office for the Environment (FOEN). PFC concentrations are generally

How do you detect substances like PCB which are poorly water soluble? Passive collectors made of special silicon rubber were attached to a pole and placed in the water where they remained for four weeks.

low, but still too little is known about their sources and how the substances spread throughout the environment. That's because the compounds are difficult to track and can only be analysed with great effort. This is a challenge that excites Müller. "I'm interested above all in the interconnections. That is, questions like: Are perfluorinated compounds more likely to arise in private households or in industrial processes? Are there large point sources such as airports? How widespread are PFC products?" She took samples at 44 locations all over Switzerland, from a variety of rivers and lakes including a remote mountain lake as well as multiple possible hot spots near airports and metal-working facilities, and determined the concentration of 14 perfluorinated compounds.

Distribution of PFCs in Switzerland

The analysis proved to be anything but simple. First of all, PFC are very surface active and tend to stick to the sample containers. Further, Müller had to pay very special attention that the samples were not "contaminated". That's because even very small traces of PFC can be found virtually everywhere, even in Empa's laboratories. Together with her colleagues in the team led by Empa researcher Andreas Gerecke, she developed a process to extract PFC from water samples and analyse them with a mass spectrometer. The result: the concentrations of various substances were generally low, between 0.02 and 10 nanogram per litre. In addition, she was able to show that the level of pollution correlates well with the overall population. This indicates that the sources of PFC emissions are consumer products, such as cleaning agents, impregnated textiles or furniture, rather than industrial processes.

So, can we issue an "all clear" signal? Not necessarily. "On the one hand," cautions Müller, "the samples only represent a snapshot." Therefore, FOEN is commissioning a study intended to examine sewage sludge for PFC using new analytical methods. "On the other hand, these substances can accumulate in nature. That's possibly a disadvantage for birds which feed on fish in certain rivers in Switzerland", she adds.

CityPOP – emissions from construction materials

Next, the Empa researchers are looking into how and from where PFC manage to get into remote mountain lakes. The first samples were recently collected within the scope of the newly initiated CityPOP project. For a month, specially prepared foam filters were exposed to air at 30 locations in the city of Zurich. This study, supported by the city and canton of Zurich as well as FOEN, is designed to determine which chemical substances are emitted from construction materials in buildings within the city.

Gerecke and ETH researcher Christian Bogdal are concentrating above all on persistent organic pollutants (POP) such as the flame retardant HCBD (hexabromcyclododecan). HCBD is used in polystyrene construction components, the light-blue or pink panels used for thermal insulation of buildings. This and other substances such as plasticisers leak out of construction materials even decades after being installed, and are thus a typical example of a "dirty legacy" in the construction branch. Based on their measurements, Gerecke and Bogdal want to create a very special city map of Zurich, one during the next few years that shows neighbourhoods are contaminated by POP emissions from construction materials and to what extent. Their findings will then help to develop improved emission-free construction materials.

Persistent and poisonous – polychlorinated biphenyl

Another inherited pollution that has emerged recently are polychlorinated biphenyl compounds (PCB), which were utilised until the late 1980s. They were used, for instance, as cooling and insulating fluids in transformers and capacitors, as hydraulic oil and as plasticiser and flame retardant in wall coatings, sealants and plastics. There has been a total ban on these toxic and carcinogenic substances in Switzerland since 1986. Even so, large amounts of PCB from previous applications still linger today, such as approximately 100 tonnes in joint sealing compounds in buildings. Additional possible sources of PCB include waste disposal sites, industrial brownfields and metal recycling facilitities.

PCB can be released into the environment from these "reservoirs" and, like PFC, bioaccumulate in the food chain. In 2007, for instance, it was discovered that fish from the Saane river in the canton of Fribourg and from the Birs river in the canton of Jura contained high levels of PCB. The highest concentration allowed in foodstuff is 8 picograms of toxic equivalents per gram of fresh weight, and this value was at times exceeded by a factor of ten. Hobby anglers were advised to limit their consumption of fish caught in said waters; for stretches of the rivers that were particularly contaminated, fishing was completely banned.

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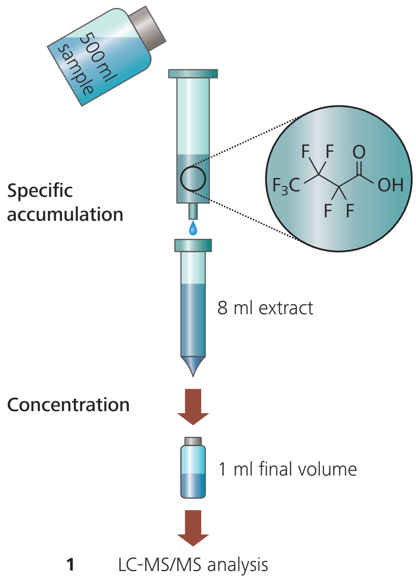
Innovative PCB collectors made of silicon

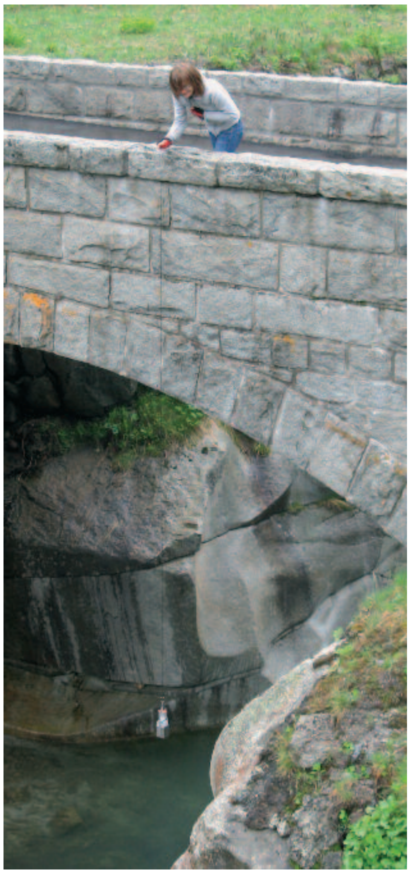
At the same time, the cantons in charge were working to identify PCB sources in the drainage basin of the rivers in order to initiate clean-up measures with the landowners. The case for the Saane could be solved quickly: the source of PCB emissions is the former La Pila landfill, roughly seven kilometres upstream from Fribourg.

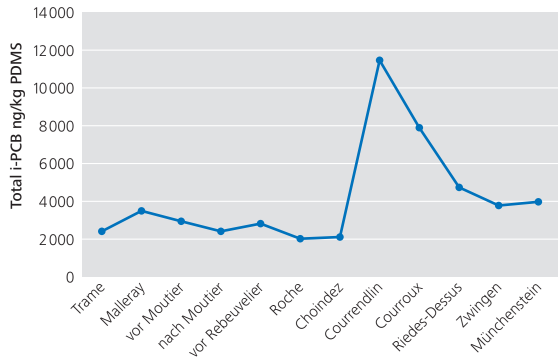
In the Birs river just downstream from the village of Choindez, Empa scientists, working on behalf of the canton of Jura, had to take a far closer look. “That’s because, for a chemist, fish are only a bio-indicator”, notes project manager Markus Zennegg. Fish are in constant motion, so a highly contaminated fish caught in one location might not necessarily indicate the immediate vicinity of the emission source. Thus, the Empa chemists, working with researchers from the Swiss Federal Institute of Aquatic Science and Technology (Eawag), developed an analysis method which, for the first time, detects even tiny traces of the dioxin-like PCB.

The “passive collector” consists of a special silicon rubber the size of a A5 sheet of paper. Akin to a flag, it is attached to a pole and placed into the river. In two sampling periods, Zennegg and his colleagues placed the flags in two sessions, each time putting 13 of them at various positions in the course of the river. In each case, after four weeks substances that are poorly water soluble accumulated on the silicon collectors' oil-like surface. “Just as a fish absorbs toxins through its gills and skin, PCB diffuse from the water phase into the plastic”, explains Zennegg.

By evaluating the data, it turned out that the source had to be a factory downstream from the village of Choindex, where steel had been produced since the mid-19th century and where, even today, steel continues to be processed and recycled. Upstream, no high PCB values were measured. The canton of Jura is currently working with the operator of the manufacturing facility to determine the origin of the PCB which made their way into the Birs, in order to be able to sketch out measures to prevent future deposits in the waters. //







1
The analysis of the different poly- and perfluorinated substances turned out to be a difficult task because the compounds are, among other things, very surface active.

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Water samples were also taken from the Aare river in the Grimsel region and checked for PFC.

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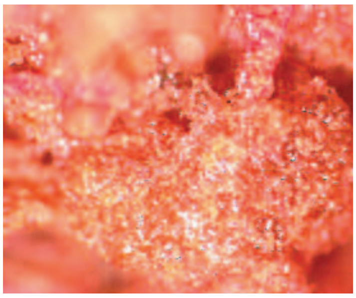
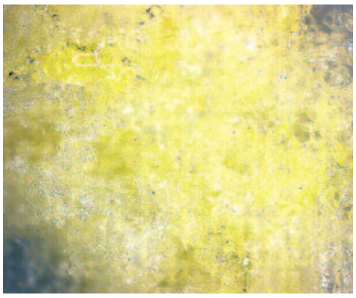
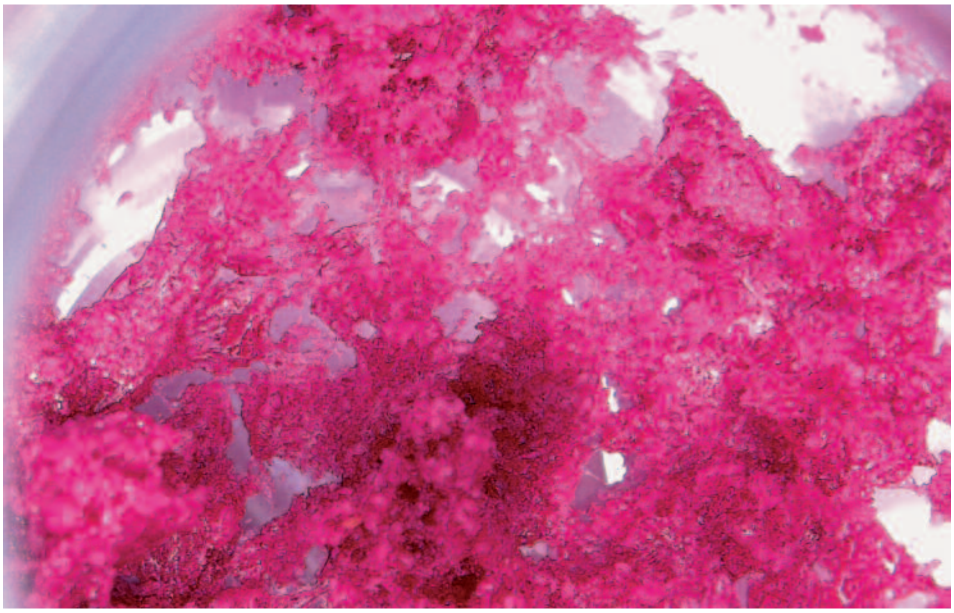
As the analysis of the passive collector showed, the largest amounts of PCB in the Birs were found downstream between Choindez and Courrendlin.







Design studio for new materials

Even everyday technologies such as catalytic converters or rechargeable batteries for mobile phones and electric vehicles use "exotic", meaning rare elements. They are expensive and also often poisonous. Chemists at Empa are studying new materials based on readily available, affordable and environmentally friendly elements.

TEXT: Beatrice Huber / PHOTOS: Empa

Chemists at Empa are working on perovskite metal oxides. Perovskites are a class of compounds with a flexible yet stable crystal structure, their chemical compositions can be varied widely and thereby the physical properties, such as colour, can be modified.

The variety of materials used in modern technology is virtually limitless. Quite frequently, these materials contain not only common chemical elements such as titanium, iron or aluminium, but also very rare elements, for instance tellurium (for solar cells) or rhodium (for catalytic converters).

Meanwhile, the search for new, improved materials proceeds continuously. The goal is, on the one hand, to optimise the material properties and, on the other hand, to find replacements for material constituents which are disadvantageous in terms of scarcity (tellurium), price (precious metals) or environmental impact (cadmium).

Multi-talented perovskite

Empa researcher Anke Weidenkaff has been working with colleagues in her Solid State Chemistry and Catalysis Laboratory for quite some time on what are known as perovskite metal oxides. Perovskites are a class of compounds with the molecular formula ABO_3, where A and B represent transition metals and O is oxygen. Due to their high temperature, pressure and oxidation stability they can be put to use in a wide range of applications and are environmentally safe. In naturally occurring perovskite, A is calcium and B

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is titanium. “Thanks to the perovskites’ flexible and yet stable crystalline structure, their chemical composition can vary widely,” Weidenkaff describes their merits. “Moreover, the specific exchange of both metal ions as well as oxygen enables us to optimise the material’s physical properties, that is magnetic behaviour, electric or thermal conductivity, colour and much more.” The underlying idea is to synthesise new materials for various applications by using readily available, affordable and environmentally friendly elements. Examples of use are rechargeable batteries in electric vehicles, catalytic converters and thermoelectrics, i.e. materials which convert heat directly into electricity.

Electricity storage as a key technology

The major drawback of renewable energy sources such as solar radiation and wind is that they are not continuously available and thus cannot be used on demand. As a result, energy conversion and storage technologies are playing a key role in aligning supply and demand and to leverage renewable energy sources. Research projects on polymer solar cells or solar water-splitting processes are further examples for activities in this field at Empa.

Batteries are the electrical energy storage systems of choice, especially for transportation purposes. Electricity is converted into chemical energy which can be easily stored. The reverse process releases the electricity again, which can be used to power electrical vehicles or plug-in hybrid vehicles. Batteries have to fulfil three basic requirements: they must be safe, reliable and affordable. These demands on quality can be illustrated by a simple calculation. In future, the operational lifespan of batteries should correspond to that of vehicles, i.e.15 years. Assuming daily recharging, a total of approximately 5500 charge/discharge cycles would arise. Today, only high-quality batteries, far too expensive for electrical vehicle application, can meet these standards.

Replacement for the “heavyweight” cobalt oxide

At present, lithium-ion batteries are considered as state-of-the-art, yet far from perfect. Cobalt contained in the frequently used cathode material lithium cobalt dioxide ($LiCoO_2$) is heavy and thus results in heavyweight batteries. What is more, cobalt is one of the most expensive transition metals due to its scarcity. Materials containing little if any cobalt but rather manganese, for example, are currently a hot research topic. Scientists at Empa are are even going beyond this. “We don’t just want to replace the cobalt”, explains Angelika Veziridis from Weidenkaff’s team. “We’re searching for completely new materials, since the battery performance in terms of energy density and reliability needs to be improved considerably.”

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1
Laboratory experiments are not performed simply by trial and error; Empa researchers deal intensively with the relationship with the relationship between crystal structure, composition, microstructure and material properties.

At room temperature, perovskite-type metal oxides exhibit a very high lithium ion conductivity, making them interesting as alternative electrolytes but also as anode or cathode materials. Empa researchers are trying to even increase this conductivity by substituting of individual elements. This is not restricted to metal ions but also includes the exchange of oxygen with nitrogen. The resulting oxynitrides exhibit an even higher lithium capacity and a better conductivity. In addition, they're chemically and thermally more stable than pure oxides or nitrides.

The relationship between composition, structure and effect

However, the chemists are not just acting upon the trial-and-error method but are rather trying to get to the bottom of how the composition and thus the microstructure influences the material properties. "Only if we have precise knowledge of the crystal structure or the locations where mobile ions are embedded or the oxidation state of the transition metal, are we able to determine how the structure influences the material properties", Weidenkaff points out. In close collaboration with researchers from other laboratories at Empa and ETH Zurich, Weidenkaff's team is synthesising various complex oxides and oxynitrides in order to investigate, among other things, their application in batteries.

Less precious metal in catalysts

In the short term, efficient transportation can not be accomplished without the use of fossil fuels. Among them, natural gas becomes increasingly important as its combustion generates less NO_x and CO_2 compared to petrol and diesel. However, the exhaust fumes from natural gas vehicles need a special treatment in order to remove traces of non-combusted methane which is a potent greenhouse gas and about 20 times more climate-damaging than CO_2.

Until now, engineers simply adapted catalytic converters from petrol-powered vehicles to the emission profile of natural gas vehicles. However, to ensure the removal of even small methane concentrations, these converters contain at least three times as much precious metal. Within the scope of a national research programme entitled "Intelligent Materials", researchers from the Solid State Chemistry and Catalysis Laboratory are working together with engineers from the Internal Combustion Engines Laboratory on new types of catalytic converters for natural gas vehicles. They are supposed to have a long service life and require less precious metal. The Empa team wants to completely eliminate rhodium, which is one of the most prevalent constituents of conventional catalytic converters but also one of the rarest and thus most expensive metals of all. Instead, the researchers are taking advantage of a well-known property of perovskite-type metal oxides: in a reducing atmosphere precious metal atoms exit the crystal lattice and are dispersed at the surface, while in an oxidising atmosphere they re-enter the structure. In this way, the precious metal particles can be stabilised and a constant catalytic activity is ensured.

The scientists are currently studying the catalytic efficiency of various perovskite-type metal oxides by analysing both the structure and chemical composition as well as the reactivity in oxidation-reduction cycles typical of catalytic converters in automobiles. First encouraging results have been achieved with $LaFe_{0.95}Pd_{0.05}O_3$. The next step is to test those materials, which have shown promising results in the laboratory, in a natural gas engine.

A replacement for the "problem child" lead telluride

A sustainable supply of energy, however, can only be achieved by a more economic and efficient use of primary energy carriers. Technical equipment and machines generate considerable amounts of waste heat, most of which simply dissipates unused – or even has to be elaborately discharged. Thermoelectric generators can convert this waste heat directly into electricity without any moving parts. Until now, however, such generators have been used only in niche applications such as space probes or buoys because inexpensive and efficient thermoelectric materials have not been available. Tellurium, for example, an integral constituent of today's most common thermoelectric materials, is scarce, expensive and also poisonous. In addition, the efficiency of these materials is modest and they are stable only up to temperatures of 300 °C.

The scientists in the Solid State Chemistry and Catalysis Laboratory strive to design perovskite-type metal oxides for thermoelectric applications, as well. Due to their high temperature stability in air, they're well suited for an operating temperature range of up to 1 000 °C. The researchers are looking for new thermoelectric materials which are further optimised, for example, by nanostructuring. That way, the undesirable thermal conductivity is reduced while at the same time the essential electrical conductivity is increased.

A nanostructured metal oxide (consisting of oxygen, calcium, manganese and niobium) has already been prepared. In contrast to oxides synthesised by conventional solid-state reaction methods, the thermoelectric figure of merit ZT is twice as high making it the best n-conducting perovskite-based thermoelectric material at present. The figure ZT is a measure of quality of a thermoelectric material. Today's best thermoelectric materials have ZT values between 0.8 and 1.1. ZT values between 1.2 and 1.5 along with a good thermal stability would be sufficient to cover the car's demand for electricity by applying a thermoelectric generator in the exhaust gas system. //

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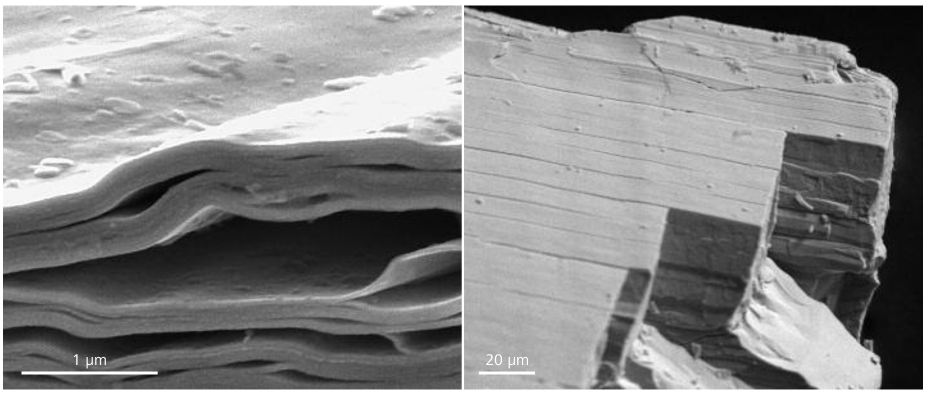
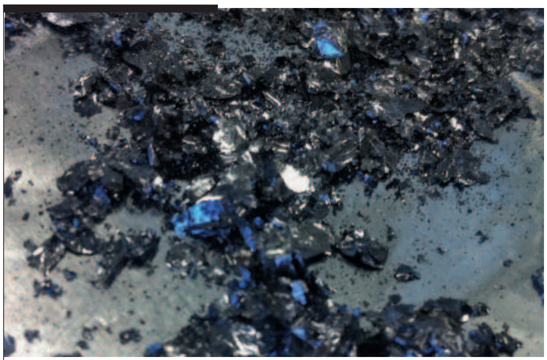


2
Not only the chemical composition but also its microstructure influences the material properties. The pictures show electron microscope images of perovskite-type metal oxides.



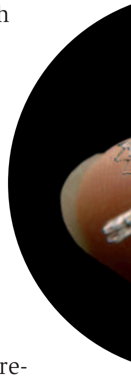
The result of a master's thesis: monocrystals with thermoelectric properties. (Photo: Empa)

Students at Empa

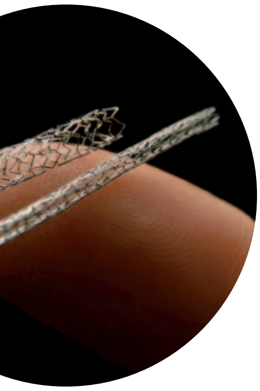
Knowledge transfer can't get any more direct than this – each autumn semester, chemistry students from the University of Bern complete part of their inorganic chemistry trainings at the Empa Solid State Chemistry and Catalysis Laboratory. It's not really worthwhile to travel from Bern to Dübendorf for just a few hours, so the trainings are organised in two-day blocks. That, in turn, makes it possible to carry out extensive experiments in the laboratory. Objects of study include perovskite compounds (ceramic oxide) for automobile catalytic converters as well as thermoelectric converters for converting heat into electricity. The students synthesise the materials and investigate them in great depth. In this way, they are introduced to a variety of methods such as for the analysis of elements and crystalline structures, or how the morphology of materials can be studied with an electron microscope.
These trainings also motivate students to continue with their master's thesis at Empa laboratories. Consider the current example of David Moser. Within the scope of the national research focal area MANeP (MAterials with Novel electronic Properties), in his master's thesis he is investigating the manufacture of thermoelectric monocrystals for studies using ARPES (angle resolved photoemission spectroscopy). "Direct access to all the instruments needed for analysis, the interdisciplinary work and the large team are, from my viewpoint, the primary advantages compared to a classic university programme", says Moser. "Here I also get enough time to study and so I can grow into my assignments."

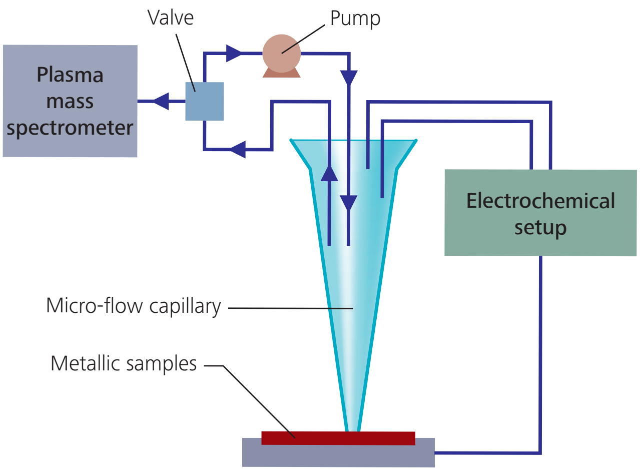
When "corroding" implants are beneficial

In most cases, corrosion is undesirable. Sometimes, though, it can be useful – for instance in biodegradable implants. Timing is, however, critical; the degradation process should be carefully controlled to avoid dissolution of the implant before it has fulfilled its function. Empa's Analytical Chemistry Laboratory has developed an analytical setup, with which they measure local dissolution processes. It is, for instance, possible to determine which elements will preferentially dissolve out of an alloy and, through automated operation, to follow the dissolution process over time. In collaboration with the Laboratory for Corrosion and Materials Integrity, this setup is currently used to study magnesium alloys, which are promising candidates for biodegradable implants because of their high biocompatibility. Their corrosion behaviour is determined, to a large extent, by the chemical composition of the alloys. Often impurities such as iron are kicking off local corrosion processes. In contrast, alloying components of the rare earth group such as yttrium seem to slow down the dissolution rate of magnesium alloys. However, Empa researchers, in collaboration with ETH Zurich and partners from industry, are still investigating their role.

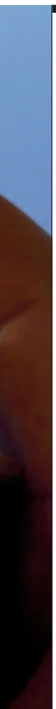


How is it possible to measure nanoparticles in a fluid medium such as the aerosol from a spray can? Empa researchers have assembled an experimental setup for this purpose. Here various spray products and their behaviour in the atmosphere are being investigated. (Photo: iStock)





Principle of the newly developed analytical setup: a thin capillary is placed on the sample, and filled with a corrosive medium (e.g. a saline solution). At defined time intervals, a small amount of the solution is taken from the capillary and sent to a plasma mass spectrometer to determine the different dissolution rates of the individual elements.



Nanoparticle release from spray products

Around the world, more than 1500 everyday products containing synthetic nanoparticles are already on the market. Among these are, for instance sprays, which contain silver nanoparticles for antibacterial applications. However, because aerosols created during spraying can be easily inhaled and also because nanoparticles can be easily absorbed, especially in the lungs, it's important to know if synthetic nanoparticles are released and how they subsequently behave. To investigate nanoparticles in solutions and aerosols in a reliable and reproducible manner, Empa's Analytical Chemistry Laboratory has assembled a new experimental setup. In cooperation with researchers from Empa's Air Pollution/Environmental Technology Laboratory and a group from ETH Zurich led by Konrad Hungerbühler, the team can determine the size, size distribution, chemical composition and morphology of the released nanoparticles.
Their findings show that, especially in those applications involving a propellant gas dispenser, aerosols often contain particles smaller than 200 nanometres, which is a critical size for cell uptake. Furthermore, even a few minutes after the use of the spray, these particles can still be detected. Whether airborne nanoparticles are present or if they clump together into larger particles mainly depends on the type of spray container: in contrast to propellant gas dispensers, the use of a pump spray vessel shows no detectable nanoparticle release. But also the composition of the spray product has an influence on the released particles. These results are establishing the fundamental data needed to model the behaviour of synthetic nanoparticles from spray products over an extended period of time, and the ability to estimate the exposure of consumers to them.

International Year of
CHEMISTRY
2011

Open house

A number of Swiss universities are taking the Year of Chemistry as an occasion to open up their laboratories to the public and provide a glimpse into the research taking place in chemistry. Most of these events will take place on Saturday, 18 June. More details can be found at the Internet addresses provided below or at *www.chemistry2011.ch*. Further information about the Year of Chemistry is available at *www.chemistry2011.org.*

- **University of Basel**
  Fest der Moleküle
  Department of Chemistry
  www.fest-der-molekuele.ch

- **University of Bern**
  Open house
  Department of Chemistry
  and Biochemistry
  Among those giving presentations
  is Anke Weidenkaff, Empa
  Laboratory Head and Professor
  at the University of Bern.
  www.dcb.unibe.ch

- **University of Fribourg**
  Fest der Chemie
  Department of Chemistry

- **University of Zurich/ETH Zurich**
  Kulturleistung Chemie
  University of Zurich, Irchel Campus
  ("Farbstoffe, Duftstoffe,
  Kunststoffe")
  ETH Zurich, Hönggerberg Campus
  ("Werkstoffe, Wirkstoffe, Naturstoffe")
  www.kulturleistungchemie.ch

Robust accelerant

It's at the very top of the industrial wish list: a robust, long-lasting catalyst for the production of polyethylene. A novel palladium-gallium compound is a candidate with great promise. In a European project, researchers are now determining whether its future use makes economic sense. Empa scientists are, for instance, observing at the atomic level how individual precursor molecules behave on the catalyst surfaces.

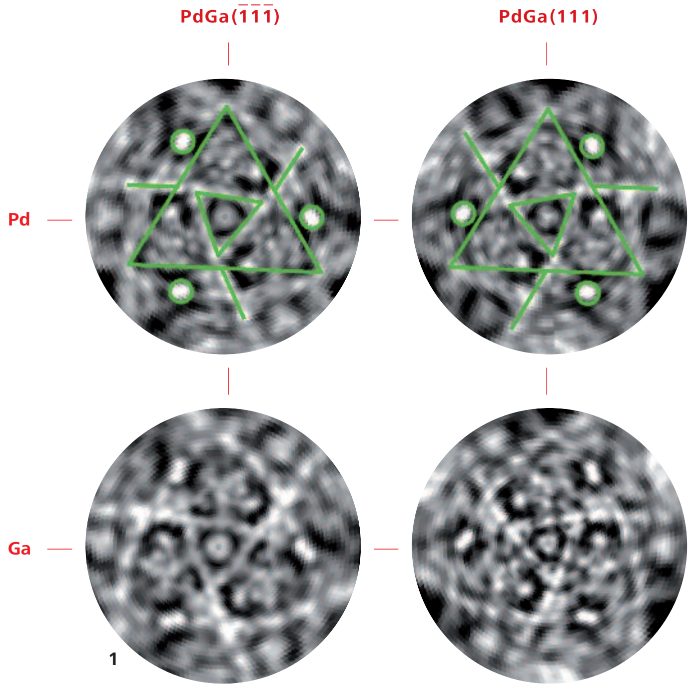
TEXT: Martina Peter / PHOTOS: Empa

1
Photoelectron spectroscopy reveals the fact that the palladium-gallium monocrystal is chiral, that is, the front and back sides are not identical but instead have a relationship to each other similar to an object and its mirror image.

2
Front and rear view of a monocrystal: in a diagrammatic representation of crystals, the numbers $(\bar{1}\bar{1}\bar{1})$ and (111), known as the Miller indices, serve to provide an unambiguous description of the crystal surface and the planes of the crystal lattice.

These days, almost 80 per cent of all chemical products result from processes which involve catalysts. In the manufacture of polymers, for instance, catalysts initiate, accelerate and direct chemical reactions so that the result is predominantly – or even sometimes exclusively – the desired product, for example the highly functional thermoplastic polyethylene. The problem, though, is that base materials are often contaminated with traces of acetylene. This "poisons" the catalysts, which typically consist of powdery palladium-silver alloys, such that the catalysts must be replaced regularly. Given a worldwide production of 60 million tonnes of polyethylene each year, this entails considerable costs.

In order to develop durable catalysts with a long lifetime, researchers at Empa are collaborating with the Max Planck Institute for Chemical Physics of Solids in Dresden, the Fritz Haber Institute in Berlin and the Ludwig Maximilian University (LMU) in Munich. In particular, they are focusing on a palladium-gallium intermetallic compound. This innovative catalyst, which in contrast to alloys has regular lattice structures, should be able to suppress undesired side reactions and prevent segregation (the separation into different elements), thereby making the chemical processes on the catalyst less complex. Palladium-gallium can withstand the "poison" by converting acetylene into ethylene through selective semi-hydrogenation.



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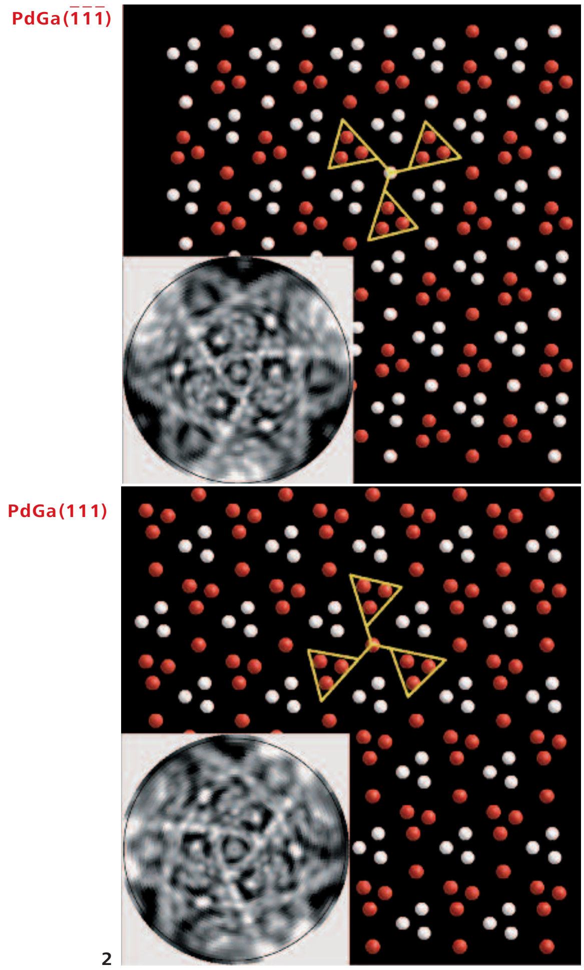

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However, because palladium-gallium is considerably more expensive than existing catalysts, the researchers have to explore ahead of time in the laboratory whether its future use would make economic sense. For industry, this innovative catalyst only becomes a viable option if it is very selective, long-lived, highly effective, and due to these factors, cost-effective.

Following chemical reactions step by step

In a project sponsored by the Swiss National Science Foundation (SNSF), scientists from Empa's nanotech@surfaces Laboratory are studying the catalyst's surface structure. "While a chemist would focus on the actual reaction, we take an atomic approach", says project leader Roland Widmer. "We take an individual acetylene molecule and want to find out exactly where it "sits" down on the palladium-gallium surface, what the hydrogen molecule does and exactly how the two react with each other." Widmer's goal is to follow the chemical reaction pathway step by step and to understand the reaction mechanism in detail. "So far, catalysts have been developed on a purely empirical basis. With our approach, we want to systematically contribute to improving their efficiency", he says. The findings should lead to the ability to design and structure the surfaces such that the catalytic process can proceed as effectively and inexpensively as possible while, at the same time, preserving the environment and our natural resources to the largest possible extent.

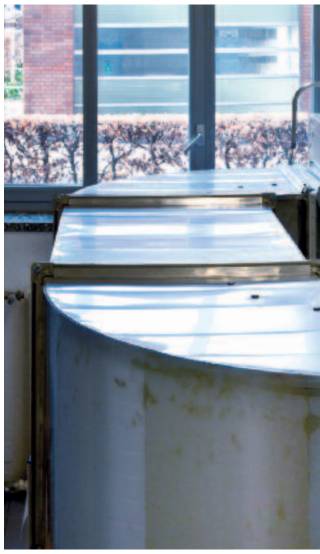
For their work, the Empa team uses palladium-gallium monocrystals which are grown by their LMU colleagues in Munich. These crystals have a homogeneous lattice, in which each atom sits in a defined location. Several layers of the crystal lattice consist primarily of palladium, others of a palladium-gallium mixture, and yet others primarily of gallium atoms. Depending on how the layers are aligned and which surface energies they have, they function differently as catalytically active surfaces in the reaction between acetylene and hydrogen – sometimes the catalyst is more efficient, sometimes less so.

Studying surfaces with different techniques

At the moment, Widmer and his colleagues are studying the catalyst surfaces with a variety of different physical methods such as scanning tunnelling microscopy and X-ray photoelectron spectroscopy, supported by computer modelling. The researchers have already obtained some initial results: the palladium-gallium monocrystal is chiral, that is, the front and back sides are not identical but instead have a relationship to each other similar to an object and its mirror image. Whether or not this influences the catalytic activities of the two mirror-image crystals is one of the questions the scientists want to examine in detail in the coming months. //

Following the path of floating particles

The newly appointed ETH professor and Empa researcher Jing Wang is investigating small and even the smallest particles floating in the air. In order to study nano-sized particles, he set up a special laboratory at Empa, including a wind tunnel.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TEXT: Remy Nideröst / PHOTOS: Empa

A room, one filled with shiny ventilation ducts. That's what the newest laboratory at Empa looks like. But what is this setup used for? No, it's not intended to make sure that researchers and engineers at Empa are able to work in very comfortable indoor conditions; rather it's needed for scientific projects. Although a wind tunnel in the Building Technologies Laboratory was just dedicated in March, tests have already been running here on a second such installation. "With it, though, we'll be doing something completely different than the wind researchers in Building Technologies," explains Chinese-born Jing Wang who recently took up his activities at Empa. "We'll be investigating nanoparticles suspended in air."

Jing Wang is taken with nanoparticles. Already his doctoral research at the University of Minnesota dealt with particles suspended in fluids and gases like air. One example is that he dispersed nanoparticles in polymer solutions to achieve new properties. "In this way we created new viscoelastic fluids" – and thus made it possible to obtain usually high extensional viscosity. Since then, he has primarily studied fine airborne particles, known as aerosols. For instance, as Research Assistant Professor in Minnesota, where starting in 2007 he became the lab manager of the university's Particle Technology Laboratory.

After all, too cold

After a total of ten years in the USA, his career has now brought Jing Wang to Switzerland. Last summer, he took on a position as Assistant Professor for industrial ecology and air-pollution control at the Institute of Environmental Engineering at ETH Zurich; at the same time he became Group Leader in the Analytical Chemistry Laboratory at Empa.

On the one hand, he had enough of the climate in Minnesota where the winters are extremely cold and long. "Last winter in Switzerland seemed like spring to me", comments Wang with a smile. On the other hand, he was also attracted to Switzerland by the professional opportunities available to him as a professor. "ETH Zurich is among the top universities in the world. For me, the combination of ETH and Empa is simply ideal", comments Wang, who raves about the excellent infrastructure and the environment offered to him at Empa for his research activities. The laboratory for the wind tunnel alone measures around 100 square metres. "That's far larger than would have been available to me in the USA."

Everything is still being set up. One of the rooms has a bit of furniture, but otherwise it's just about empty. In another a few instruments are scattered about, some just having been unpacked. One of them produces nanoparticles which will be measured by the others. An additional piece of equipment on the way is one that Wang developed himself. With it, nanoparticles or agglomerates of these tiny particles can be measured with high accuracy (primary size, morphology, and agglomerate number, surface and volume distributions). A prototype unit is already in use at the chemical company BASF, which co-financed this development. It characterises the nanoparticles being produced there, for example titanium dioxide. This material serves as a catalyst in chemical processes and has applications as a pigment in paints.

Previously, the morphology of nanoparticles produced in a flame reactor had to be analysed using a microscope. By the time it was determined if their quality was adequate, tonnes of the particles had already been produced. The test instrument Wang developed, on the other hand, measures nanoparticles "online" – the results are known within minutes. This time factor is a significant advantage, and so for the instrument, called "universal nanoparticle analyser", a patent is pending and the commercialisation is under way. "Then I'll be sure to get one of those instruments for my work", jokes Wang.

Nanoparticles in the air – largely unexplored

There's still too little known about exactly what happens to the airborne particles. Therefore, workers often protect themselves preventative with spacesuit-like clothing while cleaning production facilities. The wind tunnel is an excellent instrument for studying nanoparticles under well-defined conditions. Thanks to fans, heating and humidification, it is now possible to precisely control wind speed, temperature, humidity and other test parameters. In field

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Empa researcher Jing Wang's equipment: the wind tunnel for investigating nano-particles is an installation built with external dimensions of roughly 3 x 13 metres.

2
Jing Wang at his introductory lecture at ETH Zurich on 30 March 2011.

3
Nanofibre filters for removing particles consist of multiple layers. The fibres on the top layer, with a diameter around 100 to 150 nanometres, can provide excellent filtration performance. The fibres in the background, with diameters of about 10 to 20 micrometres, provide necessary mechanical strength for the composite filter.

studies, these parameters are largely unknown. Wang's team manufactures nanoparticles themselves and thus has precise knowledge about their size and nature. As soon as they are "set free" in a wind tunnel, they are very mobile and agile and remain in the air for a very long time; that's in contrast to larger particles which fall to the ground more quickly because they weigh more. "We investigate how long they remain in the tunnel's airstream under exactly defined conditions, how they propagate, whether they agglomerate and in this way change their size and whether they react to each other chemically", explains Wang. In addition, in the wind tunnel we've installed measurement points at various spots, and our instruments then analyse the collected samples."

In the tunnel, air-ventilation filters can also be tested so that the concentration of particles in front of the filter can be compared to that behind it. Such devices can also filter out particles with nanometre dimensions, and new challenges are emerging with new nanomaterials for filter manufacturers, with whom Wang is in very close contact, like 3M, which manufactures face masks, or Boeing for the filters installed inside aircraft interiors.

Collaboration with other research groups

At Empa there's a series of colleagues who deal with nanotechnologies and are interested in Wang's work. One of these is the Internal Combustion Engines Laboratory. Wang plans to collaborate with that group to investigate the soot particles that come from diesel engines. Their findings could lead to better soot filters and catalysts.

Furthermore, at ETH as well as at Empa, life cycle analyses (LCA) are being carried out. Until now, such analyses on products that contain nanoparticles have been somewhat imprecise because there's hardly any experimental data available showing what happens to nanoparticles when a given product is recycled or disposed of. It's possible to make precise statements about the risks only when the level of exposure and the behaviour in the environment are known. Products could therefore not be evaluated accurately afterwards using a LCA; that's a gap that will be filled thanks to the future work of Wang and his group. //


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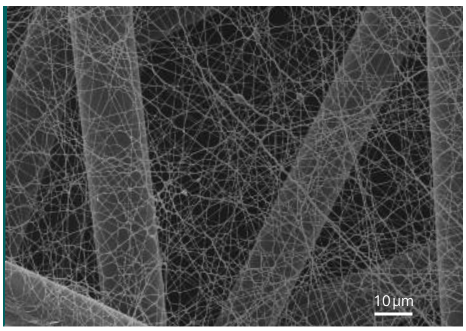

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