ONE/16

INFORMATION

Guest article
Antarctic algae for the solar cells of the future

Atmospheric research
Investigating long-range aerosol transport in Scotland

From the environmental laboratory
BSK Labs boosts productivity and profitability with Metrohm IC

Metrohm

Dear readers

There is much debate as to whether print is a dead medium for information. Metrohm, like many others, has started to move away from paper and into the digital world in the past few years. And yet I would say that print is alive and well, and Metrohm Information is perfect proof of the fact. To my mind, «print or non-print?» isn't the question we should be asking ourselves. Instead, we should be looking at which types of information are still well-suited to print media, and which can now be better served with different channels.

«Print is alive and well. But some types of information are now better served with different channels.

This edition of Metrohm Information is the first to be published not only on paper, but also as a digital version for iOS and Android tablets. This will make the magazine more accessible for you, regardless of where you live and work. But that's not the only benefit: With digital publishing, we can provide you with up-to-date information about key developments in your industry, in the field of analytics, and, of course, at Metrohm – something that simply wasn't possible with the two print editions of the magazine published each year. What's more, we can now offer you extra multimedia materials, such as the interview with Larry Tucker, who represents Metrohm at the ASTM, about the standard-compliant detrmination of the acid number in crude oil. If you don't have a tablet, you can of course watch the video online as normal at **bit.ly/Metrohm_Info**.

The «Metrohm Information» app is available to download free of charge for Android and iOS. I hope you enjoy this issue, whether you are swiping, clicking or holding a paper copy in your hand!

Markus Steinke
Head of Sales and Marketing in the Metrohm Group

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Electronic edition
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News in brief

The latest from the worlds of science, analytics, and Metrohm

TAN determination in crude oil: New standard in progress

The ASTM is currently developing a new method for determining the acid number (TAN) of crude oil and petroleum products. Thermometric titration, which is to become the new standard method, is quick and easy and ensures low reagent consumption. For refineries, which process crude oil, a high level of acid means increased risk of corrosion. It is therefore important that oil dealers state the acid content of their goods accurately.

Find out more about the new method in our interview with Larry Tucker, who represents Metrohm in the ASTM, at **bit.ly/Metrohm_Info** or via the digital edition of Metrohm Information on your iPad or Android tablet.

www.astm.org

Crude oil analytics: The ASTM is developing a new method for determining the acid number.

Feather-light gold for research and day-to-day applications

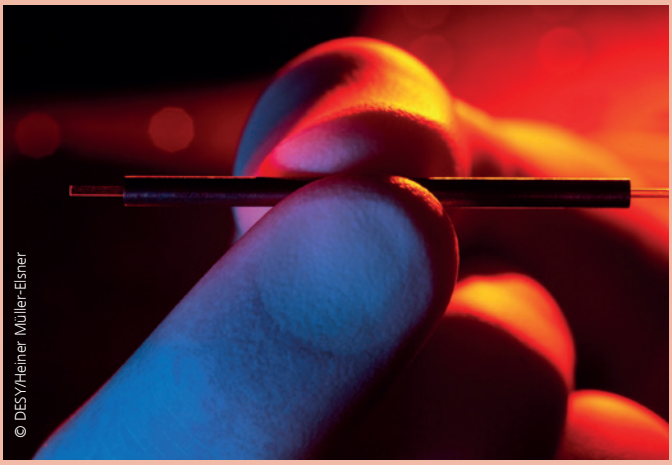
Researchers at ETH Zurich have produced a foam made of gold which is lighter than milk foam. Its composition is 98% pores, but thanks to its metallic shine, its appearance is virtually indistinguishable from that of pure gold. The first stage of the new production method is to heat milk proteins in order to produce nanometer-thin fibers. These fibers are then added to a solution of a gold salt. Here, they interlace themselves into a basic structure along which the gold crystallizes into microparticles. Thanks to its highly porous structure and correspondingly large surface, the aerogel is well-suited to use as a catalyst. There are also potential applications as a pressure sensor: when pressure is exerted on the material, contact is established between the gold particles which do not normally touch each other, and the material becomes conductive. The product could, of course, also be used in jewelry in order to reduce weight and material consumption.

www.ethz.ch

Science

A pinch of particle accelerator

When it comes to particle accelerators, the first thing most of us probably think of is gigantic machines like the 27-kilometer-long Large Hadron Collider (LHC) at CERN. At the DESY (Deutsches Elektronen-Synchrontron – German Electron Synchrotron) research center, however, a team of scientists led by Franz Kärtner has built a mini particle accelerator which fits between your thumb and forefinger. In the future, accelerator modules like this one could be used for applications involving X-rays or electron beams in materials research or medicine. The accelerator works with terahertz radiation, which is characterized by a wavelength between 100 µm and 1 mm – hundreds or thousands of times shorter than the wavelengths of the high-frequency radiation used in established particle accelerators. This makes it possible to shrink the instrument dimensions by the same factor. Although the miniature accelerators cannot compete with conventional instruments when it comes to acceleration power, the theory suggests that high acceleration is possible. Now that the principle has been proven in practice, scientists will be aiming to achieve this.



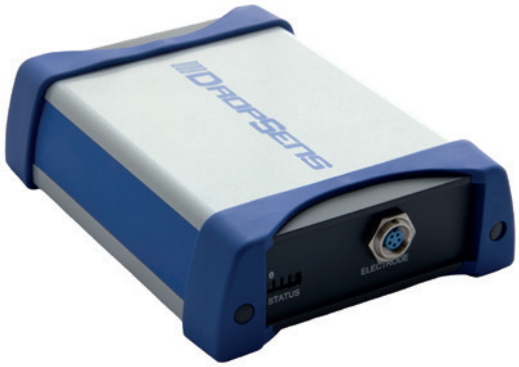
The accelerator module developed at DESY fits between your thumb and forefinger.

desy.de

Applications for research and development in the electrochemical industry

DropSens is a Spanish company which manufactures electrochemical equipment, with a portfolio that includes screen-printed electrodes and portable potentiostats. The innovative company works closely with research and development, particularly in the university environment. Metrohm sells the DropSens products as a supplement to the Metrohm Autolab electrochemical portfolio. With a focus on portable instruments, DropSens complements Metrohm's in-house range.

The DropSens products have recently been integrated into the Metrohm website. The corresponding applications can also be found in the Metrohm Application Finder alongside the Metrohm applications – at **www.metrohm.com/Applications**. This edition also features a DropSens customer article: you can find out about electrochemical research in the Antarctic starting on page 6.



Small, light, and robust: The portable DropSens µStat 400 unites the exact properties researcher María Fernanda Cerdá was looking for to study the electrochemical properties of algae pigments in Antarctica – read more starting on page 6!

New industry pages online

There are now new pages for the energy and polymer industries on the Metrohm website. The industry pages, which can be found at **www.metrohm.com** under the «Industries» menu item, contain extensive information about the analytical challenges faced in the relevant industry, including the applicable standards, and offer suitable solutions. Our web editors are constantly updating the pages with news and information.

Industry brochures updated

Metrohm provides free brochures which give an overview of the chemical analyses required in a range of different industries. Many of these brochures have recently been revised, including those for the following industries: pharmaceuticals, environment, water, waste water, beverages, power plants, petrochemistry, and biofuels. You can access the brochures via the product search at **www.metrohm.com**.

New instruments from Metrohm

Easy routine determination of water traces

The new 917 Coulometer makes it possible to determine traces of water using coulometric Karl Fischer titration. It is the latest addition to Metrohm's range of instruments for titrimetric routine analysis. Like its «siblings» – the 916 Ti-Touch for potentiometric titration and the 915 KF Ti-Touch for water determination using volumetric Karl Fischer titration – the compact 917 Coulometer boasts full system integration: the magnetic stirrer, operating module, and the pump for changing the reagents are all housed in one compact unit. The touchscreen enables clean, easy operation of the analyzer.

Find out more about the 917 Coulometer:
bit.ly/KFTitrators

Once you have saved an application as a favorite, it only takes a single tap to start it! The 917 Coulometer can be fully automated for routine operation with the 885 Compact Oven Sample Changer. With its USB and Ethernet connectors, the compact titrator also makes it much easier to input sample data, e.g., using a balance or barcode reader, and enables external storage, archiving, and printing of measured data and results.

Antarctic solar cells

or A step-by-step guide to being a researcher at the end of the world

Traveling to Antarctica might sound like traveling to the very end of the world for many – even more so when you come from a small country, for instance, Uruguay, where the longest distance between two points does not exceed 1000 kilometers. Still, scientists from the University of the Republic in Uruguay take this trip upon them to do research at the country's Scientific Antarctic Base «Artigas» (BCAA in Spanish), situated at 3012 kilometers from the Uruguayan capital Montevideo. Among them is our guest author, María Fernanda Cerdá. Here she is on the joys and strains of being a researcher in Antarctica.

Step 1: Know what you're getting yourself into

The BCAA (figure 1) is located at Collins Bay on King George Island, roughly 1000 kilometers south of Cape Horn (figure 2). Traveling there is not without its complications, and traveling there to do science is again a completely different story. As a researcher, there is only one person responsible for transporting all necessary materials for your work to the Antarctic Base: you. This means that you have to take with you absolutely everything that you might need – and might not need, too, just in case. Anything that you forget stays at home.

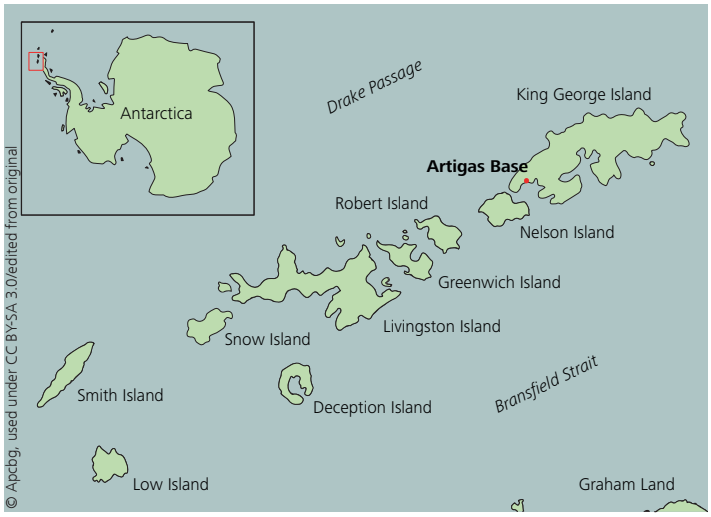


Figure 2. The Uruguayan Antarctic base «Artigas» is on King George Island, the largest of the South Shetland Islands. It is situated roughly 1000 kilometers south of Cape Horn, the southernmost point of South America.

The rough climate at Antarctica requires special adaptation. This includes the means of transportation – here's our track vehicle.

Step 2: Plan around uncertainties

So far, so good. But keep in mind that a research trip to Antarctica takes luggage planning to a whole new level, because you never know exactly how long you are going to stay. Crossing from the South American continent to King George Island and back is only possible when climatic conditions are good. This means that maybe you'll only spend 10 days at the base, but you might have to stay for 3 months until our plane can return to pick you up. In Antarctica, weather and nature dictate the lives and activities of all.

If you look for a «real» laboratory at the BCAA, you will look in vain. A small room with a table is all we have (figure 3)! There is no access to the instrumental equipment that is necessary for many analytical purposes. Moreover, you cannot carry with you all the equipment you have at the university, as the plane is needed to transport many things to the base, e.g., supplies for those who are going to spend the worst part of the year isolated in Antarctica. So, if you're lucky enough to get the opportunity to travel to the BCAA, you will need foresight and good planning to pack your «scientific luggage».

Figure 1. Panoramic view of the Scientific Antarctic Base on King George Island. *Picture by Gabriela Rufener*

Figure 3. The «lab» at the BCAA is nothing more than a small room with a table.

Step 3: Get to work

So, you have arrived at the BCAA. What now? If you're a chemist and you work with dye-sensitized solar cells, your first task may be quite simple: walk across the island and collect samples of algae (figure 4).

My project at the Antarctic base was to collect red algae on King George Island, extract the dyes responsible for their color, and select those with the proper characteristics to assemble a dye-sensitized solar cell, which I was going to do after returning to Montevideo. The first part of the work can be done without any special equipment: all you need to do is compare the color of the extracts obtained with different solvents and select those with the deepest red. To be suitable for solar cells, however, the dyes have to combine two properties: in addition to high extinction coefficients at suitable wavelengths, high oxidation potentials are required. Only a dye exhibiting both properties can transfer the electrons to the semiconductor of the cell, and thereby make it possible to harvest electricity from the cell.

Step 4: Use the instrument that suits your application

Unlike the extinction coefficients which can be estimated by an experienced eye, you will need the help of an instrument to measure the oxidation potentials of your dyes – preferably a small instrument that is light and easy to use, such as the ones from DropSens. Weighing less than half a kilogram, the

Figure 4. Red algae can be found in abundance on King George Island. Here I am collecting some samples. *Picture by Patricia Valdespino*

portable potentiostat «µStat 400» is well within your luggage restrictions and solves your problem (figures 5 and 6)! The device works with screen-printed electrodes that combine the working electrode, reference electrode, and counter electrode in one handy sensor and require only a drop of solution. This means that only small quantities of sample and of electrolyte solution are required for the measurements. This again comes in handy when packing: you won't need to bring more than 20 milliliters of electrolyte solution to the Antarctic base.

Figure 5 (top). To determine the oxidation potentials of the dyes I had extracted, I used an experimental setup that consisted only of the 400 µStat potentiostat and a laptop. **Figure 6 (left).** Here I am measuring the oxidation potential of a dye using the µStat 400 from DropSens.

Step 5: Evaluate your data

When you analyze a dye, you will obtain a curve similar to the one in figure 7: a cyclic voltammogram. To produce this, the potentiostat performs a potential sweep on the working electrode and measures the current that results in the electrolytic cell. The electrolytic cell is made up of the sensor with its three electrodes and the sample solution containing dye extract and electrolyte solution. The sweep starts at a small potential that increases to the point at which the analyte – your dye – has been oxidized. Afterwards, a backward scan is performed during which the dye is reduced. The voltammogram plots the current in the electrolytic cell against the applied potential.

The voltammogram in figure 7 unveils that the dye in question has a promising oxidation behavior: there is a strong peak at 1.0 V at positive current values, i.e, in the oxidation quadrant (upper right) of the graph. This means that the oxidation potential is high. Other samples that I've analyzed didn't show such a peak, or exhibited contributions at a lower potential (around 0.6 V) and therefore weren't good candidates for a dye-sensitized solar cell.

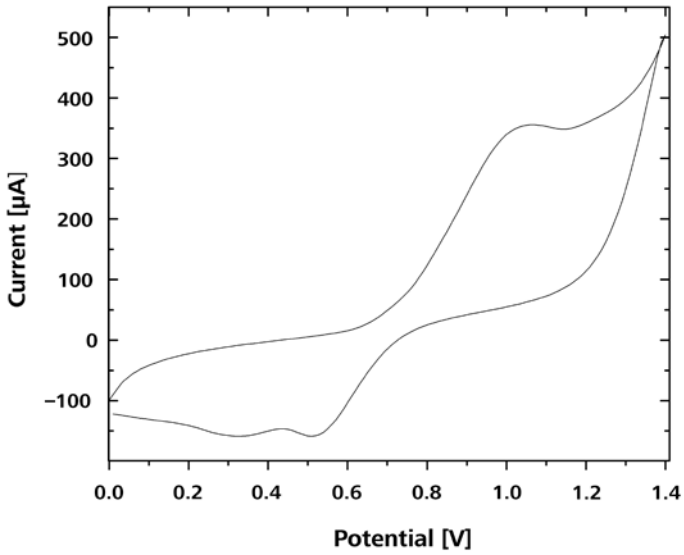


Figure 7. A dye-extract from red algae was analyzed by cyclic voltammetry at a potential sweep rate of 0.1 V/s. The strong peak at 1.0 V in the oxidation quadrant (upper right) of the graph reveals a high oxidation potential.

My tiny helper

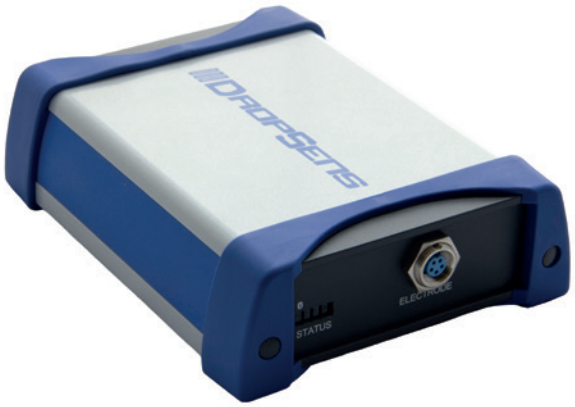
The µStat 400 helped me identify potentially suitable dyes for solar cells by shedding light on their oxidation behavior. In addition to that, there are three main reasons to choose this potentiostat – especially when working at a place like the BCAA: its small size, its light weight, and the fact that measurements don't generate waste that has to be flown back to the continent.

My colleagues at the BCAA. *Picture by Cap. (Nav.) Esteban Carrero*

About the author

María Fernanda Cerdá graduated with a PhD from the Faculty of Chemistry of the University of the Republic (Udelar) in Montevideo, Uruguay. Today, she is Associated Professor at the Faculty of Sciences of her alma mater. Fernanda has been working on the topic of dye-sensitized solar cells for 4 years, in which she has evaluated the suitability of dyes coming from flowers and fruits native to Uruguay for use in solar cells.

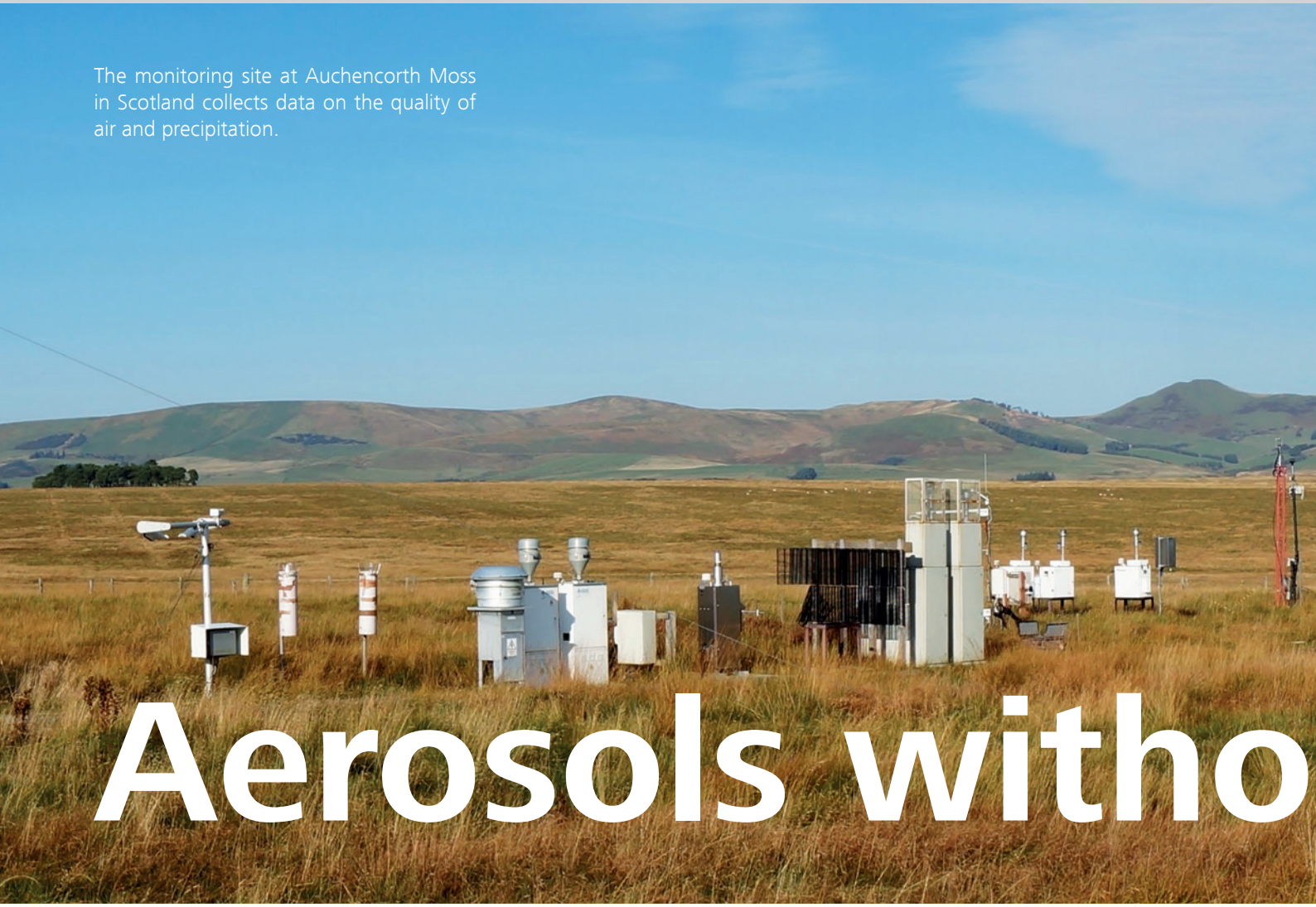
In hopes of extending her research to dyes from Antarctic red algae, she presented her project at the Uruguayan Antarctic Institute (IAU) in 2013. In the end of 2014, she finally got the news that her project was selected, but wasn't able to travel on the fixed dates. After signing up again, she waited all summer for news from the IAU. «I was looking at the stars, wondering what the Southern Cross constellation looks like from Antarctica» says Fernanda. «I felt like haunted by Antarctica. I took my youngest daughter to two movies, and both were full of references to Antarctica. And then I finally got the invitation to travel on the last flight»! And after a week of cloudy skies, just some nights before returning home, she could finally see the Southern Cross, this time from the furthest south she had ever been.



The µStat 400 from DropSens weighs only 480 g and measures 13.2 cm × 10.0 cm × 3.6 cm.

DropSens

DropSens is specialized in the design and manufacture of instruments for electrochemistry research and is based in Oviedo, Spain. The product range includes, among others, potentiostats, screen-printed electrodes, and accessories for screen-printed electrodes. Metrohm recently added DropSens to the portfolio of instruments and accessories to provide an even wider range of low-cost to high-end solutions for electrochemical research.



The monitoring site at Auchencorth Moss in Scotland collects data on the quality of air and precipitation.

Aerosols witho

To gain insight into the effects of particulate matter on health and the environment, we need long-term measurements that determine the quantity and chemical composition of suspended particles at high temporal resolution. In the south-east of Scotland, such measurements are being taken as part of «EMEP», a program that focuses on the monitoring and evaluation of the long-range, transboundary transmission of air-polluting substances in Europe. The program serves to regularly equip European governments with the scientific knowledge required to reduce air pollution and mitigate its effects.

ut borders

©Ian Leith/Centre for Ecology & Hydrology

The Auchencorth Moss monitoring site

Auchencorth Moss is about 20 kilometers south of Edinburgh in Scotland. The landscape is a raised bog, that is, a bog which is exclusively precipitation-fed. In this remote place, the Centre for Ecology & Hydrology (CEH) operates a monitoring site which collects specialized data on the quality of air and precipitation (title image). Scientists at CEH and other British research institutes analyze this data as part of research initiatives including EMEP. Isolated from urban and industrial areas, as well as other local sources of emissions, the area qualifies as a «rural background location»[1]. It is therefore ideal for analyzing to what degree crops and natural ecosystems, as well as the rural population, are exposed to airborne pollutants.

A convention for clean air

The UNECE (United Nations Economic Commission for Europe) Convention on Long-range Transboundary Air Pollution entered into force in 1983. The signatory states agreed to take specific action, such as combating air pollution and building a monitoring network across Europe. EMEP operates under this convention and provides it with a scientific foundation. In order to collect the relevant data, the program follows a monitoring strategy[2]. This strategy determines, for example, that long-term, comprehensive monitoring of air pollutants is to take place, whereby temporal resolution is sufficient to investigate not only atmospheric processes, but also individual pollution events.

Hourly air pollutant measurements

The data collected at Auchencorth Moss includes, for example, the concentrations of inorganic aerosol components and inorganic reactive gases in the ambient air. These are determined entirely automatically on an hourly basis by the Monitor for AeRosols and Gases in ambient Air (MARGA). Marsailidh M. Twigg and her colleagues at the CEH, at Metrohm Applikon, and at the School of Chemistry in Edinburgh, recently published an evaluation of the results collected between 2006 and 2012 – a period of six-and-a-half years. It was published in the open-access journal «Atmospheric Chemistry and Physics Discussions»[3].

Measurements with MARGA

MARGA analyzes water-soluble aerosols and trace gases by ion chromatography. The system at Auchencorth Moss takes in ambient air and aerosols contained therein up to a diameter of 10 µm (PM_{10}, where PM stands for *particulate matter*) through a suitable inlet opening. The tube then separates: The first line leads directly into a sampling box. The other directs the air flow initially into a cyclone which removes particles with a diameter greater than 2.5 µm from the mixture. This ensures that only aerosols in the $PM_{2.5}$ fraction are led into the second sampling box. Each sampling box contains a «Wet Rotating Denuder» (WRD) which dissolves the water-soluble gases from the passing air flow, and a «Steam-Jet Aerosol Collector» (SJAC) which transfers the water-soluble aerosols into a second solution. The sample solutions are then continuously transferred into the analysis box where they are analyzed by anion and cation chromatography. Further information on the analytical procedure can be found in the original publication which can be downloaded free of charge from **bit.ly/MARGApub**.

Making one-off pollution events visible

The hourly rhythm of the measurements reveals variations in the composition of aerosols throughout the day, including one-off pollution events. Given the consistently low concentrations of pollutants, these variations are particularly striking at the rural location of the Auchencorth Moss monitoring site. For example, on the night of November 5, 2012 – called «Guy Fawkes Night» in the United Kingdom and celebrated with fireworks – the site measured a sharp increase of K^+ concentration around midnight; at 2.61 µg m^{-3} the figure was forty times the annual average of 0.07 µg m^{-3}.

In addition to variations throughout the day, Twigg and her colleagues were also able to observe more long-term trends such as seasonal differences in the concentrations of Na^+ and Cl^-: the ions primarily originate from the sea and enter the atmosphere in greater quantities due to the increase in wind speeds during the winter months (figure 1).

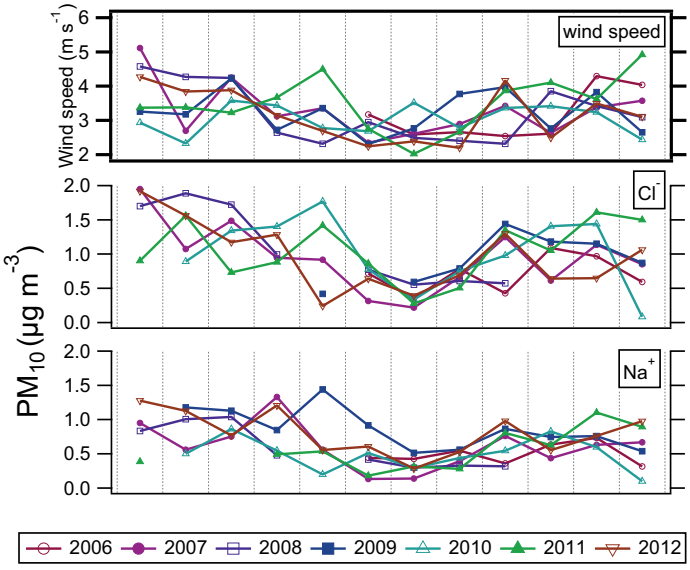


Figure 1. The mass concentration of Cl^- and Na^+ in the PM_{10} fraction is considerably lower in the summer than in winter. During the winter, the transference of these mostly marine ions into the atmosphere is much higher because of increased wind speeds (Twigg et al. 2015).

Ions originating from the sea

Auchencorth Moss is not far from the sea in any wind direction, meaning that the quantity of marine ions is relatively high. Typical ion species of marine origin are Na^+, Cl^-, SO_4^{2-}, Mg^{2+}, Ca^{2+}, and K^+ – the ions are, however, not necessarily exclusively of marine origin. The proportion that is of marine origin can nonetheless be calculated, since they occur in the sea in fixed proportions. Twigg and her colleagues take the entire Na^+ concentration measured and calculate the marine fractions of the other species from this. In the coarse fraction of aerosols (PM_{10} minus $PM_{2.5}$), the marine ions make up 73%, whereas in the fine fraction ($PM_{2.5}$), they constitute around 30% of the inorganic ions.

When calculating the marine proportion of Cl^- from the Na^+ concentration, the scientists found a deficit of Cl^- in many of the individual measurements as well as in the average of all measurements: in the coarse fraction, the concentration of marine Cl^- calculated exceeded the Cl^- concentration measured. This, in combination with the measured surplus of NO_3^- which is not of marine origin, suggests an exchange of chlorides and nitrates. The exchange takes place by reaction with HNO_3 during the long-range transmission of sea salt. This hypothesis is supported by the fact that increased nitrate quantities are generally accompanied by a Cl^- deficit which was found in an analysis of the measurements taken in 2012 (figure 2).

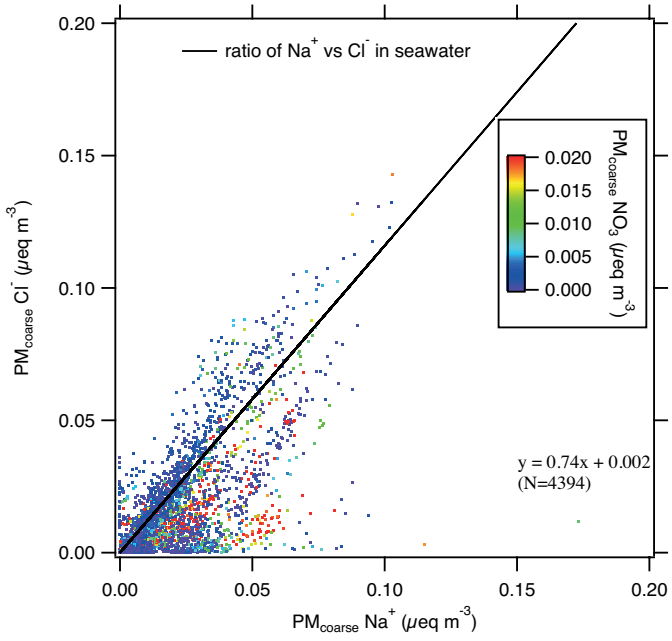


Figure 2. Each point represents a measurement during 2012 and shows the ratio of sodium to chloride. If a point appears below the black line, there is a deficit of Cl^-. The quantity of NO_3^- in the measurement is shown by the color coding. High concentrations of NO_3^- are often accompanied by a deficit of Cl^- (Twigg et al. 2015).

Toward the origin of air masses using computer simulation

There are no sources of emissions in the immediate vicinity of the monitoring site. The long-range transmission of air masses therefore has a considerable impact on the composition of aerosols at Auchencorth Moss. Using backwards trajectories, which are created by computer simulations on the basis of meteorological data, the origin of air masses can be ascertained. In order to retrace the path of air masses, these trajectories were simulated in three-hour intervals for a measuring period between 2007 and 2012 – 17,370 simulations in total. A cluster analysis helped Twigg and her colleagues to group together similar trajectories (figure 3) and to establish the relationships between aerosol composition and the origin of air masses.

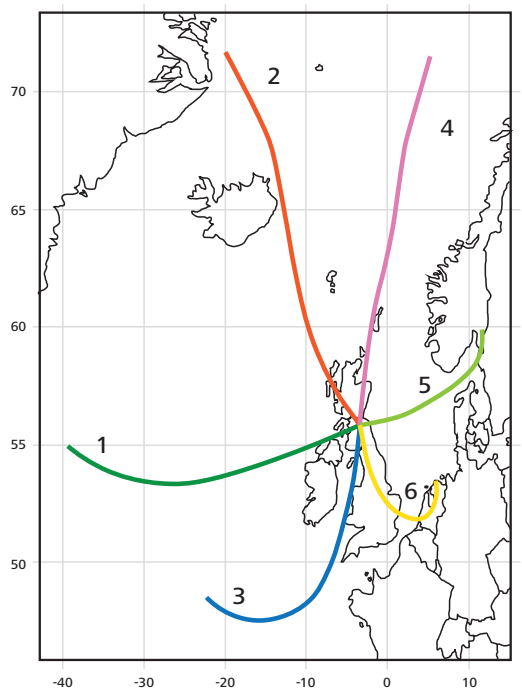


Figure 3. The backwards trajectories of the air masses were grouped into six clusters. This shows the averaged path for each cluster (Twigg et al. 2015).

Trajectories 1, 2, and 4, originating from the Atlantic Ocean and the Arctic Circle, were linked with high quantities of Na^+ and Cl^- (figure 4). This is even true for the $PM_{2.5}$ fraction, which is usually determined by secondary (anthropogenic) ions. By contrast, air masses which cross land (trajectories 5 and 6) carry considerably more secondary inorganic aerosols such as NO_3^- and NH_4^+.

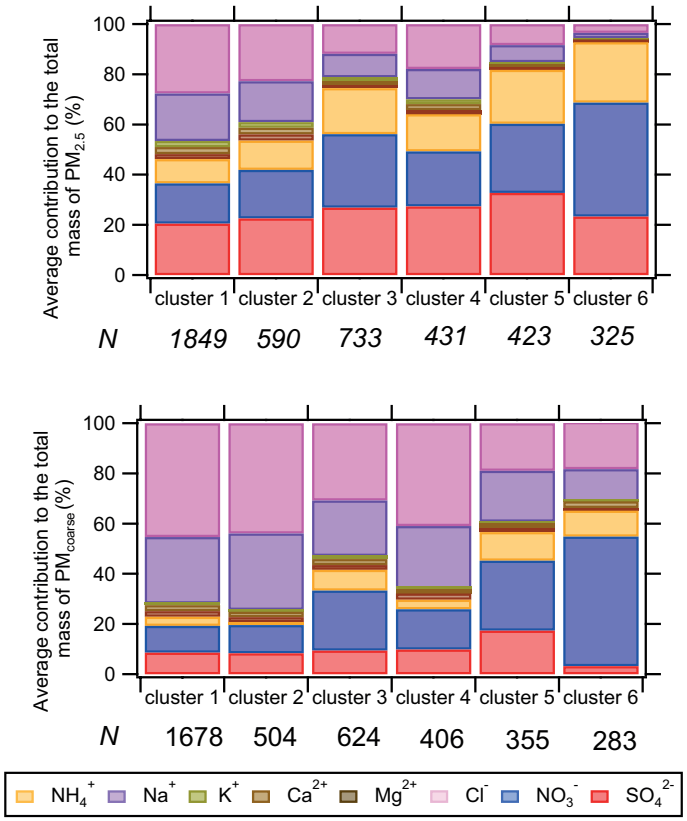


Figure 4. For each cluster of backwards trajectories, the proportions of individual ion species in $PM_{2.5}$ (top) and PM_{coarse} (bottom) are shown (Twigg et al. 2015).

Conclusion

The semicontinuous determination of inorganic aerosol components at Auchencorth Moss enables the analysis of both one-off pollution events and long-term trends. When combined with computer simulations, the origin of the air masses and aerosols can also be determined. Twigg and her colleagues were able to establish that a significant proportion of the aerosols, and therefore also air pollution, detected at rural locations like Auchencorth Moss have traveled a great distance. This underlines the importance of international cooperation in order to control emissions.

References

[1] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe

[2] Unece.org, (2015): «EMEP Strategies». Retrieved August 27, 2015 from http://www.unece.org/env/lrtap/emep/strategies.html.

[3] Twigg, M. M. et al. (2015) Atmos. Chem. Phys. 15, 8131–8145

For more information on air analysis using MARGA, visit **bit.ly/MetrohmMARGA**

The productive environmental laboratory

Brad Meadows is Vice President and Lab Director at the US company BSK Labs, which runs a number of environmental laboratories and service centers. Brad is an analytical chemist and has been working in analytical lab management for 15 years. He shared his experiences with Metrohm ion chromatography with us in the form of concrete facts and figures.

BSK Labs runs a number of environmental laboratories and service centers along the west coast of the US. A total of 70 employees – including microbiologists, chemists, lab technicians, and support staff – make sure that the 200 to 350 samples that come in every week are analyzed. BSK Labs specializes in potable water chemistry, ground water monitoring, storm water runoff, solid waste characterization, and wastewater discharge compliance. The company's portfolio is rounded off with services including project consultation, sample collection, and small public water system operation and management.

The challenges of the environmental lab

One of the most important analysis methods for American environmental labs is the determination of inorganic anions in accordance with EPA 300.1 Part A. In this standard, the United States Environmental Protection Agency (EPA) describes how to analyze various substances including chloride, sulfate, bromide, nitrate, and nitrite not only in different types of water and waste water, but also in solids (following extraction) and leachates, using ion chromatography.

The nature of the samples measured in environmental labs is such that sample preparation is required – this always involves filtering the samples, and in many cases diluting them as well. This is the only way to prevent damage to the analysis system and to achieve accurate results. Sample preparation is expensive for BSK Labs, as it involves a lot of work as well as costly consumables.

Considerations when buying the new system

BSK Labs processes a high volume of samples, including some with a limited shelf life. Reliability is therefore a particularly important criterion when it comes to buying a new system. Economic considerations also play a key role: a new system should pay for itself as quickly as possible; it needs to be generating a return on investment after a year at the latest. A 30-day trial run should demonstrate whether the system offered by Metrohm meets the requirements. BSK Labs tested a Metrohm ion chromatography system with automatic ultrafiltration and dilution.

Fully automated Inline Ultrafiltration protects the separation column – and the budget

At BSK Labs, all samples are filtered before being analyzed. This prevents dirt from the sample contaminating the separation column – which significantly improves its service life. The high volume of samples drove material cost down substantiallly, to only 1 US dollar per filter. However, since each sample requires a new filter, with 14,300 samples a year this still amounts to $14,300 – just for filtration materials.

Filtration ROI*

	Ultrafiltration	Syringe Filter
Filter cost per sample	$ 0.11	$ 1.00
Labor cost per sample	None	3 min
Total	$ 1,586	$ 27,170
Savings	**$ 25,584 per year**	

*Return on investment

The integrated ultrafiltration in the ion chromatography system from Metrohm only needs one filter change per day, saving BSK Labs over $12,000 per year. What's more, the ultrafiltration process is fully automated. Compared to the manual filtration previously used at BSK Labs, this saves three minutes' working time per sample. With labor costs of $18 per hour, this again corresponds to savings of around $13,000 per year. Overall, therefore, using ultrafiltration saves over $25,000 in annual expenditure.

Suppressor ROI

	Metrohm	ERS
Replacement cost	$ 0	$ 1,200
Replacements per year	0	4
Regeneration	$ 52 after 1,000 samples	$ 0
Total	$ 750	$ 4,800
Suppressor Savings	**$ 4,050 per year**	

Long-lasting: The Metrohm anion suppressor

Suppression reduces the conductivity of the eluent, resulting in a more sensitive conductivity detection of the analyte. This makes it possible to achieve particularly low limits of detection and quantification. The instrument previously used at BSK Labs (from a different supplier) employed membrane-based suppressors. These suppressors have to be replaced every three months, costing $1,200 each time. The Metrohm Suppressor Module (MSM), on the other hand, is a one-off purchase because it uses ion exchanger particles in a robust micro packed bed for suppression instead of

Environmental laboratories often need to analyze heavily contaminated samples which must be filtered and diluted first.

membranes. The three suppression cartridges of the MSM alternate between suppression, rinsing, and regeneration, thereby ensuring continuous suppression at all times. The regeneration reagents are not expensive at $52 per 1,000 samples, resulting in total annual costs of $750 for 14,300 samples. This is much cheaper than the cost of replacing a membrane suppressor multiple times.

Columns ROI

	A Supp 5	AS4A
Injections	7,000	1,200
Column cost	$ 1,420	$ 1,751
Total	$ 2,900	$ 20,866
Savings	**$ 17,966 per year**	

High-performance separation columns

With Metrohm columns, BSK Labs achieved better separation of the analytes and a much longer column service life – on average, 7,000 injections compared to 1,200 with the previous columns. There appear to be two factors which are key to the reduced wear on the separation column: Firstly, the Metrohm ion chromatography system provides measuring signals which are four to five times stronger. This results in a much higher detection limit, which makes it possible to reduce the injection volume by a factor of five. Secondly, Metrohm Inline Ultrafiltration removes particles down to a size of 0.2 µm – whereas manual filtration with syringe filters can only remove particles down to 20 µm.

Dilution ROI

	Metrohm	Competitive System
Samples	4,290	4,290
Labor	None	3 min/sample
Total	$ 0	$ 3,861
Savings	**$ 3,861 per year**	

Automatic dilution increases sample throughput

If the determination indicates that the analyte concentration is too high, i.e., outside the permissible determination range, the sample must be diluted and reanalyzed. At BSK Labs, this is the case for around 30% of the samples. Manual dilution takes the lab staff at least three minutes which, with labor costs of $18 an hour, results in annual costs of $3,800. Automatic Inline Dilution eliminates this expense: the analysis system dilutes the relevant samples fully automatically and then measures them again. This makes the laboratory much more efficient: the daily sample throughput increases and samples with a limited shelf life are always analyzed in good time.

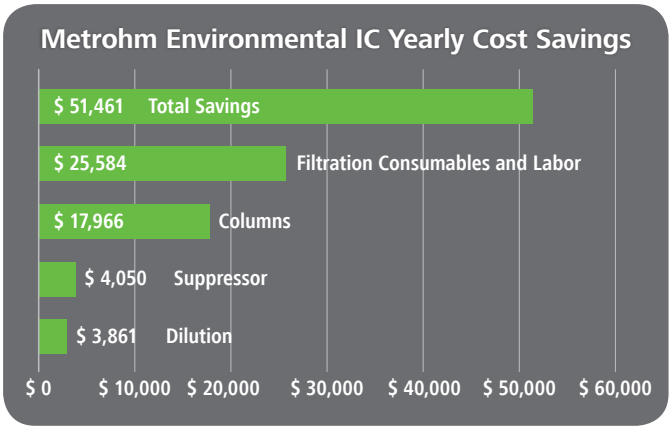
Improved performance

Significant cost savings weren't the only benefit of the Metrohm analysis system for BSK Labs – the 30-day trial run also revealed a number of other advantages. The company was impressed with the robustness of the instrument and with its ability to measure the entire range of samples processed at BSK Labs. Its stable calibration also made it possible to reduce the calibration frequency: the new system only needs calibrating every two to three weeks instead of two to three days. The most impressive features, though, were the high measuring sensitivity and the large linear range of the detector. Thanks to the latter, only 2% of the samples remain outside the measuring range and have to be diluted – compared to 30% with the old system.

Conclusion

The 30-day test proved to BSK Labs that the Metrohm ion chromatography system with automatic Inline Ultrafiltration and Dilution saves both material and labor. Furthermore, it also offers a number of improvements in terms of analysis performance compared to the systems previously used at BSK Labs.

Based on the test run, BSK Labs calculated the annual savings that could be achieved with the Metrohm analysis system and came to a final figure of $50,000. The most significant savings are those for labor and material costs as a result of using ultrafiltration, followed by those resulting from the longer separation column service life.



It's all made of plastic!

«Plastic» has become something of a dirty word. It makes us think of trash and environmental pollution, inferior quality, mass-produced goods, and excess. But if you take a look around, you will realize that a lot of the objects that surround us – including those that we couldn't live without – are also made of plastic.

That's no accident: as synthetic organic polymers, plastics have the advantage that their properties can be perfectly adapted to their intended use – unlike most natural materials – and they can also be manufactured inexpensively. Thanks to their versatility, plastics have become established in all areas of our lives.

Whatever their use – whether it is food packaging, flooring, or textile fibers – plastics have to meet quality criteria which are often determined by standards. To ensure that they satisfy the quality requirements, analyses must be carried out at every stage of production, from the raw materials to the reaction conditions and intermediate products, right up to the final product.

Quality control for raw materials

Identifying the raw materials

High-quality raw materials form the basis of a good product. Before being processed, the raw materials must be identified reliably and undergo quality control. When the goods are received, spectroscopic methods – particularly Raman spectroscopy – can be used to confirm that the raw materials are correct. Practical hand-held instruments such as the Mira M-1 from Metrohm make this especially easy. They measure the Raman spectrum of the sample and identify the sample by comparing the spectrum with a spectrum database – all within a few seconds.

How does Raman spectroscopy work?
The spectrometer first shines monochromatic light on the sample and then detects the scattered photons. When detected, elastically scattered photons have the same frequency as they did before being scattered on the sample, so they do not provide any information about the properties of the sample. They are of no value for the determination. In the case of inelastic scattering, however, the photons transfer part of their energy to the sample, changing their own frequency. The change in frequency provides information about the sample, as the energy absorbed induces rotational and vibrational states which are characteristic of the molecular structure and require specific amounts of energy. The absorption pattern – the Raman spectrum – of each substance is unique, and the determination is therefore unambiguous. Figure 1 shows the Raman spectra of some common monomers.

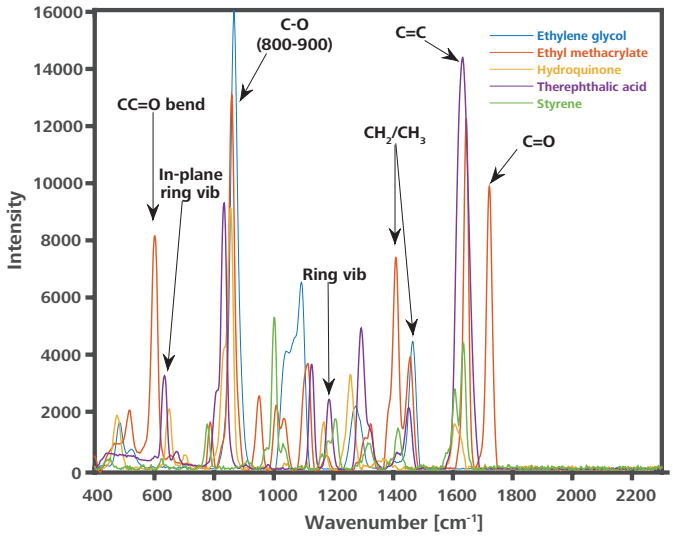


Figure 1. The Raman spectra of some common monomers are depicted. The peak positions of the Raman spectra provide information about functional groups of the sample molecule: the difference between the frequency of the scattered photons and the starting frequency corresponds to vibrations and rotations which are characteristic of them, and which are initiated using a specific amount of energy which is absorbed from the photons.

Quality of the raw materials

The quality control involves examining a wide range of physical and chemical parameters, from pH value and viscosity to determining the functional groups of the monomer, to contaminants, polymerization inhibitors, and the proportion of dimerized/oligomerized raw material.

> *A significant proportion of the acrylic acid from which, for example, polyacrylic acid is produced, may be in the form of a dimer. This reduces the polymerization speed.*

Determining monomer quality through end-group titration
Acrylic acid is used to manufacture polyacrylic acid – the «superabsorber» that can be found in diapers – as well as many copolymers which are employed as photo-resistant and hydrolysis-resistant industrial coatings. Acrylic acid polymers also have countless applications in medical products such as creams and gels. Acrylic acid dimerizes spontaneously (Figure 2). Even when inhibitors are used (usually monomethyl ether hydroquinone, or MEHQ for short) and optimum storage conditions are ensured, this cannot be avoided entirely. Depending on the storage time, a significant proportion of the raw material may be in the form of a dimer, which reduces the polymerization speed. Determining the dimer content is, therefore, a key part of the quality control for acrylic acid.

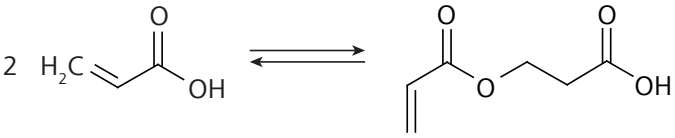


Figure 2. The acrylic acid monomer dimerizes spontaneously. The dimer content must therefore be determined as part of the raw material quality control when the goods are received.

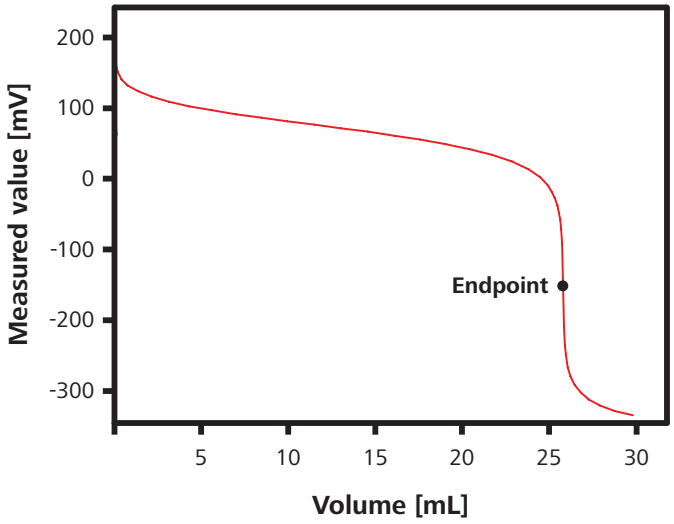


Figure 3. Acid number determination in acrylic acid monomer

The Solvotrode enables precise potentiometric endpoint determination even in a nonaqueous medium with low conductivity.

When acrylic acid dimerizes, the acid group of one of the monomers reacts with another monomer to form a carboxylic ester. The number of free acid functions per gram of material thus reflects the dimer content. The acid number – i.e., the amount of potassium hydroxide (KOH) in milligrams which is required to neutralize one gram of sample – is therefore determined as a quality indicator. This is done by end-group titration (Figure 3). The titration takes place in a nonaqueous solution. The low conductivity of the medium makes it harder to determine the endpoint potentiometrically, but suitable sensors such as the Solvotrode from Metrohm enable precise determinations nonetheless. The process can be fully automated.

End-group titration can also be used to determine other functional groups in a similar way to the acid functions. For the polymer industry, the most important of these groups are hydroxyl and isocyanate groups (hydroxyl and isocyanate number). Their titrimetric determination complies with the ASTM and ISO standards.

Contamination of the raw material

In addition to dimers and oligomers, there are other contaminants present in raw materials which, in some cases, can significantly hinder the production process. These include water, which can be quantified using Karl Fischer titration regardless of the physical state of the monomer, as well as certain metals with catalytic activity such as iron (determined by voltammetry) or sodium and potassium (determined by ion chromatography, Figure 4).

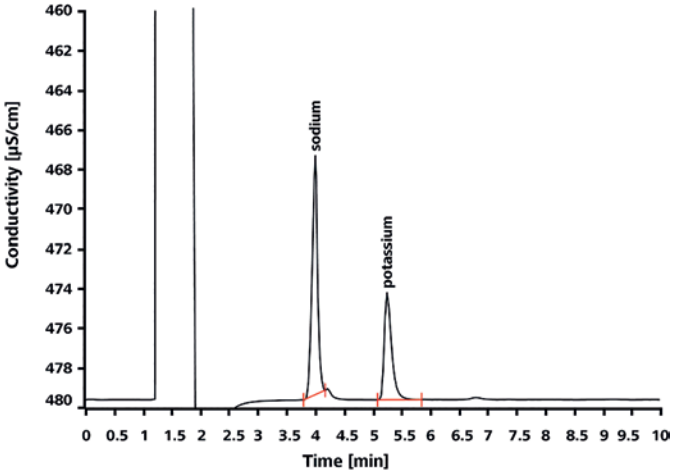


Figure 4. Determination of sodium and potassium in a polyol solution. Polyols are raw materials used in the production of polyurethane.

Reaction monitoring

Process optimization through real-time analyses

During polymer production, real-time analyses help to achieve the desired product quality and ensure an efficient production process. Online analyses, which provide results continuously and immediately, make it possible to monitor reaction conditions, for example. If necessary, these conditions can then be optimized without delay.

Viscose production: Conditions in the wet-spinning bath

More than four million tonnes of viscose fibers are produced worldwide each year for the textiles industry. Viscose is produced from cellulose, a natural polymer which is obtained from pulp. The fibers are produced using the wet-spinning method in a bath containing sulfuric acid, sodium sulfate, and zinc sulfate. Each of these substances has a different task in the production process. Altering their concentrations changes the properties of the fibers, enabling different types of viscose fibers to be produced. Online determination of the acid and zinc concentrations is essential for controlled production. Online determination of sulfuric acid and zinc can be carried out simultaneously with the ADI 2045TI Process Analyzer from Metrohm Process Analytics. Being an online analyzer, the ADI 2045TI works fully independently. Its robust design makes it well-suited to the harsh conditions in the process.

The production of nylon and nylon products can be optimized with process monitoring using near-infrared spectroscopy.

Near-infrared spectroscopy

Alongside wet-chemical methods, near-infrared spectroscopy (NIRS) is ideal for process monitoring. It works with mathematical models which correlate the measured spectra with reference methods. This enables NIRS to measure both chemical and physical parameters within seconds. One measurement can determine numerous parameters.

When manufacturing nylon fibers, NIRS helps to achieve the best possible properties: as the protective oil layer is being applied to the fibers, its thickness can be monitored in real time. This means that the process can be stopped as soon as the optimum thickness is reached.

The ADI 2045TI Process Analyzer carries out analyses automatically and is ideally adapted to the harsh conditions in the process.

Quality control for the finished polymers

Analyses before and during plastics production form the basis of a high-quality product. A final quality control step provides assurance that the production process has gone as planned and that the plastic meets the requirements of its intended application.

> *Each polymer contains a small amount of residual monomer. In the case of the toxic styrene monomer, this can be a problem.*

Residual monomer in the finished product

Each polymer contains a small amount of residual monomer which has not reacted. In the case of polystyrene, which is used for food packaging such as yogurt pots among other things, this can be a problem, as styrene is toxic and carcinogenic. It goes without saying, therefore, that sensitive determination of the monomer as part of quality control is indispensable. Voltammetry is a cost-effective, reliable analysis technique that is well-suited to this task, and can be used to determine quantities of styrene as small as of 5 mg/L. This sensitive analysis technique can also determine traces of metallic contaminants.

Polymer water content

The water content of the finished plastic affects its properties. Sensitive coulometric Karl Fischer titration is the ideal method for determining the low water content. As most polymers are not soluble, the water determination is carried out using the Karl Fischer oven method: the residual moisture in the plastic is heated in order to evaporate it and then titrated. Figure 5 shows the progression of the Karl Fischer titration for a PVC sample. Before the analysis, the sample was ground into a powder to ensure complete extraction of the contained water.

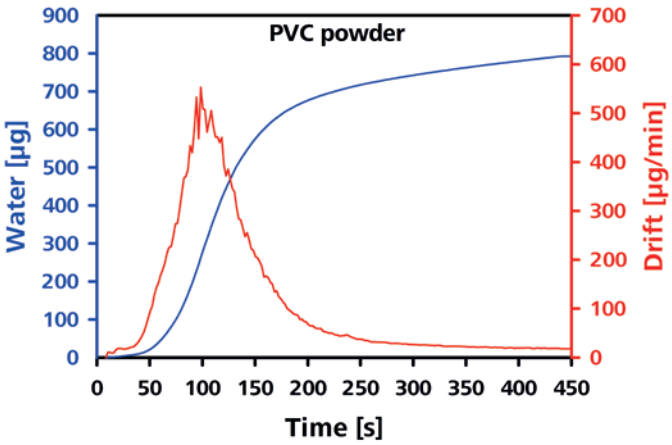


Figure 5. Curve for a coulometric Karl Fischer titration in PVC. The determination was carried out using the oven method, i.e., the sample was heated to extract the water by means of evaporation before determining the water content.

Halogens and sulfur: Safety in the event of a fire

Plastics that contain halogens and sulfur release dangerous toxic gases when they burn. Halogen-free plastics are therefore becoming increasingly popular for certain applications, such as power cables. Determining the sulfur and halogen content is an indispensable part of quality control in this case, and combustion ion chromatography, or CIC, can be used to complete this task. The sample is burned and the resulting gases are absorbed by a carrier solution which is ultimately analyzed using ion chromatography. Figure 6 shows a schematic depiction of the entire process. Metrohm provides a complete CIC solution that combines sample digestion and analysis. This saves time and ensures highly accurate analysis: a certified polyethylene granulate was used to demonstrate that the recovery rate of the method lies between 99 and 102.4%.

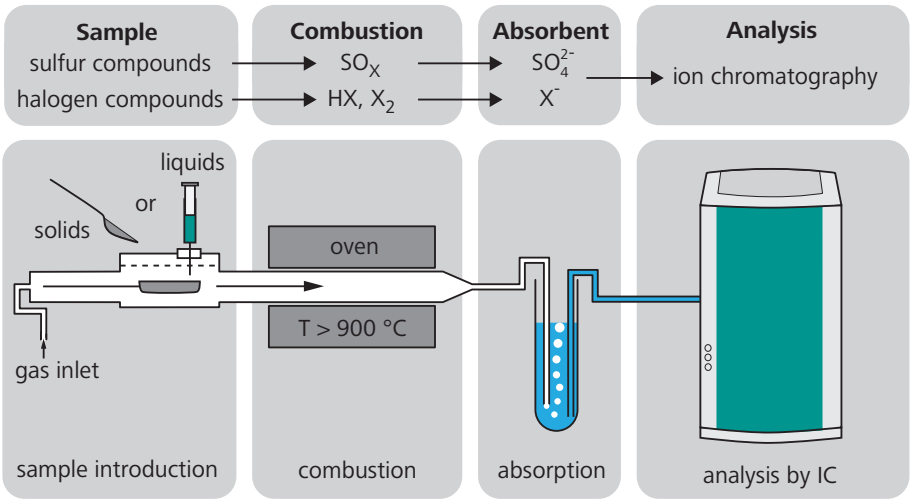


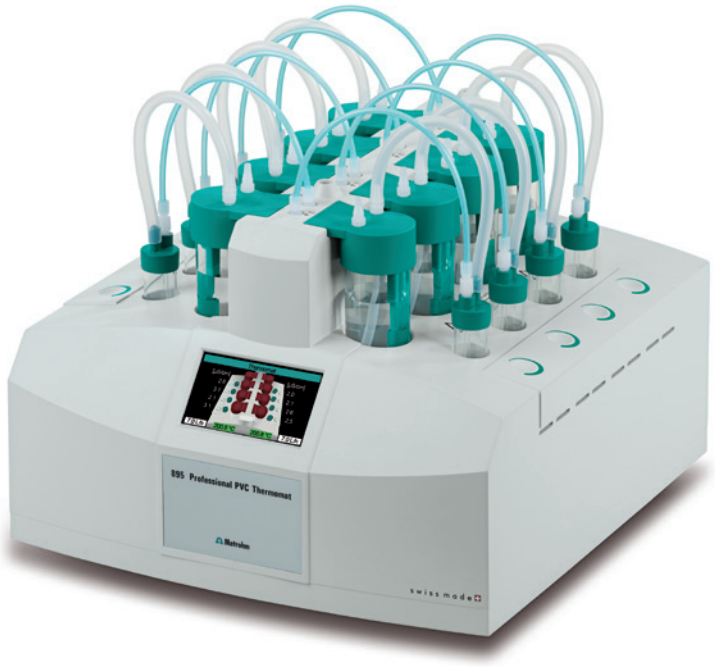
Figure 6. Combustion ion chromatography is used to analyze sulfur and halogens in solids and liquids. Once the sample has been added, the complete solution from Metrohm carries out the sample digestion and the analysis by itself: First, the sample is burned and the resulting gases are absorbed by a solution. The solution is then automatically injected into the integrated ion chromatograph where it is analyzed.

Heat resistance of PVC

PVC and other polymers which contain chloride can also release toxic gases – specifically, hydrogen chloride (HCl) – when exposed to elevated temperatures. However, these polymers are still widely used, as they are particularly versatile. The «dechlorination» effect can be prevented using heat stabilizers. To ensure quality control in accordance with ISO 182 Part 3, Metrohm offers the PVC Thermomat, which heats the sample and transfers the resulting HCl gas into a solution where it is detected by conductivity measurement.

Electrically conductive polymers

The field of electrically conductive polymers is still in its infancy. They were discovered in 1977 by the researchers Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa, who were awarded the Nobel Prize in 2000 in honor of this discovery. The conductivity in these plastics is created by conjugated double bonds. There are many promising applications for conductive polymers – organic light-emitting diodes (OLEDs), photovoltaic cells, and rechargeable batteries to name but a few. When it comes to studying the electrochemical properties of polymers, cyclic voltammetry and electrochemical impedance spectroscopy are the methods of choice.



The PVC Thermomat (right) tests samples of polymers which contain chloride, e.g., PVC, to examine their heat resistance.

A future with or without plastic?

Almost all of the items that we use every day contain plastic. And their presence is likely to continue to grow: new areas of application are constantly being opened up for synthetic polymers, with notable developments in the applications of conductive polymers as just one example. With their low costs and flexible properties, plastics are attractive materials. That does not mean, however, that we should become blind to the problems they pose. In most cases, plastics are produced using fossil fuels as raw materials, which means that they consume valuable resources. They also create waste that takes a long time to decompose in the environment – from several decades (plastic bags) to many centuries (drink bottles).

Recycling provides a partial solution to this problem. Here, chemical analyses come into play again: for plastics to be recycled, they need to be sorted by material. Raman spectroscopy, which identifies substances within seconds, is ideal for this type of application.

«Plastics have long been an essential part of our everyday lives. The important thing now is to make plastics sustainable.

In the future, bioplastics could be the way forward: these are polymers that are based on renewable raw materials or are completely biodegradable – ideally, both. Examples include polyhydroxyalkanoates (PHA) and polylactic acids (PLA). Their properties are similar to those of conventional plastics, which means that they can be used in similar ways. Bioplastics are already in use in some areas, but they are a long way from covering the broad range of applications of conventional plastics. Bioplastics are constantly being optimized through intensive research, both in terms of their application properties and their degradation.

Plastics have long been an essential part of our everyday lives. The important thing now is to make plastics sustainable in order to minimize environmental pollution and oil consumption. Chemical analysis plays a central role not only in the development of sustainable, biodegradable plastics, but also in recycling and in routine work within the polymer industry. Metrohm offers suitable solutions at all stages of research, development, production, and further processing.

You can find detailed information about analytics in the polymer industry at **www.metrohm.com/Industries**

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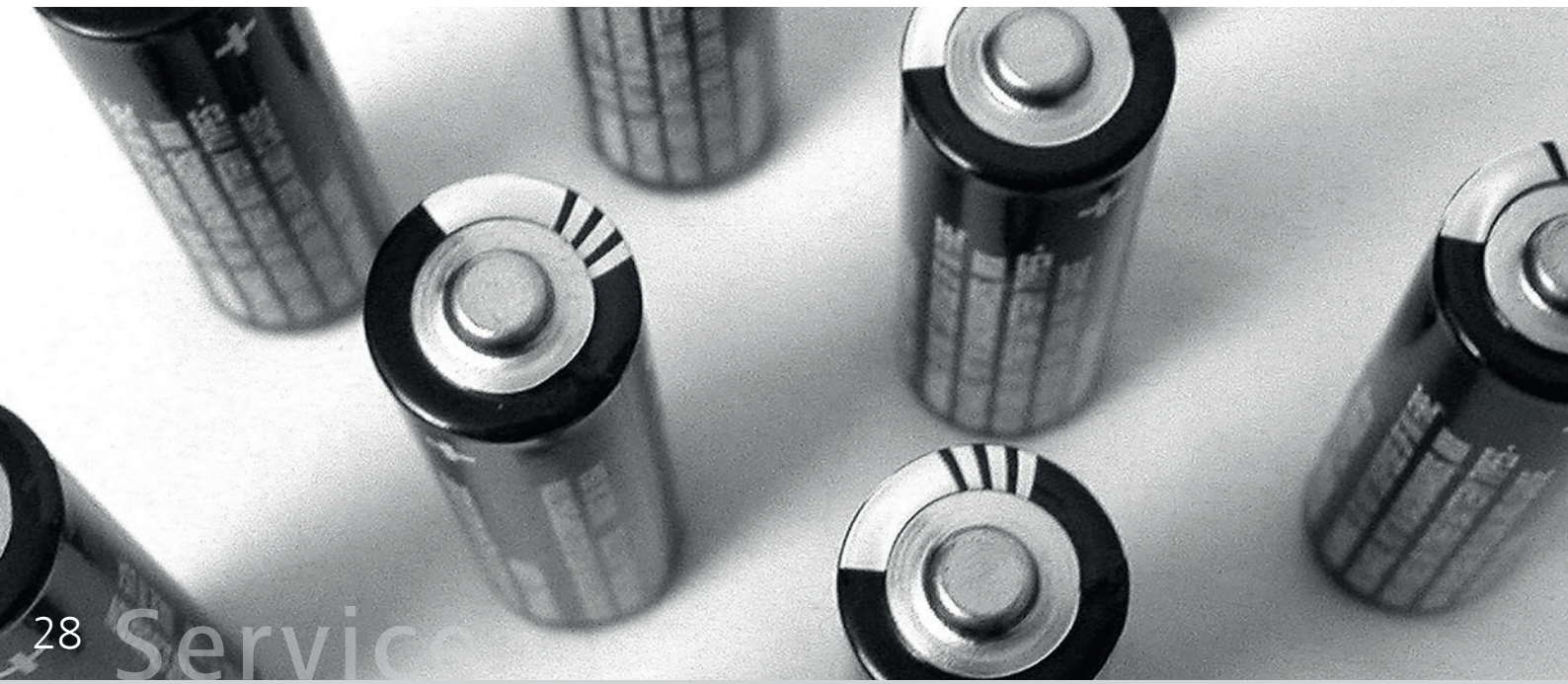
Energy storage systems of the future

The NEAMTECS symposium, hosted by the Metrohm Academy, provided a platform for scientists to discuss their research into fuel cells, batteries, and photovoltaics.

Our hopes for the future are pinned on renewable energy sources: they enable us to avoid the risks involved in nuclear power and to eliminate the CO_2 emissions generated by fossil energy production. But they do pose a problem: the production of solar and wind energy – the most widely used renewable energy sources after water power – is dependent on weather conditions. This means that the energy is not available precisely when it is needed. Scientists all over the world are working on ways of storing and converting energy with minimal losses.

A key part of this research takes place in the field of electrochemistry. Metrohm organized an international symposium at the company headquarters in Herisau, Switzerland, on the subject of «New Electrochemical Analytical Methods and Techniques for Energy Conversion and Storage – NEAMTECS 2015». The aim was to share with customers Metrohm's own in-house expertise with regard to storing and converting energy, as well as its extensive network of experts. The main focus of the event was the presentation of research into fuel cells, batteries, and photovoltaics.

The symposium was held last October at the Metrohm Academy site. The modern lecture halls, laboratories, and seminar rooms provided the ideal location for a varied program which included practical and interactive elements as well as presentations. The speakers, who came from Germany, the UK, and the Netherlands, presented new methods for analyzing electrolytes as well as innovative ways of combining different analytical techniques. The participants were able to gain an insight into the next generations of the polymer electrolyte membrane fuel cell (PEMFC) and the batteries of the future, as well as having the opportunity to discuss ionic liquids with the experts. The workshops and the introductions to different applications covered design of experiments as well as trace analysis of iron ions, temperature-controlled electrochemical measurements, and an introduction to the software used. The range of topics covered and the expert knowledge of the invited speakers ensured that the symposium lived up to the standards expected of academic conferences.



Crowning glory after three days of intense work at the symposium: the NEAMTECS participants on their trip to Säntis

Both the symposium participants and the guest speakers benefited from the interesting presentations and fruitful discussions. They were particularly impressed by the friendly, open atmosphere and the outstanding facilities. After two days packed full of academic presentations, lively discussions, and in-depth workshops, NEAMTECS came to a close with a tour of the historic village of Appenzell and a fantastic panoramic view from Säntis, a mountain standing at 2,500 m.

NEAMTECS was the first in Metrohm's series of international symposiums. Their organization is coordinated by the Metrohm Academy, which hosts customer courses and events. Metrohm Autolab, the competence centers at Metrohm International Headquarters, Metrohm Deutschland, and Metrohm UK were also involved in organizing the NEAMTECS symposium.

We hope to see you at our next event in September 2016: the Global IC User Meeting 2016. This event is aimed at our long-standing users and gives them a unique opportunity to share their experiences in the field of ion chromatography with their colleagues.

Register now for the three-day Global IC User Meeting 2016: **bit.ly/gumic**

Tips and tricks

Ion chromatography

Leaching test for different vial types when determining traces of cations

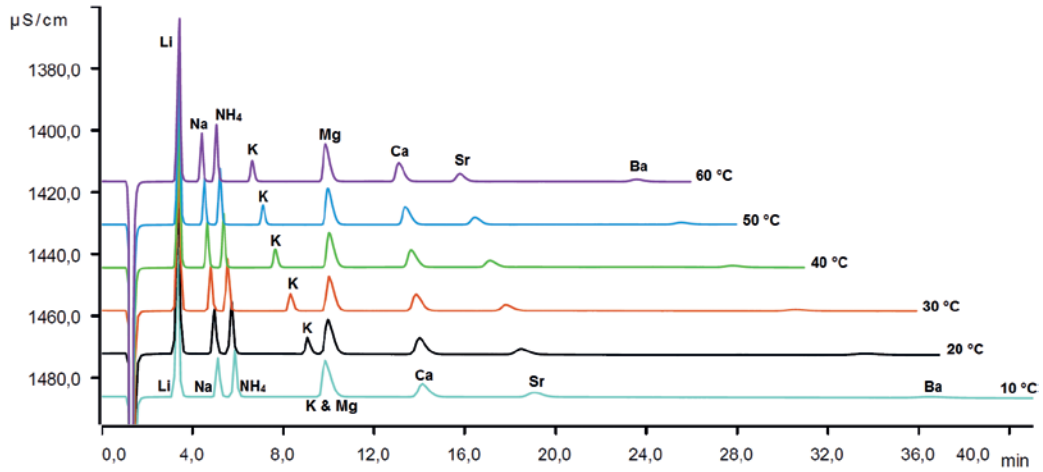
Cation suppression makes it possible to achieve extremely low detection limits when determining cations by ion chromatography. Even minor interference factors have an impact on the sensitive measurements – for example, the blind concentration of the analyte in the sample vial. It is therefore advisable to carry out a leaching test before determining traces of cations. By doing so, the cation contribution of the vial can be quantified and taken into account when the results are evaluated.

« The blind concentration of the analyte in the sample vial has an impact on the sensitive measurements when using cation suppression.

You can find information on different vial types and on the leaching test procedure in Application Note AN-CS-009.

Optimizing cation determination by adjusting the column temperature

The separation of standard cations on the high-capacity Metrosep C 6 - 150/4.0 column depends on the temperature. Potassium, strontium, and barium elute much earlier when the temperature is increased. By contrast, the retention times of lithium, sodium, ammonium, magnesium, and calcium are hardly reduced at all at higher temperatures. Adjusting the temperature can improve the separation of ammonium, potassium, and magnesium (see figure below). All of the relevant information is summarized in Application Note AN-C-156.



The retention times of magnesium and ammonium are largely unaffected by the temperature. Potassium, on the other hand, elutes earlier at high temperatures than it does at low temperatures. The separation of these three species can therefore be optimized by adjusting the temperature.

Basics and troubleshooting in titration

At the end of October last year, Metrohm held two webinars in conjunction with «G.I.T. Laboratory Journal»: «Basics of Titration» and «Troubleshooting in Titration». The webinars contain lots of practical tips that help you with your titrations during everyday work in the lab. Once you have registered, you can view the webinars free of charge. You can access them at the following link:
bit.ly/titration-webinar

A concise summary of the tips can be found in the accompanying article which appeared in G.I.T. 9-10/2015. Like all Metrohm applications, you can download the article from our website free of charge. Visit the Application Finder and search for article number TA-058.

Accurate dosing guaranteed

It is essential that dosing and exchange units work precisely in order to provide accurate and precise measurement results. Performing dosing tests at regular intervals ensures that this is the case. Certain chemicals can corrode dosing units and exchange units, which can in turn affect the dosing volume. Intensive use or simply the effects of aging can also cause unsatisfactory system performance. The dosing test is carried out by trained Metrohm service engineers – at your site – on the basis of recognized standards and methods. It can either be carried out on request or at the same time as the annual instrument maintenance, and can be included in a Metrohm Care Contract if you wish.

More information on the standards and methods used in the dosing test can be found in the «Metrohm Dosing Test» brochure, which you can download from our website.

All applications can be downloaded free of charge at:
www.metrohm.com/Applications

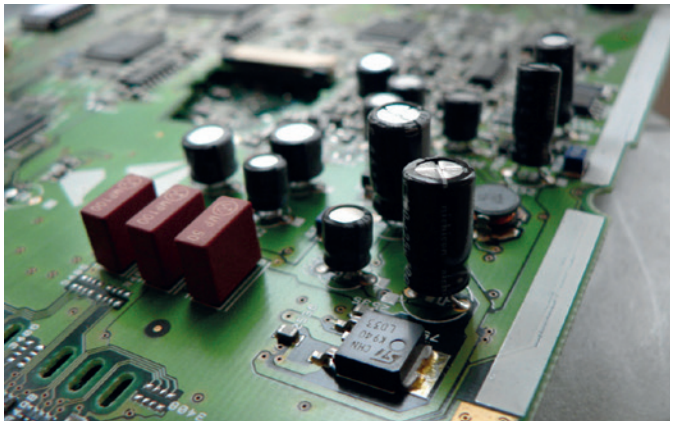
Do your dosing and exchange units work accurately and precisely? With regular dosing tests, you can be sure that they do.

New application literature

The past year has seen the laboratories at our competence centers create yet another extensive range of applications. The graphic opposite shows a selection of these, arranged according to sector and technology. For a full list of the new applications and technical articles, visit **bit.ly/Metrohm_Info**.


Tetrabutyl-ammonium in atorvastatin applying sequential suppression (AN-CS-005)
Determination of dimethylamine in meropenem applying sequential suppression (AN-CS-008)
Determination of choline in baby milk powder (AN-CS-004)
Monitoring Peracetic Acid (PAA) in Bottling Line Sanitization Processes (AN-PAN-1029)
Titration of alpha acids in hop products according to EBC 7.4 (AN-T-154)
Shorter citrate retention times in beverage analysis using a step gradient (AN-S-327)
Polydextrose in biscuits with IC-PAD in line to AOAC 2000.11 (AN-P-057)
Maleic and kojic acid in starch using UV/VIS detection (AN-O-041)
Monitoring the purity of recovered solvents by NIRS (AN-NIR-021)
Raman-spectroscopic analyses of road construction materials (AN-RS-004)
Identification of commonly used organic solvents using Raman spectroscopy (AN-RS-003)
Determination of water in propene (AN-K-066)
Determination of water in iso-butane before and after drying (AN-K-065)
Determination of water in a refrigerant (AN-K-062)
Halogens in LPG applying Metrohm Combustion IC (AN-CIC-018)
Automated determination of mercaptans in refinery products (AN-T-152)
Titration
Ion chromatography
Karl Fischer titration
Voltammetry
Spectroscopy
Process analysis

Literature references



Voltammetry

The dissolution of palladium as a function of glucose concentration in chloride containing solutions of acidic pH

M. Gerstl, M. Joksch, and G. Fafilek

A strong anodic peak observed in cyclic voltammetry measurements of palladium electrodes when adding glucose to chloride containing (0.1 M) slightly acidic (pH 5.3) unbuffered media was studied in detail. The peak was highly sensitive to glucose concentration (5–20 g/L). Experiments were conducted by variation of pH (1–13) and chloride concentration (0.5–50 g/L) of the medium over a wide range, as well as substituting chloride with bromide. The resulting data suggests dissolution of the electrode as a chloride complex as the root cause for the peak, which is triggered by the addition of glucose to the electrolyte. The organic substances are oxidised thereby removing the protecting oxide layer and enabling the dissolution. This reaction is only observed in a certain window confined by both pH and halide concentration.

J. Electroanal. Chem. (2015) 741 1–7

Ion chromatography

Thermal decomposition of tetrabromobisphenol-A containing printed circuit boards in the presence of calcium hydroxide

S. Kumagai, G. Grause, T. Kameda, and T. Yoshioka

Recycling of printed circuit boards (PCBs) is complicated by the presence of flame retardants containing halogen and phosphorus, as the degradation products of these retardants reduce the quality of the produced gases and liquids. Moreover, during thermal treatment, corrosive and toxic compounds are released and the volatilization of undesirable metals incorporated in the PCB matrix is enhanced. To combat this problem, we investigated the effects of calcium hydroxide ($Ca(OH)_2$) on the thermal decomposition of both phenol and epoxy resin paper-laminated PCBs containing tetrabromobisphenol-A. Pyrolysis experiments revealed a maximum removal of 94% HBr, 98% brominated phenols, and 98% phosphorus from the gaseous and liquid pyrolysis products. In addition, Br-induced metal volatilization was inhibited, improving the recovery amount in the solid fraction. Thermogravimetry–mass spectrometry revealed that $Ca(OH)_2$ enhanced the evolution of phenolic compounds produced from the PCB matrix, mainly below 300 °C, while the fixation of brominated compounds took place primarily above 300 °C.

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Titration

Ocean acidification alters the material properties of *Mytilus edulis* shells

S. C. Fitzer, W. Zhu, K. E. Tanner, V. R. Phoenix, N. A. Kamenos, and M. Cusack

Ocean acidification (OA) and the resultant changing carbonate saturation states is threatening the formation of calcium carbonate shells and exoskeletons of marine organisms. The production of biominerals in such organisms relies on the availability of carbonate and the ability of the organism to biomineralize in changing environments. To understand how biomineralizers will respond to OA the common blue mussel, *Mytilus edulis*, was cultured at projected levels of pCO_2 (380, 550, 750, 1000 µatm) and increased temperatures (ambient, ambient plus 2 °C). Nanoindentation (a single mussel shell) and microhardness testing were used to assess the material properties of the shells. Young's modulus (E), hardness (H) and toughness (K_{IC}) were measured in mussel shells grown in multiple stressor conditions. OA caused mussels to produce

shell calcite that is stiffer (higher modulus of elasticity) and harder than shells grown in control conditions. The outer shell (calcite) is more brittle in OA conditions while the inner shell (aragonite) is softer and less stiff in shells grown under OA conditions. Combining increasing ocean pCO_2 and temperatures as projected for future global ocean appears to reduce the impact of increasing pCO_2 on the material properties of the mussel shell. OA may cause changes in shell material properties that could prove problematic under predation scenarios for the mussels; however, this may be partially mitigated by increasing temperature.

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Stability measurement

Moringa oleifera: A potential source for production of biodiesel and antioxidant additives

D. M. Fernandes, R. M. F. Sousa, A. de oliveira, S. A. L. Morais, E. M. Richter, and R. A. A. Muñoz

This work reports the use of *Moringa oleifera* oil and leaves as potential sources for the production of biodiesel and antioxidant additives for biodiesels, respectively. The *M. oleifera* methyl ester was prepared by a two-step reaction and exhibited physical-chemical properties that met the minimum or maximum limits of the EN 14214, emphasizing the high induction period (IP) of 19.3 h. Ethanolic extracts of *M. oleifera* leaves were evaluated as additives to increase the IP value of biodiesels. The results indicate that the 98% (v/v) ethanolic extract increased IP values of soybean biodiesel from 3.8 to 10.3 h using the 100 μg g^{-1} of extract, showing better performance than the synthetic antioxidant tert-butyl-hydroquinone. The extract also provided similar efficiency to methyl esters produced from sunflower, colza, corn and residual cooking oils. These results evidence the promising use of *M. oleifera* not only for biodiesel production but also as a source of antioxidant additives for biodiesels with low oxidation stability.

Fuel (2015) 146 75–80

Spectroscopy

Near-Infrared Spatially Resolved Spectroscopy for Tablet Quality Determination

B. Igne, S. Talwar, H. Feng, J. K. Drennen, and C. A. Anderson

Near-infrared (NIR) spectroscopy has become a well-established tool for the characterization of solid oral dosage forms manufacturing processes and finished products. In this work, the utility of a traditional single-point NIR measurement was compared with that of a spatially resolved spectroscopic (SRS) measurement for the determination of tablet assay. Experimental designs were used to create samples that allowed for calibration models to be developed and tested on both instruments. Samples possessing a poor distribution of ingredients (highly heterogeneous) were prepared by under-blending constituents prior to compaction to compare the analytical capabilities of the two NIR methods. The results indicate that SRS can provide spatial information that is usually obtainable only through imaging experiments for the determination of local heterogeneity and detection of abnormal tablets that would not be detected with single-point spectroscopy, thus complementing traditional NIR measurement systems for in-line, and in real-time tablet analysis.

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