NPL
National Physical Laboratory

Environmental *Measures*

A National Measurement Newsletter

Winter 2007 | Issue 4

Sampling instrument at the network site at Weston Point near Runcorn

Twenty five years of monitoring airborne metal pollutants

Nationwide monitoring of metal pollutants in ambient air began in the late 1970s. The data produced by NPL, the current scientific operator of the national measurement network, marks a quarter of a century of ambient heavy metal monitoring in the UK.

Air pollution is an issue of great concern to the general public and the scientific and medical communities alike. Over the last 20 years or so understanding of the toxic effects of metals in ambient air on human health and the environment has increased and the permissible concentration levels of many are now the subject of European legislation.

In the UK, airborne particulate concentrations are measured at a network of 17 sites across the country, at industrial, urban, roadside and rural locations, operated on behalf of DEFRA by NPL and known as the UK Heavy Metals Monitoring Network (UKHMMN). The list of toxic metals currently monitored includes longstanding industrial pollutants such as lead, arsenic and nickel, emerging pollutants like platinum from automobile catalytic converters and mercury from crematoria, and metals of which the adverse health effects have recently become more apparent, for example iron. The latter is in fact the most abundant by far of the metals monitored in ambient air.

During the 25 year period of operation of UKHMMN the measured ambient concentrations of most of the metals monitored have fallen steadily, especially since 1991. This has been as a result of a combination of abatement strategies, legislation and changing fuel usage. In fact the current annual average concentrations of lead, nickel, arsenic, cadmium and mercury in the UK are well below the limiting values set by EU directives.

The future challenge is to find more accurate and efficient ways of performing the measurements including monitoring even more pollutant species at each site. Toxicity of a metal often depends on its chemical form in the environment and therefore analytical techniques will be required to determine the exact chemical composition of airborne particulates.

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Inside:

High standards for energy efficiency and climate change

NPL is at the forefront of developing new high temperature fixed point standards that should lead to greater energy efficiency of industrial processes and contribute to a better understanding of climate change.

High-temperature industrial processing in the UK uses the energy equivalent of 120 million barrels of oil per annum. At temperatures below 1350 K reference standards are available to provide known points against which instruments can be checked to improve efficiency and save energy. However there are no internationally agreed high temperature references that are sufficiently well understood to aid efficient operation of industrial processes at higher temperatures and improve product yield.

In the last few years fixed-point standards based on the melting temperature of particular alloys of metals and carbon have made improvements at temperatures above 1350 K a real possibility. An additional goal is to develop higher temperature standards (over 3000 K) to be used for radiometry. This would improve measurements of solar radiation and its interaction with the atmosphere and enable us to gain a better understanding of climate change.

NPL is leading Europe in the development of these high-temperature fixed points, but demonstrating equivalence at such high temperatures has been difficult. Working at NPL, Tiejun Wang of the National Metrology Institute in China (NIM) compared an NPL platinum-carbon eutectic fixed point with one from NIM using an NPL furnace and radiation thermometer. The agreement was within 50 mK at 1738 K. Dave Lowe of NPL subsequently used facilities at PTB, Germany, to construct a platinum-carbon eutectic fixed point which compared with a standard from the National Measurement Institute Japan (NMIJ) to the same level of accuracy. These results are the best ever agreement achieved at this temperature. More recently a fixed point has been constructed at NPL using titanium carbide alloyed with carbon in a graphite crucible. This gives a reference at over 3000K which could be used to help quantify the stability of the sun and its effect on the Earth's atmosphere.

Fixed points from NPL are currently being compared with those from national metrology institutes in

A high temperature reference – the intensity of the light emitted from the furnace is a fixed quantity and allows calibration of both radiation thermometers and detectors.

Japan, China, France and Germany to establish long term stability during repeated melt and freeze cycles. A concerted international effort is now underway, coordinated by Graham Machin of NPL, that should ultimately lead to adoption of globally accepted standards for the benefit of both temperature and radiometric metrology.

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NPL Training framework

Do you use measurement equipment or rely on measurements within your processes?

Are you aware that knowing how to use a measurement tool is not the same as knowing how to use measurement as a tool?

How confident are you in challenging a measurement as being fit for purpose?

Measurement is a science to be applied with skill, not a manual.

The NPL Training framework is the only independent, hands-on measurement focused training course. Understanding the principles of measurement can lead to better decisions in product purchasing, a reduced need for technical support and fewer operational mistakes with expensive consequences. A better understanding of measurement will reduce the risks to your business.

Dates of Level 1 Dimensional courses are now available for 2008 - Find out more at www.npl.co.uk/training

Reliable standards for measuring atmospheric organic pollutants

The environmental measurements team at NPL have carried out a comparison of the methods normally used to prepare standards for calculating concentration data from atmospheric organic pollutant samplers.

Measurement of toxic volatile organic compounds (VOCs) in the environment, such as benzene and other hydrocarbons, is usually carried out using sorbent-based samplers. Concentration data are then obtained by thermal desorption and comparison with calibration standards prepared in the laboratory by one of two methods: liquid or gas loading of the appropriate VOC onto the selected sorbent, the former being much the more cost effective and easier option. However doubts have been raised over the equivalence of the standards produced by the two processes, and hence the accuracy of concentration results.

A comparison undertaken at NPL for a number of common environmental hydrocarbons has shown that for the methods to deliver essentially identical results the selection of a suitable combination of sorbent material and solvent is critical for some VOCs. The team recommend that users should first consider obtaining gas-loaded standards from accredited laboratories which should then be intercompared with in-house liquid-loaded standards. Only then should the decision be taken on whether to adopt the more cost-effective method of liquid loading.

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Calibrated pressure sensors for engine efficiency

In order for internal combustion engine manufacturers to meet increasingly tough regulations for carbon emissions and efficiency there is a need for more accurate measurements of in-cylinder and fuel injection pressures.

There is a drive among manufacturers of petrol engines to continuously improve the accuracy of intake manifold and in-cylinder pressure measurements, whilst diesel engine production aims for better control of injector performance by direct measurement of pressures at the injectors. Under these demanding applications, where the combustion of air/fuel mixtures results in flame fronts that reach temperatures of 2000 °C, sensor performance is critical, and the detection of events such as engine knocking requires sensor response times that are measured in microseconds. Sensor accuracy is currently limited by the absence of a means to calibrate them under conditions similar to those encountered under normal engine working conditions and, in particular, by only calibrating at static pressures. Parameters such as the resonance frequency of the sensors and associated fittings (e.g. connectors and pipe work), and the damping and rise-times have to be estimated through computer modelling, further increasing uncertainty in the sensor output during use.

To help address this problem, NPL is working with Loughborough and Cranfield Universities, Perkins Engines, Kistler, and independent automotive engine consultants, to develop a method or methods to calibrate 'gold standard' reference pressure sensors at amplitudes, frequencies, and temperatures that are encountered in engines, and to build pressure waveform generators that are suitable for in-house use by manufacturers and researchers alike. The latter will enable calibration of engine sensors by direct comparison with the 'gold standards'.

Work towards the first aim is likely to include the further development of shock-tube and combustion-bomb facilities already existing at Cranfield and Loughborough, and the development of a piezoelectric sonar transducer-based system at NPL.

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Compositional profiling of organic coatings

The Nano analysis group at NPL is exploring a novel technique for measuring the distribution of organic components in coatings and thin films.

Virtually every object in the world is coated with organic material. Usually this is a result of the adventitious accumulation of environmental molecules and serves no useful purpose. In a wide variety of products, however, the coating is deliberately applied to enhance performance or enable the product to function. In everyday life organic and polymeric thin films have become ubiquitous as a glance around any home or workplace will reveal. Examples include lubricants, paints, inks, adhesives, laminations for paper, coatings for glass and the many functional layers in a common crisp packet. A number of emerging technologies rely upon controlling the thickness and composition of organic layers and ensuring that the distribution of organic components is fully understood when used or exposed to different environments. Significant examples of emerging technologies include plastic electronics and the controlled release of drugs. Plastic electronics are potentially a more environmentally friendly alternative to semiconductor technology. Individual devices comprise of a minimum of two organic layers: control of the absolute and relative thickness of these layers as well as homogeneity across the device are critical for reliable operation. Controlled release systems commonly comprise of a therapeutic agent (a drug) dispersed in a biodegradable polymer: the distribution of the drug determines the release rate, and this must be above a minimal therapeutic level but below toxic levels throughout the lifetime of the system. The advantage of controlled release is that it avoids the fluctuating levels of drug associated with repeat injections and removes the risk of patients or carers forgetting to administer the drug, or administering the incorrect dose.

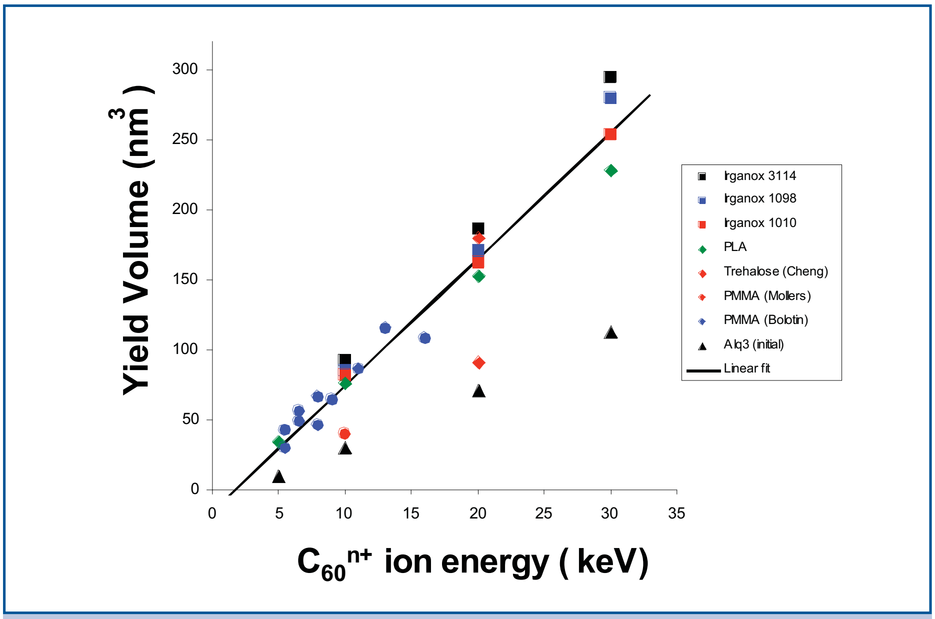

Figure 1: The volume of material sputtered per incident C_{60} ion (Yield Volume) as a function of C_{60} kinetic energy from a variety of materials. The initial Yield Volume is shown to be very similar for most organic materials and appears to increase linearly with energy. It should be appreciated that the volume of a C_{60} molecule is less than 1 nm^3.

Having a means to measure the distribution of organic components in thin films will enable designers to confirm that the predicted distributions have been achieved and to determine the cause of poor function or failure. Appropriate methods must be able to deliver the necessary depth resolution of a few tens of nanometres and have the ability to uniquely identify delicate organic species. Until recently, this was thought to be impossible and indirect methods were employed which either did not have the chemical specificity required to uniquely identify organic components or did not have the requisite depth resolution. However, in the last ten years it has been recognised that organic material may be sputtered with cluster ions without causing significant damage to the

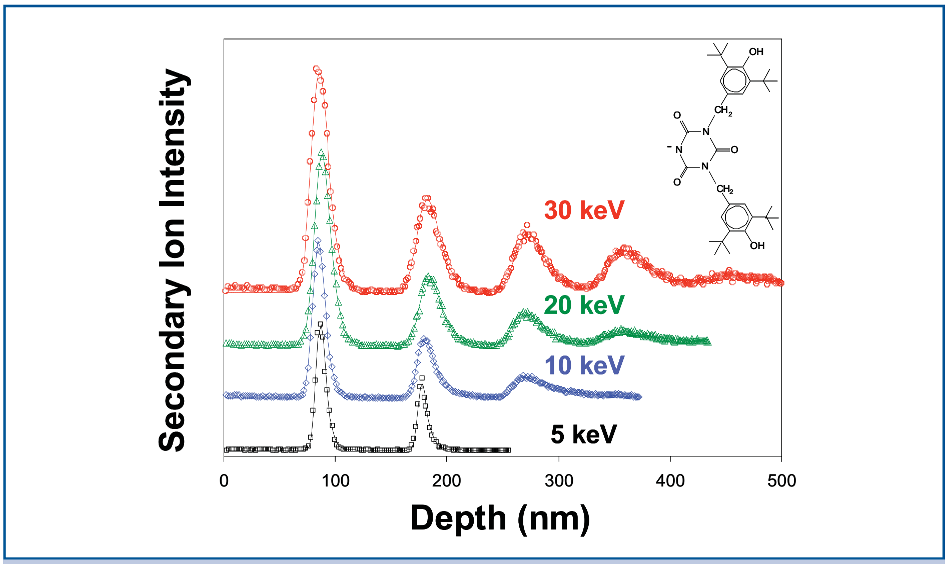

Figure 2: C_{60} sputter depth profile of an NPL organic delta layer, the ion detected is shown in the inset. The signal from a delicate organic compound deposited in 2.5 nm thick layers within another organic material reveals the sputter rate, depth resolution and sensitivity during a profile. Higher energies have poorer depth resolution, but a greater useful depth of sputtering. Analysis shows that the relative concentration of the compound in each layer can be determined to within 10%

underlying material. By using a surface sensitive and chemically specific spectroscopy, such as secondary ion mass spectrometry (SIMS) it is possible to record signals from individual organic components as a function of depth by repetitively 'shaving' a thin layer of material with a cluster ion beam and analysing the remaining surface. In this way a depth profile of organic components can be achieved.

One of the most promising set of cluster ions for organic depth profiling are fullerene ions, particularly C_{60}^{n+}. Seminal work using C_{60}^{n+} ion sources has been carried out at Pennsylvania State University, USA and the University of Manchester. The research has demonstrated that organic depth profiling is possible, but has not demonstrated the general utility of the technique. NPL (in partnership with the University of Nottingham, Cambridge Display Technologies, Novalia, Kodak, ICI and NTERA) has been developing C_{60} depth profiling to determine important metrological parameters, explore the limitations of the technique and to demonstrate its utility on real devices.

By accurately measuring the sputtering rate of a variety of organic materials (Figure 1), we have shown that most organic materials initially sputter at the same rate. This observation is very encouraging, as it suggests that the application of a depth scale to data from mixed organic materials should be straightforward. The volume of material liberated by each ion impact is very large and is the key to the success of the technique. The sputtered volume is large enough to remove most of the damage created by previous impacts. However, for some materials the remaining damage acts to decrease the sputtering rate and the yield rapidly declines until sputtering rates are a hundred times lower, more typical of inorganic materials such as silicon. Our investigations indicate that there are two limiting factors that undermine the success of organic depth profiling. Some materials cross-link under ion bombardment and this leads to a rapid decline in sputtering yield. Others develop

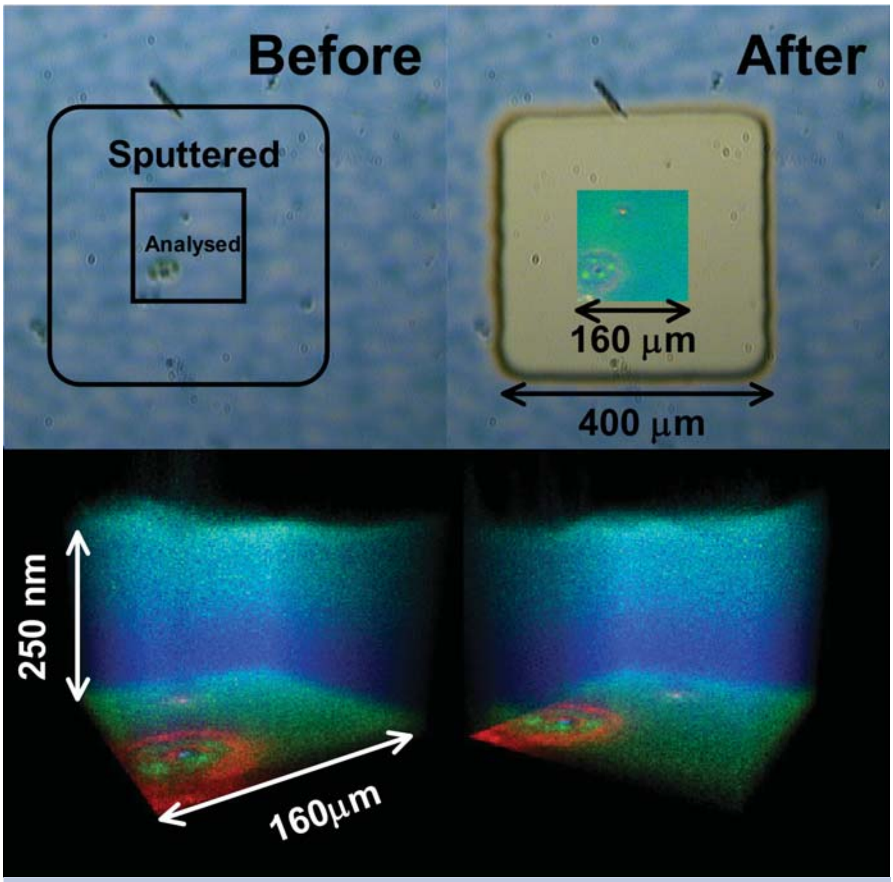

Figure 3: Upper images show optical micrographs of a defective drug-loaded polymer film before and after analysis. The 'after' image is overlaid with a composite image to show that the optical features correlate with components in the film. The lower images show two views of a 3 dimensional reconstruction of the film components, sodium contamination is red, intact drug molecules are green and polymer is blue. Defects are associated with sodium contamination on the underlying substrate and the drug has segregated to the top and bottom of the film.

a high degree of roughness and this leads to a slow decline in sputtering yield. We are currently exploring experimental methods to reduce these effects, yet a wide range of materials do not display these limiting behaviours and profiles of up to a micrometer in depth with a depth resolution of 50 nm at the end of the profile have been achieved.

To obtain a deep understanding of organic depth profiling, we have constructed novel layered organic films. By making some of the layers very thin, the resolution of the technique can be directly visualised (Figure 2). Such films are called 'delta-layers' and have been used to understand the depth profiling process within inorganic materials, particularly by the semiconductor industry. Experiments on the NPL organic delta layers have provided a wealth of understanding of the depth profiling process. For example, by comparison with atomic force measurements we have proven that the resolution is determined solely by the roughness of the sputtered surface and not by any mixing processes. NPL organic delta layers will be used to find ways to limit the development of surface roughness and to compare different cluster ion sources.

Having obtained a thorough and detailed understanding of the organic depth profiling process, the interpretation of results from samples of technological importance becomes possible. In Figure 3 we show example results from a drug delivery material. Because SIMS can be used as an imaging spectroscopy with good spatial resolution, three-dimensional reconstructions are possible. Processing, visualising and understanding the results of such an experiment are all extremely challenging. The surface and nanoanalysis team at NPL is world-leading in providing analysts with the necessary tools for this task.

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A measurement platform for tapping solar energy

Solar energy is available the world over - it is, in practical terms, inexhaustible, and is by far the largest energy source available to mankind. NPL is supporting UK development of existing and emerging photovoltaic technologies to harness solar energy economically.

Photovoltaic (PV) cells are semiconductor devices used to convert light energy into electrical energy and hence a key way to tap into solar energy for energy generation. PV cells provide a carbon-neutral, sustainable form of energy generation, which is portable, free from geopolitical instability and can provide energy at the point of use – albeit at a higher cost compared to conventional means. As a result, electricity provided by PV cells only accounts for less than 1% of global consumption – a step change in PV technology (with respect to light capture, energy conversion and storage) is needed for it to be competitive, estimated as a reduction by a factor of 5 to 10 in the cost per watt of delivered solar generated electricity.

In order to meet this challenge new materials and device architectures are being explored that could potentially hold the key to a revolution in the way that PV cells are conceived, designed, implemented, and manufactured.

NPL is developing a measurement and testing platform to support UK development, competitiveness, and exploitation of existing and emerging PV technologies. Consequently, NPL has established links with key PV academic and industrial players in the UK. In addition, NPL is supporting an EPSRC CASE award for a PhD on dye sensitised nanocrystalline solar cells with the University of Bath.

Research at NPL is focusing on providing solutions to the crucial measurement issues that are limiting PV technology and encompass all three generations of photovoltaic materials and devices. Specifically, interest lies in studying the structure-activity link in PV systems, i.e. relating material properties from the macro- to the nano- scale with the optical characteristics, both local and bulk. Techniques to be used include electron microscopies (transmission electron microscopy, scanning electron microscopy, field emission scanning electron microscopy); scan probe techniques (atomic force microscopy, conducting atomic force microscopy); local electrochemical techniques (scanning electrochemical microscopy) and spatial mapping of PV conversion efficiency as a function of specific wavelength, incident angle and irradiance using wavelength-tuneable monochromatic radiation (which can be generated across the UV, visible and infra-red using either lamp/grating monochromator facilities or a suite of lasers covering much of the 210 nm to 1700 nm range).

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New NMS Innovation R&D Programme

In April 2007, the NMS projects funded by the former DTI (now DIUS) were rearranged into a new set of programmes following the recommendation of the NMS Review in 2005-2006. With a simplified structure of fewer and larger programmes that group together projects with similar objectives, timescales and impacts, the programmes will be more efficient to operate and manage.

The NMS Innovation R&D programme within the NMS portfolio takes over from the Measurement for Emerging Technologies Programme, which comes to a close at the end of March 2008. It will have a new scope in line with the new NMS structure, focussing on developing new measurement capabilities in the government's Technology Strategy priority areas of advanced manufacturing, information and communication technologies, healthcare, security, transport, energy and the environment.

For more information on the NMS please contact the NPL Helpline 020 8943 6880
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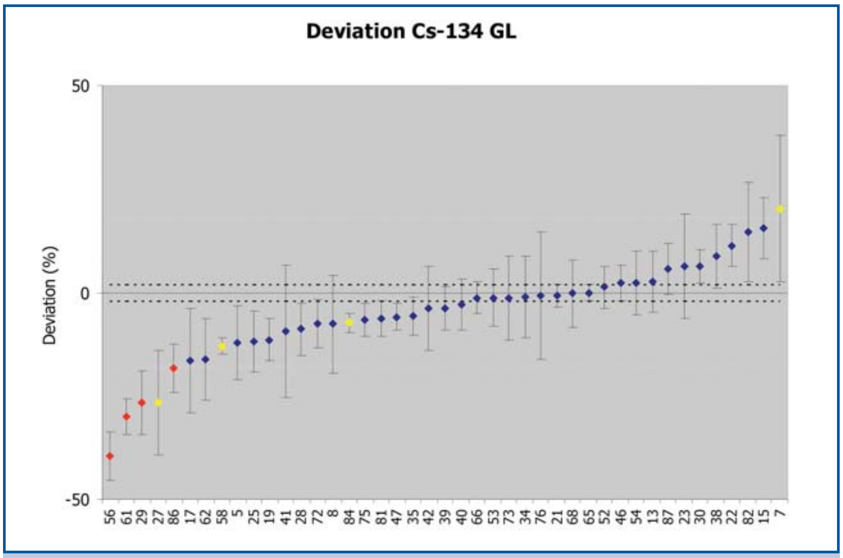
NPL Environmental radioactivity proficiency test exercise 2007

A network of analytical laboratories in the UK monitors radioactivity in the environment to ensure that radioactivity present in the foodchain is within acceptable limits.

Given the public concern over radioactivity, NPL has a key role in helping the laboratories demonstrate that their measurements are accurate, consistent, and independent of the nuclear industry. NPL has recently completed a proficiency test exercise for these laboratories; the exercise included preparing more than 200 radioactive samples and distributing them to 32 laboratories in the UK and, in addition, to 33 overseas organisations. These were based on primary radioactivity standards developed by NPL over the last few years. Eight different sample types were offered: an aqueous mixture of seven alpha emitters at two concentration levels, an aqueous mixture of six beta emitters at two concentration levels, an aqueous mixture of ten gamma emitters at two concentration levels, an aqueous mixture of four beta emitters and a solid neutron-activated concrete powder sample containing a variety of activation products. The results were discussed at a workshop held at NPL in September 2007; 73% of the results returned by the laboratories were in good agreement. NPL has produced a report on the 2007 Proficiency Test Exercise. This report can be downloaded at: www.npl.co.uk/server.php?show=ConWebDoc.2309



Deviation of Caesium – 134, one of the samples tested

The next environmental radioactivity proficiency test exercise is planned for June 2008.

If you would like to take part in the 2008 exercise, please contact Chris Gilligan 020 8943 8598 chris.gilligan@npl.co.uk

Assessing measurement software

NPL and PTB are collaborating on a guide to developing and assessing measurement software, to ensure it is fit-for-purpose.

Software is an intrinsic part of measurement. It is used in instruments to control experiments, store and process measurement data, analyse and display results and to implement many mathematical techniques. A great number of innovations in measurement have been enabled through the use of software for simulations or complex analysis. For example, the international temperature scale ITS90 requires the processing of high order polynomials and can only be implemented using software. Improving the quality of software and reducing the cost of its development are vital to the effective delivery of metrology. Due to the increasing complexity and dependency on software, there are considerable concerns over its quality. A study by NIST in 2000 stated that "Software bugs, or errors, are so prevalent and so detrimental that they cost the U.S. economy an estimated $59.5 billion annually". There is every reason to believe that Europe suffers in a similar way. NPL's recent audits of instrument manufacturers, based on Software Support for Metrology Best Practice Guide 1, Validation of Software in Measurement Systems (BPG1), and several examinations of measurement software carried out by the PTB's (Physikalisch-Technische Bundesanstalt, the German National Metrology Institute) Software Testing Laboratory, have indicated that software engineering techniques are not widely used.

A software guide that has been developed and accepted by leading NMI's would be more widely used and effective in the measurement community. For this reason NPL and PTB are currently collaborating on a guide to allow developers of measurement software to know what is required to produce fit-for-purpose software. This guide will also allow assessors of measurement software to confirm that the developed software meets these standards.

For more information, please contact Graeme Parkin 020 8943 7104 graeme.parkin@npl.co.uk

If you would like further information on any aspect of **Environmental Measures,** *please contact:*
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Forthcoming events

www.npl.co.uk/events

Nanoscale Surface Analysis for the Characterisation of Fibres
19 March 2008 (11:00)
Joanna Lee – NPL (Interwise Event Number 308065)
Join this online meeting via mset.org.uk

Power Harvesting for MEMS
26 March 2008 (11:00)
Markys Cain – NPL (Interwise Event Number 361045)
Join this online meeting via mset.org.uk

Thermal Analysis and Calorimetry (TAC) – Ensuring Accuracy and Relevance
Specialist annual event hosted at NPL on behalf of the Thermal Methods Group of the Royal Society of Chemistry
1 – 2 April 2008
NPL, Teddington
Contact:
Sam Gnaniah (tac2008@npl.co.uk)
http://conferences.npl.co.uk/tac2008/

Third Millimetre-Wave Users Group Meeting
4 April 2008
NPL, Teddington
Contact: gill.roe@npl.co.uk

CEM 2008
Seventh International Conference on Computational Electronics
7 – 10 April 2008
Brighton
http://conferences.theiet.org/cem

NPL / EMAN @ MACH 2008
21 - 25 April 2008
NEC, Birmingham
MACH is the UK's premier manufacturing technologies event
http://www.mach2008.com/

EURAMET 732 Workshop 2008
Towards more accurate fixed points
3 - 4 June 2008
NPL, Teddington
http://conferences.npl.co.uk/euramet732/
Contact: npl_clubs@npl.co.uk

Image Capture, Recognition and Reproduction
NPL Optical Technologies and Measurement Network
26 June 2008
NPL, Teddington
Contact: npl_clubs@npl.co.uk

Micro and Nano Scale Characterisation of Fibres
3 July 2008
University of Ulster, Jordanstown, Belfast
http://www.npl.co.uk/fibresworkshop

CompTest 2008
Fourth International Conference on Composites Testing and Model Identification
20 – 22 October 2008
Contact: bill.broughton@npl.co.uk
http://academic.udayton.edu/stevendonaldson/conf_overview.html

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"Nanomolecular Analysis for Emerging Technologies III" and "Surface Science of Biologically Important Interfaces 10"
5 – 6 November 2008
NPL, Teddington
http://conferences.npl.co.uk/nmaet/

NPL Training level 1 courses:
For information on training courses being run contact helen.white@npl.co.uk
or see http://www.npl.co.uk/training

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