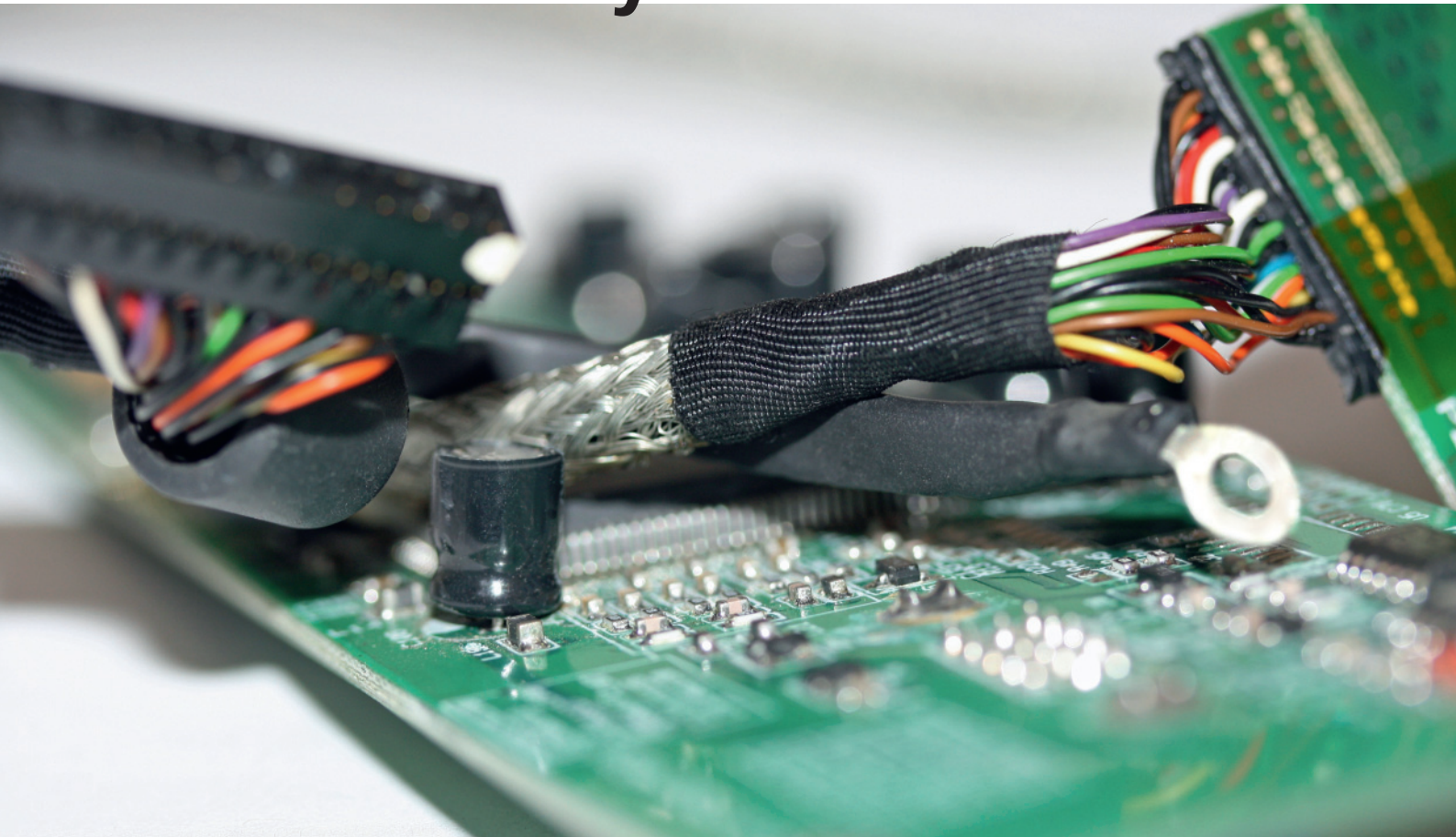


RoHS analysis



Determination of hazardous substances in
electrical and electronic equipment



Metrohm...

- is the global market leader in titration
- is the only company to offer a complete range of ion analysis equipment – titration, voltammetry and ion chromatography
- is a Swiss company and manufactures exclusively in Switzerland
- grants a 3-year instrument warranty and a 10-year warranty on chemical suppressors for ion chromatography
- provides you with unparalleled application expertise
- offers you more than 1300 applications free of charge
- supports you with expert service through local representatives and regional support centers
- is not listed on the stock exchange, but is owned by a foundation
- Gives the interest of customers and employees priority over maximizing profit

Metrohm – customized RoHS analysis for the determination of hazardous substances in electrical and electronic equipment

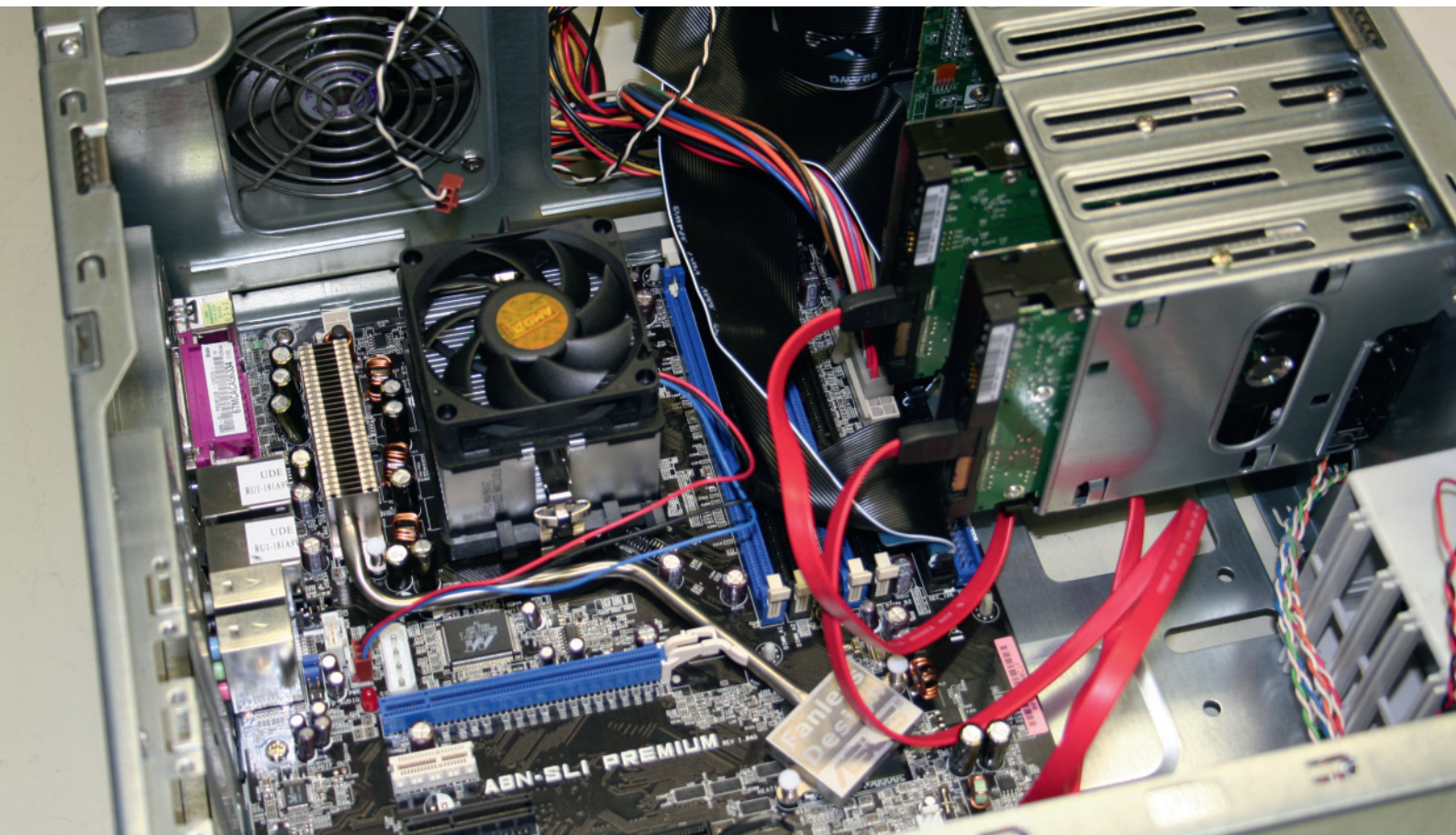
The Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) Directive, which has been in effect since 2006, stipulates maximum limits for various hazardous substances in electrical and electronic equipment. Its importance has almost made it a world standard. In many countries, similar directives are being discussed, being implemented, or already in force (China RoHS, Korea RoHS).

Meeting the RoHS Directive requires reliable equipment and methods.

You can count on our support

As a leading manufacturer of precision instruments for chemical analysis, we are aware of these challenges. For this reason, Metrohm offers you not only the most advanced equipment, but rather complete solutions for the particular tasks at hand. Your partners at Metrohm are experienced professionals who develop customized applications for you and provide you with competent support concerning all RoHS-related matters.

On the following pages, discover the solutions Metrohm offers to ensure the quality and safety of your products.



The RoHS Directive

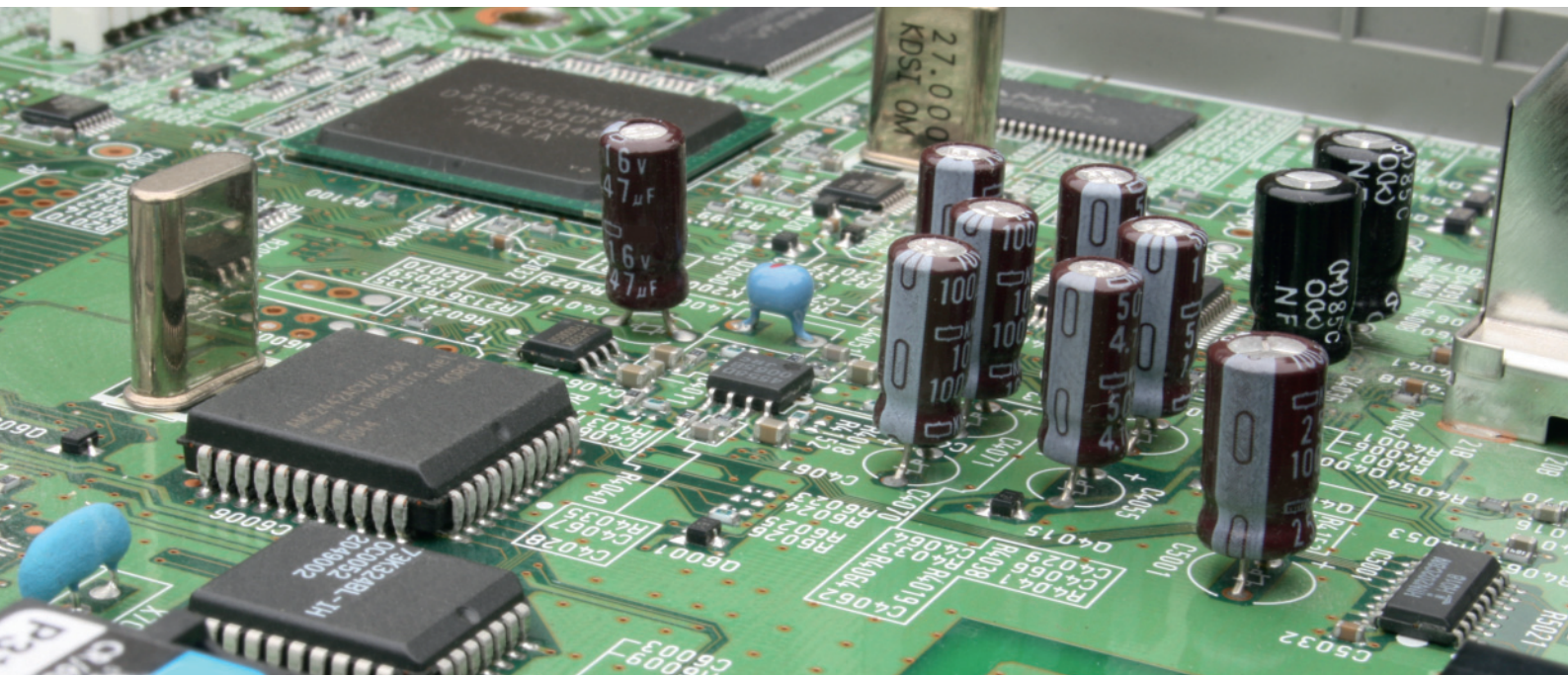
Hazardous substances in electrical and electronic equipment

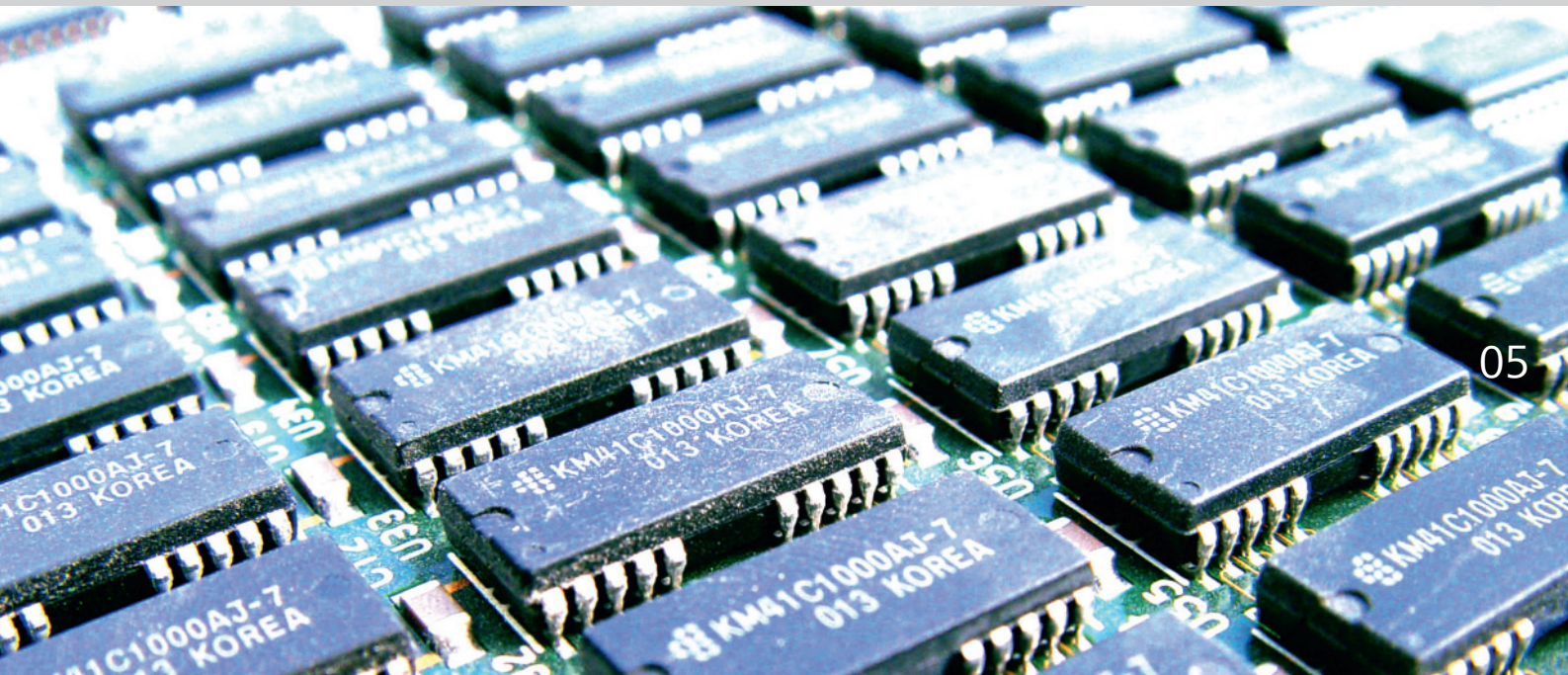
As a result of increased production and continuously decreasing lifetimes of electronic and electrical equipment, the global volume of electronic waste is increasing at three times the rate of any other type of household waste. Worldwide, nearly 40 million tons of electronic waste is now generated annually – and the rate is increasing. Improper disposal prevents the recycling of valuable raw materials such as precious metals and the rare elements indium or ruthenium. Furthermore, the toxic heavy metals and persistent brominated flame retardants used in electronic equipment represent an environmental hazard.

The EU Directives RoHS (2002/95/EC) and WEEE (2002/96/EC)

To counteract this development, two EU directives were adopted that aim to significantly reduce the amount of electronic waste through recycling targets and to protect humans and the environment from toxic substances by establishing limit values:

- The Waste Electrical and Electronic Equipment (WEEE) Directive has been in effect since May 2005 and stipulates the environmentally friendly disposal of electrical and electronic devices at the end of their working life.
- The RoHS Directive has been in effect since July 2006. It supplements the WEEE Directive and limits the use of certain hazardous substances in electrical and electronic equipment.





Selecting the right analysis equipment and methods

Maximum concentration in homogeneous materials

The RoHS Directive stipulates maximum concentration levels for lead, cadmium, mercury, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) for homogeneous materials in electrical and electronic devices. The limit values are 100 mg/kg for cadmium and 1000 mg/kg for each of the remaining elements and compounds. By definition, a homogeneous material, such as a plastic housing or a metal frame, is of uniform composition throughout and cannot be further mechanically disjointed into different materials.

Wet chemical analyses

If an initial routine inspection of a material points to an elevated concentration of a RoHS-regulated substance, conformity must be assessed via a more detailed (wet) chemical elemental analysis. Metrohm offers you a comprehensive range of equipment and methods for the rapid and precise detection of hazardous substances in electrical and electronic devices.

Analyte	Technique	Page
Lead and cadmium	Voltammetry	8
Mercury	Voltammetry	9
Chromium(VI)	Voltammetry	10
	Ion chromatography	12
Polybrominated biphenyls and diphenyl ethers	Ion chromatography	14
Bromine and other halogens	Combustion ion chromatography	15





Voltammetry

The RoHS Directive limits the use of the heavy metals lead, cadmium, mercury and hexavalent chromium in electrical and electronic equipment. A versatile, sensitive and robust analysis method is required to minimize the instrument costs associated with monitoring the established maximum concentration values. Voltammetry meets these requirements. It is used to quantify redox active substances – which includes the heavy metals listed above. Voltammetry is frequently employed to complement and validate spectroscopic methods. In addition

to its high precision and sensitivity, voltammetry has a compact equipment and is associated with low investment and operating costs.

Samples are prepared according to the recommendations by the International Electrotechnical Commission in compliance with the IEC 62321 standard. Thereafter, Voltammetry can be used to determine all four heavy metals in polymers, metals and electronic components within the required concentration ranges.

797 VA Computrace

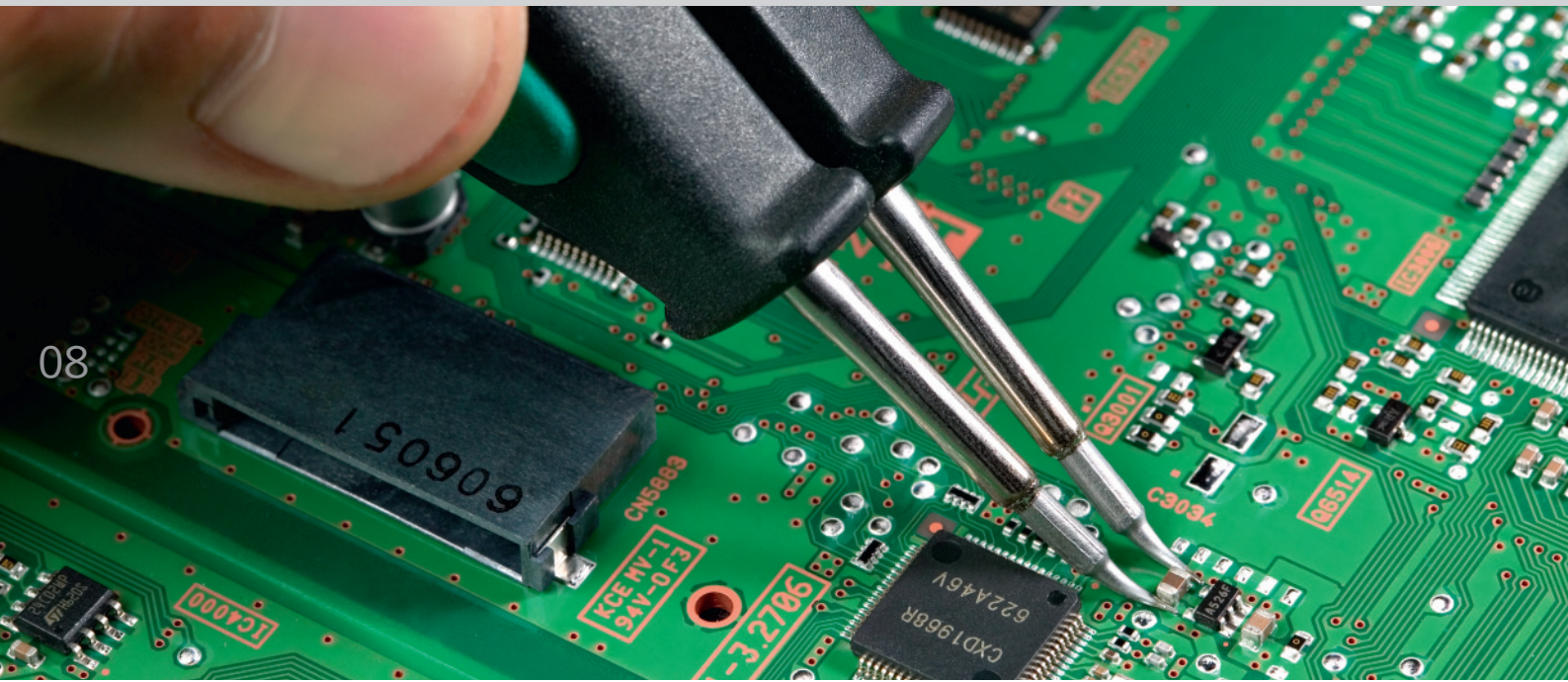
With the 797 VA Computrace, Metrohm offers you a user-friendly, modern, all-round measuring stand. Beyond covering the analytes required by the RoHS Directive, it permits the precise and sensitive trace analysis of metals and nonmetals using voltammetric and polarographic methods. Depending on the matrix, detection limits are in the ppt range (ng/L). Unlike spectroscopic methods, voltammetry distinguishes between the different oxidation states as well as between free and bound metal ions (speciation).

Detection limits in voltammetry

Element		Detection limit [ng/L]
Antimony	Sb ^{III} /Sb ^V	200
Arsenic	As ^{III} /As ^V	100
Bismuth	Bi	500
Cadmium	Cd	50
Chromium	Cr ^{III} /Cr ^{VI}	25
Cobalt	Co	50
Copper	Cu	50
Iron	Fe ^{II} /Fe ^{III}	50
Lead	Pb	50
Mercury	Hg	100
Molybdenum	Mo ^{IV} /Mo ^{VI}	50
Nickel	Ni	50
Platinum	Pt	0.1
Rhodium	Rh	0.1
Selenium	Se ^{IV} /Se ^{VI}	300
Thallium	Tl	50
Tungsten	W	200
Uranium	U	25
Zinc	Zn	50



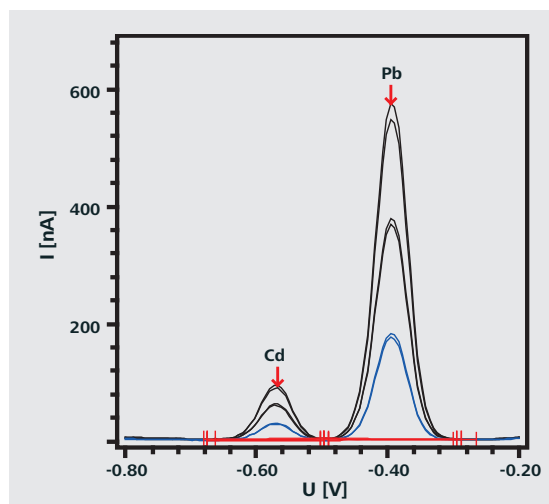
Economical and compact – the modern, computer-controlled 797 VA Computrace



Lead and cadmium

Lead and cadmium levels are determined using anodic stripping voltammetry (ASV). The two metals first undergo cathodic enrichment at the Multi-Mode Electrode and are then anodically stripped during the detection phase. The current flowing during this process is proportional to the amount of material previously deposited and hence to the metal concentration in the measured solution.

Since the oxidation for the two metals takes place at different potentials, lead and cadmium can be selectively determined in parallel. Quantification is easy and reliable with the standard addition method. Thus, matrix effects do not influence the accuracy of the results. Concentrations of 10 mg/kg lead and cadmium can be easily determined.

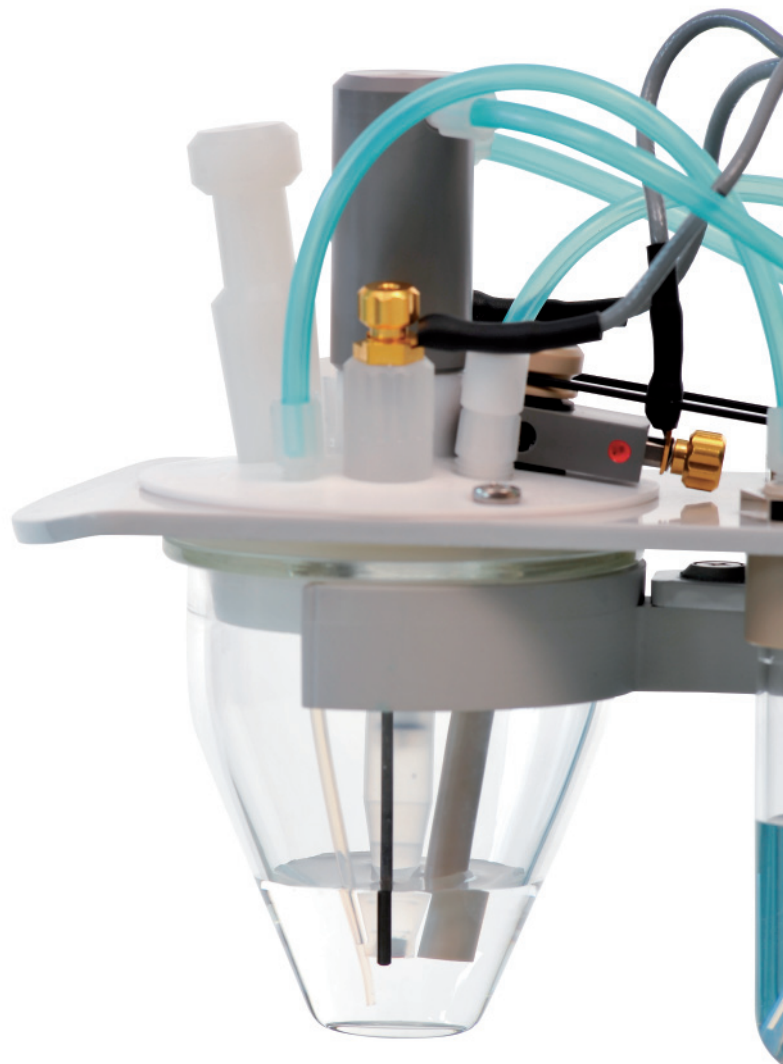


Simultaneous voltammetric determination of lead and cadmium in the range of the prescribed limit values (100 mg/kg Cd and 1000 mg/kg Pb)

Mercury

Mercury can also be determined using anodic stripping voltammetry. The determination process differs from that of lead and cadmium in that a gold rotating disk electrode is used for enrichment. The amount of deposited mercury and therefore the sensitivity of the determination can be controlled via the deposition time. In the subsequent determination, 1/10 of the required limit value can be easily detected.

As the determination of lead and cadmium, mercury determination can be accurately performed with the 797 VA Computrace. This merely requires exchanging the electrode set, which is quickly done since the electrodes are easily accessible.



Voltammetric measuring cell with gold rotating disk electrode, reference electrode and glassy carbon auxiliary electrode

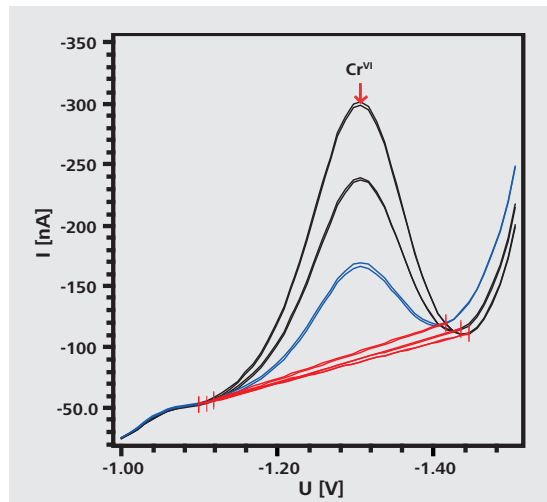


Chromium(VI)

Determining chromium levels in the context of the RoHS Directive is a special case since the concentration of the highly toxic hexavalent chromium – rather than the total concentration of the metal – must be identified. With voltammetry, Cr(VI) can be determined besides other chromium species without difficulty.

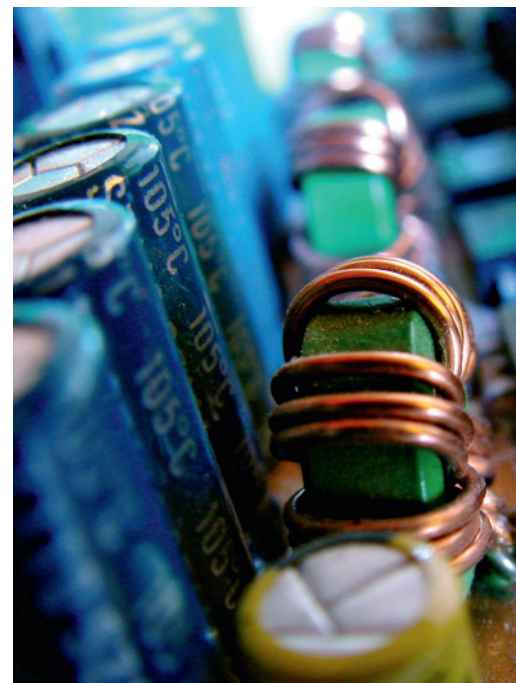
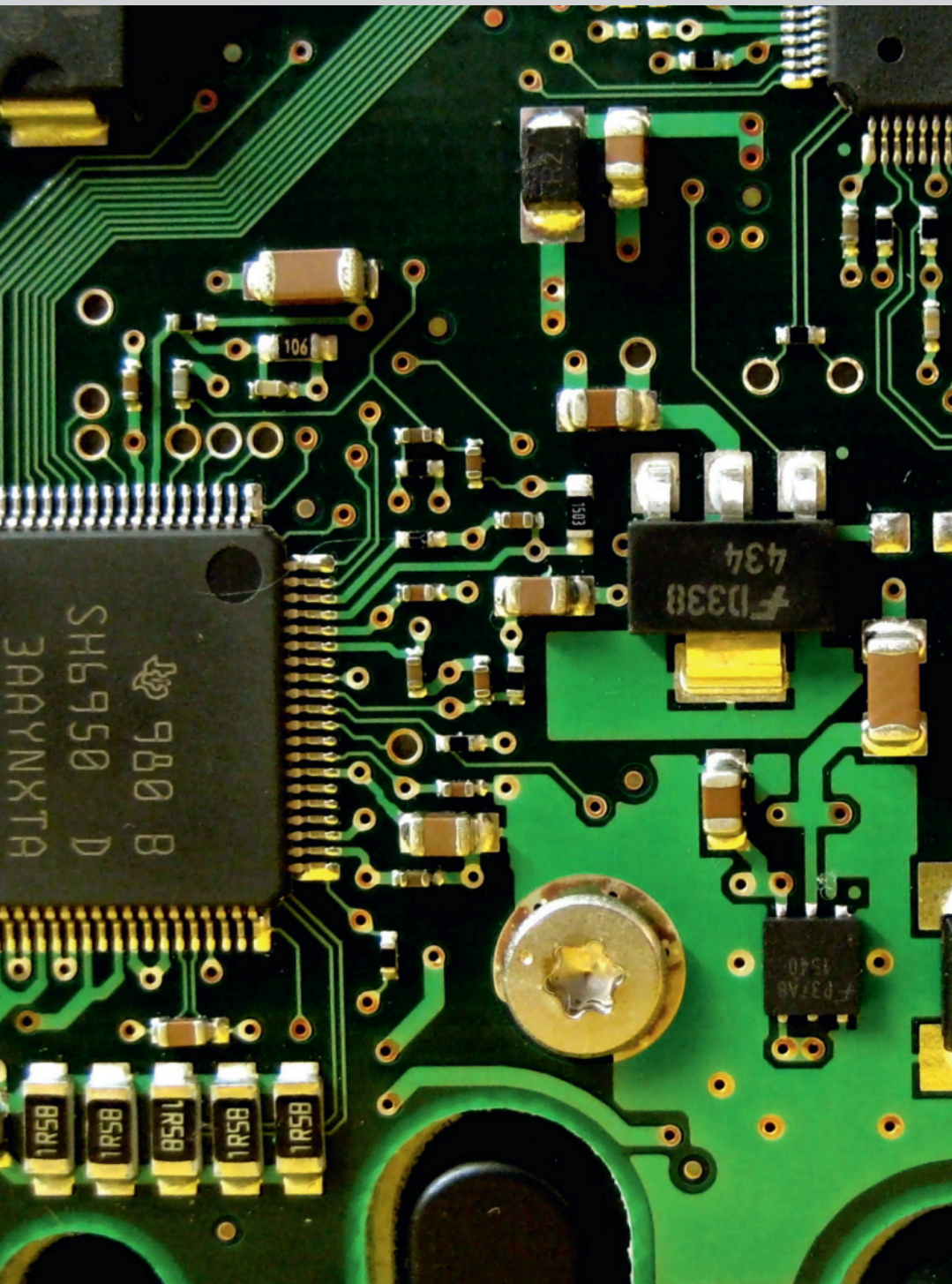
To rule out errors that derive from conversions between trivalent and hexavalent chromium, only extraction

methods, as specified by the IEC 62321 standard, are used in sample preparation. In order to comply with the limit value, Cr(VI) concentrations in the extracts of polymers and electronic components have to be around 50 mg/L. In case of chromium coatings, 0.02 mg/L must be accurately detected. Voltammetry meets this difficult analytical challenge thanks to its high sensitivity and great flexibility.



Determination of hexavalent chromium in a chromium coating in the range of the permissible limit value (0.02 mg/L)





Ion chromatography

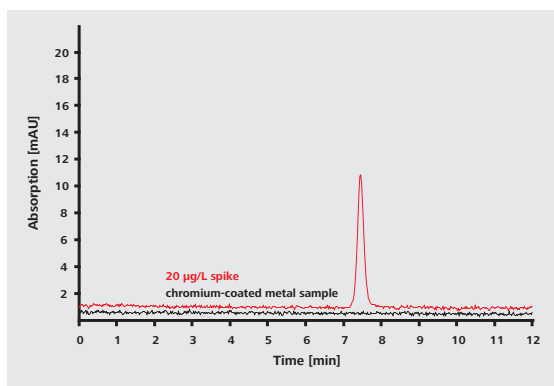
Ion chromatography (IC) permits the efficient separation and determination of inorganic and low-molecular-weight organic anions and cations. It can determine chemically similar substances within a very short time in a single analysis. Different separation mechanisms and detection types as well as the possibility of automation and sample preparation render IC a versatile analytical technique.

Chromium(VI)

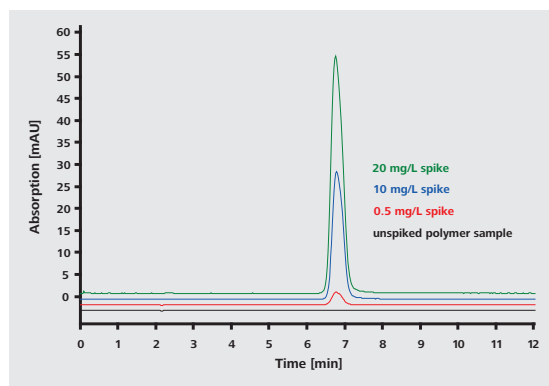
In addition to voltammetric measuring methods, ion chromatography is often used in the determination of

chromium(VI). After separation on a polyalcohol anion-exchange column and subsequent post-column derivatization with 1,5-diphenylcarbazide, chromium(VI) is detected with high sensitivity as a violet chromium-diphenylcarbazone complex at 540 nm. When using a 1000 μL sample loop, the chromate detection limit determined in accordance with DIN 32645 is less than 10 ng/L.

For polymers and chromium coatings, the RoHS Directive requires the analysis of chromium(VI) in different concentration ranges.



Chromium(VI) analysis in a chromium-coated metal sample, unmodified (black) and with the addition of 20 $\mu\text{g/L}$ of chromium(VI) (red). The recovery rate is 100%. Column: Metrosep A Supp 5 - 150/4.0; eluent: 10 mmol/L Na_2CO_3 , 1 mmol/L NaHCO_3 , 0.7 mL/min; sample volume: 200 μL ; post-column derivatization with 1,5-diphenylcarbazide.



Chromatograms of a polymer sample (black) and with the addition of 0.5 mg/L (red), 10 mg/L (blue) and 20 mg/L (green) chromium(VI): The analysis is linear over the entire determination range. Extension is possible through varying the sample amount as well as the dilution and injection volume. Column: Metrosep A Supp 5 - 150/4.0; eluent: 10 mmol/L Na_2CO_3 , 1 mmol/L NaHCO_3 , 0.7 mL/min; sample volume: 20 μL ; sample amount: 5 g finely ground polymer in 1000 mL $\text{Na}_2\text{CO}_3/\text{NaOH}$ solution; post-column derivatization with 1,5-diphenylcarbazide.

844 UV/VIS Compact IC

The 844 UV/VIS Compact IC can be used for the accurate and sensitive determination of chromium(VI) in chromium-coated metal and polymer samples. The instrument also allows to determine the organobromine compounds as required by the RoHS Directive (see page 14).



For the fully automated determination of chromium(VI), an 844 UV/VIS Compact IC is used in combination with an 863 Compact IC Autosampler. The analysis method provides excellent precision: 1.49% relative standard deviation for a 10 µg/L chromium(VI) standard (n = 6).

Polybrominated organic compounds

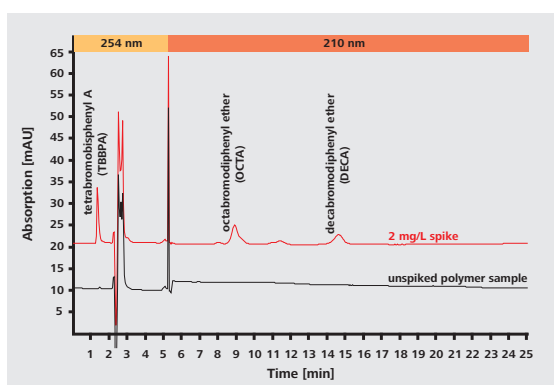
Determining flame retardants, such as polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE), in polymers is also part of RoHS Directive 2002/95/EC. Their concentration in electrical and electronic equipment is limited to 1000 mg/kg.

Using GC-MS, monobrominated to decabrominated biphenyls and monobrominated to decabrominated diphenyl ethers can be quantified after Soxhlet extraction. Two alternative analysis methods are presented below:

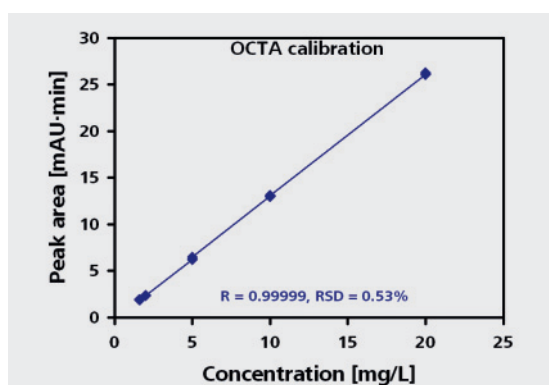
Determining PBBs and PBDEs using liquid chromatography

The polybrominated substances in the plastic are concentrated in a suitable solvent using Soxhlet extraction. The extract is then filtered and injected. After chromatographic separation of the polybrominated compounds on a rever-

sed-phase C18 column, their absorption is recorded at different wavelengths in a UV detector. Both polybrominated compounds and chromium(VI) can be determined using the 844 UV/VIS Compact IC (see page 13).



Determination of various polybrominated compounds in a polymer sample using UV detection at 254 and 210 nm. In the original sample (black), neither PBBs nor PBDEs can be detected. With the addition of merely 2 mg/L TBBPA, OCTA and DECA (red), the bromine-containing organic substances can be easily determined. This concentration is one order of magnitude below the limit value. Column: Nucleosil EC 100-7-C18; eluent: 97% methanol with 3% phosphate buffer (17.5 mmol/L Na_2HPO_4 and 11.0 mmol/L KH_2PO_4) at pH 7 (H_3PO_4), 1 mL/min; sample volume: 20 μL ; sample amount: 2 g finely ground polymer in 100 mL n-propanol.



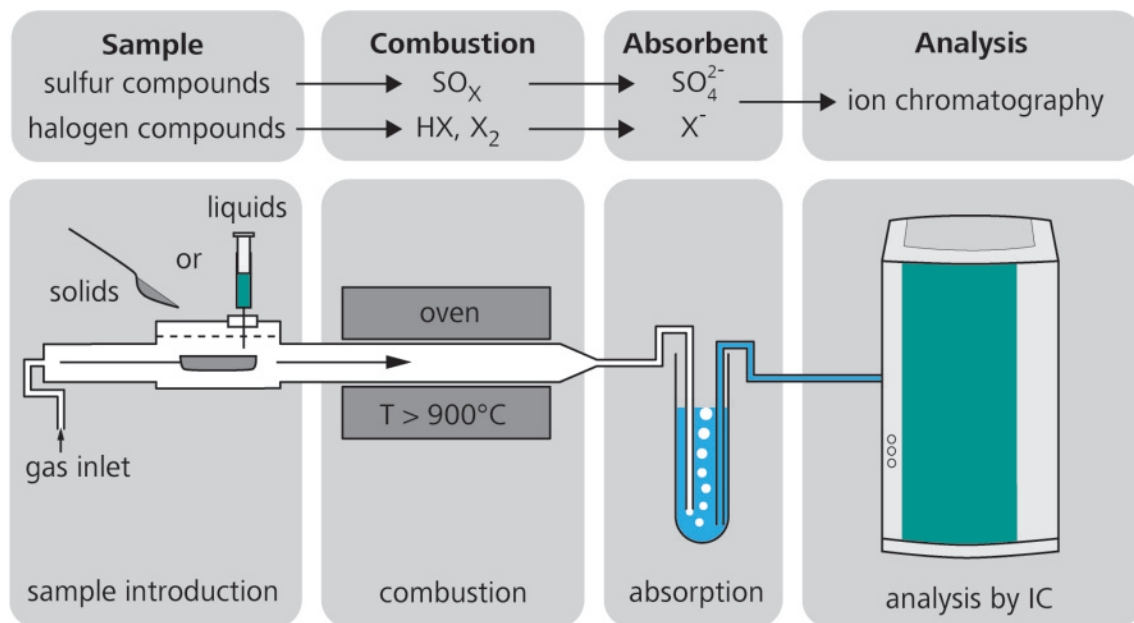
The detector signal is linear over a large concentration range. For OCTA, a correlation coefficient of 0.99999 and a relative standard deviation of only 0.53% ($n = 3$) were found.

Combustion IC for the simultaneous quantification of halogens in polymers

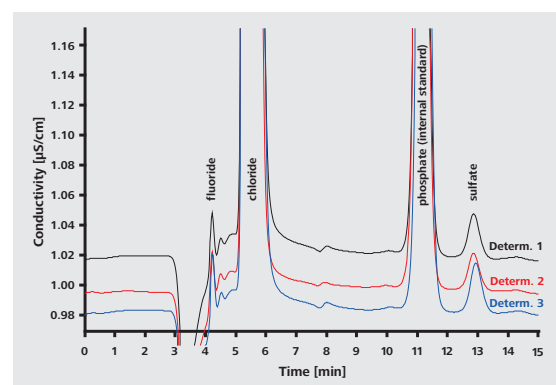
Combustion IC is a modern and powerful analysis method for the simultaneous determination of halogens and sulfur in all solid and liquid combustible samples. Electronic components, colors, pharmaceutical products, soil samples as well as fossil and biogenic fuels can be examined in addition to plastics. In contrast to the times of the oxygen bomb, no lengthy sample preparation is required. The completely automated Combustion IC features high sample throughput, low detection limits as well as excellent precision and accuracy.

The principle

After inline pyrolysis of the polymer matrix, the gaseous combustion products are led into an oxidizing absorption solution that is then fed into an ion chromatograph for analysis. Combustion IC can differentiate the halogen content of combustible samples and is thus ideally suited for determining if a material can be labeled «halogen-free» in accordance with the requirements of IEC 61249-2-21.



Halogen and sulfur determination in three PVC-containing power cable insulation materials using combustion IC. In addition to a high chloride content of up to 25%, low amounts of fluoride (< 30 mg/L) and sulfate (< 75 mg/L) were determined. Bromide, which elutes at approx. 9 min, was not detected. Column: Metrosep A Supp 4 - 250/4.0; eluent: 1.7 mmol/L Na_2CO_3 , 1.8 mmol/L NaHCO_3 , 1 mL/min; sample volume: 10 μL ; sample amount: 10 mg finely cut polymer material; internal standard: 10 mg/L phosphate.





Metrohm Quality Service®



Reliable results – for the lifetime of your analyzer

Metrohm analysis equipment is highly suitable for RoHS analysis. In combination with the comprehensive services of the Metrohm Quality Service®, our equipment ensures that laboratory managers can depend 100% on the measurement results – for the entire lifetime of the equipment.

Metrohm Compliance Service®

Benefit from Metrohm Compliance Service®, for instance for the professional initial qualification of your analysis equipment. With Initial Qualification/Operational Qualifi-

cation (IQ/OQ), you can significantly reduce costs and save time, since the analysis system is configured according to your needs. As a result your system can be put into operation quickly and professionally. User orientation and training then ensure safety and operator accuracy. Metrohm Compliance Service® includes complete documentation and guarantees conformity with common requirements of quality management systems such as GLP/GMP and ISO.

Metrohm Quality Service®

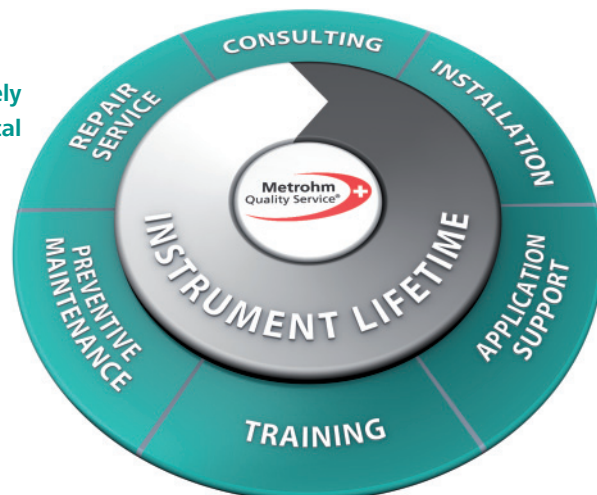
The Metrohm Quality Service® is available worldwide. Preventive maintenance carried out on a regular basis extends your instrument's lifetime while providing trouble-free operation. All maintenance work done under the label Metrohm Quality Service® is carried out by our own certified service experts. You can choose

between different types of service contracts. With a full service contract, for example, you can rely on the optimum performance of your Metrohm instruments at any time, whilst giving you complete control of costs and providing fully compliant verification documentation.

An overview of Metrohm Quality Service®

Our Services	Benefit for the Customer
Application support by means of our vast selection of Application Bulletins, Applications Notes, monographs, validation brochures, technical posters and articles Personal consultation by our specialists per telephone or e-mail	Quick and professional solution to all arising application questions and complex analytical challenges
Training courses	Competent users contribute substantially to reliable results
Certified calibrations, for example of dosing and exchange units	Accurate results Verification documentation for compliance with regulations and for efficient audits
Remote maintenance	Expeditious resolution of software questions
Back-up support	High data security
Emergency service, for example express on-site repairs	Short response times and thus rapid problem resolution Minimization of downtimes
Original spare parts, made in Switzerland and available world wide	Lasting, successful repair; short delivery times Minimization of downtime
Guaranteed spare parts available for at least 10 years beyond instrument discontinuation date	Protection of your investment through long-term availability of spare parts and accessories
Regional repair workshops available worldwide and a central workshop in Switzerland	Quality repairs done quickly, so your instruments are ready for use again

Thanks to Metrohm Quality Service®, you can rely on your results for the lifetime of the analytical instrument.



Ordering information

Voltammetry

2.797.0010	797 VA Computrace for manual operation
MVA-2	VA Computrace system with automatic standard addition consisting of 797 VA Computrace with two 800 Dosinos for automatic addition of auxiliary solutions
MVA-3	Fully automated VA Computrace system consisting of 797 VA Computrace with 863 Compact VA Autosampler and two 800 Dosinos for automatic addition of auxiliary solutions. Allows the automatic processing of up to 18 samples. This system is the optimum solution for automatic analysis of small sample series.
MVA-Hg	Complete equipment for mercury determination at the gold rotating disk electrode

Ion chromatography

Chromium (VI) determination

2.844.0020	844 UV/VIS Compact IC with post-column reactor
2.863.0010	863 Compact IC Autosampler
6.1006.520	Metrosep A Supp 5 - 150/4.0

Determination of polybrominated organic compounds – LC

2.844.0010	844 UV/VIS Compact IC Nucleosil EC 100-7-C18
------------	---

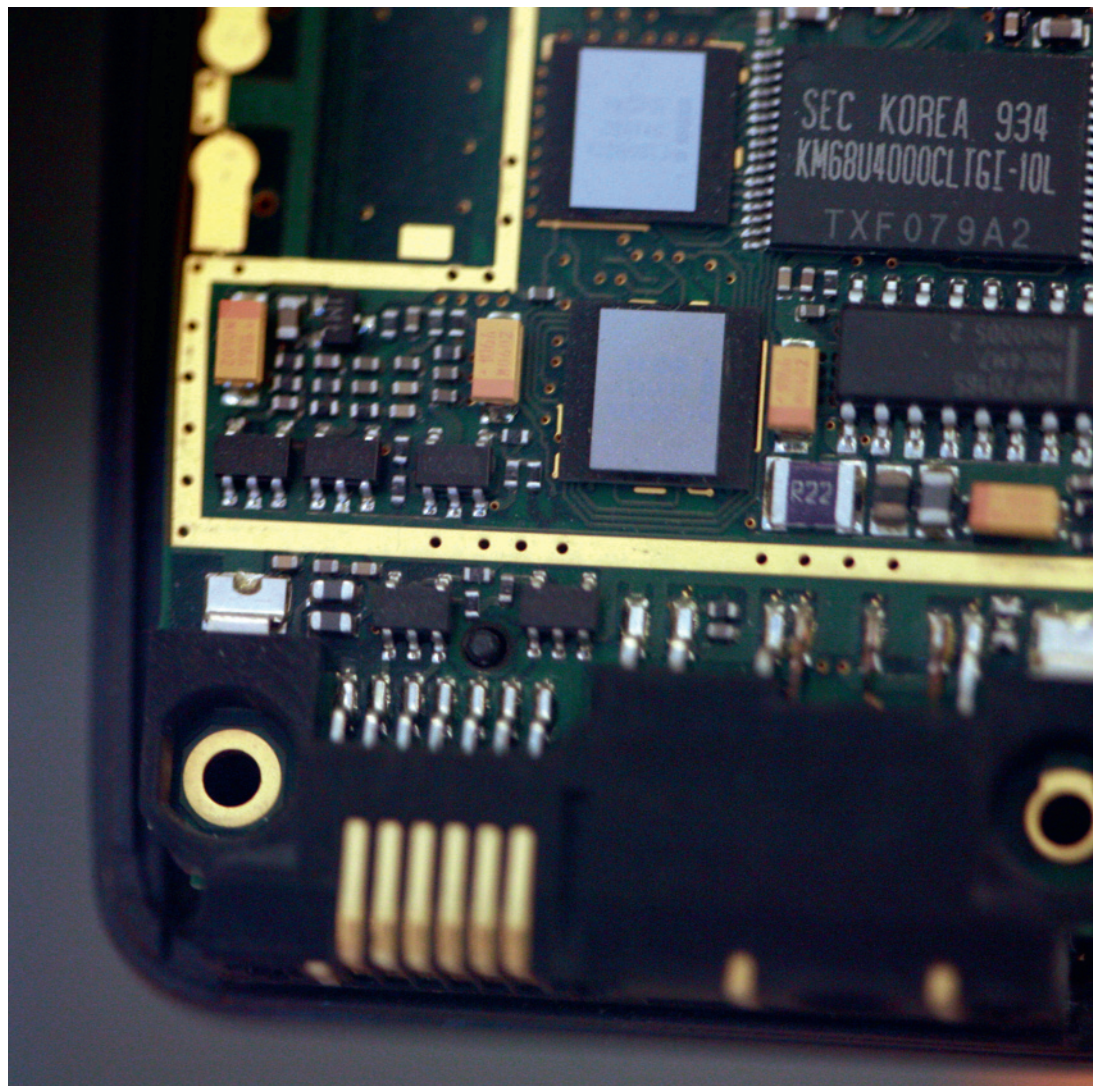
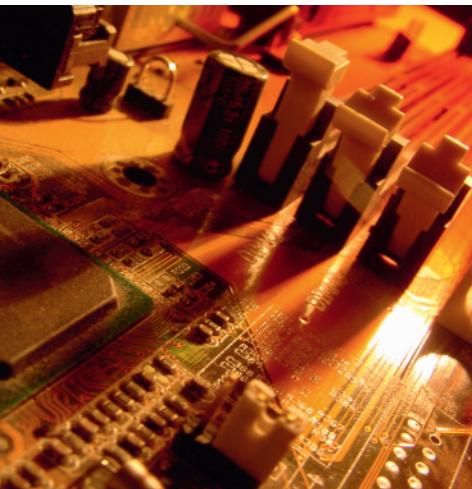
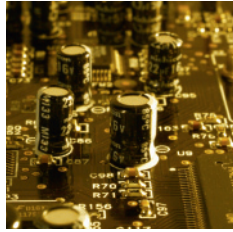
Determination of polybrominated organic compounds – Combustion IC

2.881.0030	881 Compact IC pro Anion – MCS
6.6059.211	MagiC Net™ 2.1 Compact CD: 1 license
6.2148.010	Remote Box MSB
6.2141.370	Cable for connecting Metrohm IC – PAC Combustion System
6.2141.140	Cable for connecting Metrohm IC – Mitsubishi Combustion System
6.1006.520	Metrosep A Supp 5 - 150/4.0
6.1006.500	Metrosep A Supp 4/5 Guard/4.0

Equipment for combustion can be purchased from PAC, L.P. and Mitsubishi Chemical Corporation.

The described determinations are based on the following Application Notes, which can be downloaded from <http://products.metrohm.com>

AN-V-185	Cadmium and lead in electronic components as part of electrotechnical products
AN-V-186	Chromium(VI) in electronic components as part of electrotechnical products
AN-V-187	Mercury in electronic components as part of electrotechnical products
AN-V-188	Cadmium and lead in polymer materials as part of electrotechnical products
AN-V-189	Chromium(VI) in polymer materials as part of electrotechnical products
AN-V-190	Mercury in polymer materials as part of electrotechnical products
AN-V-191	Cadmium and lead in metallic materials as part of electrotechnical products
AN-V-192	Chromium(VI) in chromate coating on metallic materials as part of electrotechnical products
AN-V-193	Mercury in metallic materials as part of electrotechnical products
AN-U-039	Polybrominated diphenyl ethers in polymers by UV detection, as per IEC 62321 method for RoHS testing
AN-U-040	Chromium(VI) in colorless and colored chromate coating on metallic samples as per IEC 62321 method for RoHS testing
AN-U-041	Chromium(VI) in polymers as per IEC 62321 method for RoHS testing



rohs.metrohm.com