Application of Ion Chromatography to the Polymer Industry

Shibu Paul, Ph.D, Product Manager – Ion Chromatography, Metrohm USA, Inc.

Introduction

Synthetic polymers offer us an incredible array of properties that can be custom-tailored to applications across a wide range of consumer products. Being synthetic, however, we must be conscious of the impact of their interaction with the environment. Ion chromatography (IC) has proven to be an effective technology for final production testing and environmental monitoring applications in the polymer industry.

Combustion ion chromatography (CIC) is well suited to analysis of halogens and PCBs in raw materials and finished products. Enabled by recent technical advances in automation, CIC has improved both its accuracy and ease of use. Standard IC is routinely used for the measurement of various anions and cations in the effluent discharge water for NPDES (National Pollutant Discharge Elimination System) compliance, and for quantification of amines in raw material and effluent monitoring.

Impact of Halogens on the Environment

According to the US Environmental Protection Agency, the amount of consumer electronic waste in the U.S. has nearly doubled since 2000. Given the widespread and growing use of electronic and electrical products, it can only be expected to grow further, increasing concern about the potential effects on our environment and human health. While we tend to think of hazardous metals like mercury and lead when considering the environmental impact of electronic waste, the traditional use of halogens in the polymer components of consumer products is equally important.

The halogens present in polymer waste can potentially make their way into the environment as carcinogenic compounds. This has led to efforts to reduce halogen content in the components used in the manufacturing of various electronic, electrical and consumable goods and materials. Regulations affecting composition, waste and energy use related to the production of polymer products have already been adopted in many countries all over the world.

The Restriction of the Use of Certain Hazardous Substances (RoHS) in Electrical and Electronic Equipment stipulates maximum limits for various hazardous substances in components, and has been widely accepted. In many countries, similar directives are being discussed, being implemented, or are already in place (China RoHS, Korea RoHS).

RoHS Directive 2002/95/EC specifies a limit of 1000 mg/kg for flame retardants such as polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in polymers. Going further, the International Electrochemical Commission defines “halogen free” to be no more than 900 mg/kg of chlorine (Cl), 900 mg/kg of bromine (Br) and 1500 mg/kg total of all halogens (IEC 61249-2-21). Other regulatory agencies have also issued or are in the process of issuing limits for halogens:

- JPCA (Japan Printed Circuit Association): JPCA-ES-01-2003
- IEC (International Electrochemical Commission): IEC 60502-1 (governing power cables)
- Waste Electrical and Electronic Equipment Directive (WEEE) 2002/96/EC
- Restriction of Hazardous Substances Directive (RoHS) 2002/95/EC (polybrominated biphenyls, polybrominated diphenyl ether, lead, mercury, cadmium, chromium (VI)

Methods for Halogen Analysis

Several conventional methods have been used or are currently being used for extracting ionic components or eliminating interfering matrices from polymers for ion chromatograhy (IC) analysis. The downside of these extraction methods is that they tend to be costly, labor intensive and not very reproducible.

The Schöniger flask method requires that the sample be placed on an ashless filter paper in a platinum holder inside an oxygen filled flask and burned. The potential for

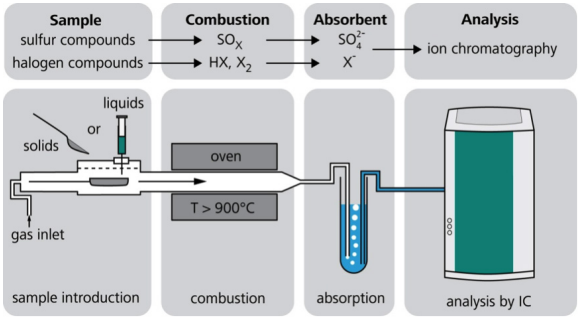
Metrohm USA Inc.

explosion, the boiling and splattering of wet materials and rapid deterioration of the combustion chamber are some of the inherent problems with this method, to name just a few.

The Parr bomb method involves oxidation of the sample with oxidizing agents such as sodium peroxide at elevated temperatures, and substantial time is required to complete the combustion. Another combustion method, the oxygen bomb, sees the sample being ignited by electrodes in a 25-40 bar oxygen atmosphere. Again, the labor involved is significant, reproducibility is poor, and sample filtration is often needed prior to successful analysis. The process is typically capable of testing only one sample at a time, and cleaning of the combustion vessel is required between each sample.

Combustion IC eliminates the need for the majority of the front-end sample preparation by combusting the sample in an oxidizing environment and absorbing the resulting gaseous hydrogen halide in an absorption solution followed by direct injection to the IC. This tremendous simplification of the method both reduces analysis time and yields reproducible results.

Combustion Ion Chromatography (CIC) Principles



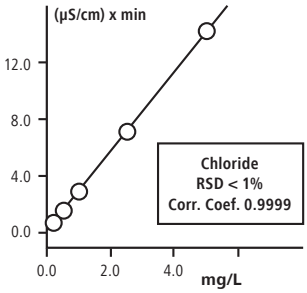
In combustion ion chromatography, sulfur and halogen compounds are combusted in an argon/oxygen gas mix and then oxidized to their respective ions (SO^{2-}_4, F^-, Cl^-, Br^-, I^-) by bubbling through an absorption solution such as hydrogen peroxide. The solution containing the analytes is then transferred to an anion pre-concentration column. The pre-concentration column is washed with deionized water to remove the absorption solution which eliminates potential interference with the ion chromatography (IC) analysis. The ions, which have become trapped or concentrated in the pre-concentration column, are then injected into the IC instrument for separation and detection.

Several technological advances have been made in automating the combustion sample analysis. Some of the more significant ones include flame sensor technology, automated multipoint calibration from a single standard, matrix elimination (to wash out hydrogen peroxide, if used in the absorption solution), use of multimatrix autosamplers and elimination of internal standards.

Flame sensor technology

The combustion portion of a CIC instrument consists of a combustion oven and auto boat driver (ABD). When the combustion oven features a flame sensor (http://misp.metrohm.com/solids/combustionIC/Flame-Sensor-Technology.html), method development is dramatically simplified. This is because the flame sensor serves to control the speed at which the sample boat moves, optimizing the combustion process. It prevents soot formation and generates more accurate and precise analytical data.

Multipoint calibration from single standard



Metrohm's Dosino technology automates liquid handling via software programmable burettes. Consisting of a drive unit and an exchangeable dosing unit, it provides the capability for automated multipoint calibration from a single standard. A Dosino system can fill the injection loop with variable sample volume, allowing a calibration curve to be developed with ease. This feature saves analysts time and provides both improved accuracy and precision.

Matrix elimination

If sulfur analysis of the sample is required, hydrogen peroxide is most often used in the absorption solution to facilitate the conversion of SO_2 to SO^{2-}_4. Instruments configured for matrix elimination selectively trap anions

in a trap column, removing hydrogen peroxide from the sample before injection. This effectively minimizes interference when performing fluoride quantitation.

Multi-matrix Autosampler

Traditionally, separate autosamplers were needed for solids and liquids. Autosamplers are now available with a novel design that allows both solid and liquid samples to be run quickly and interchangeably on the same device, simply by swapping a solid gripper with a liquid syringe. Analytik Jena's MMS-5000 is an example of a multi-matrix autosampler.

Elimination of Internal Standards

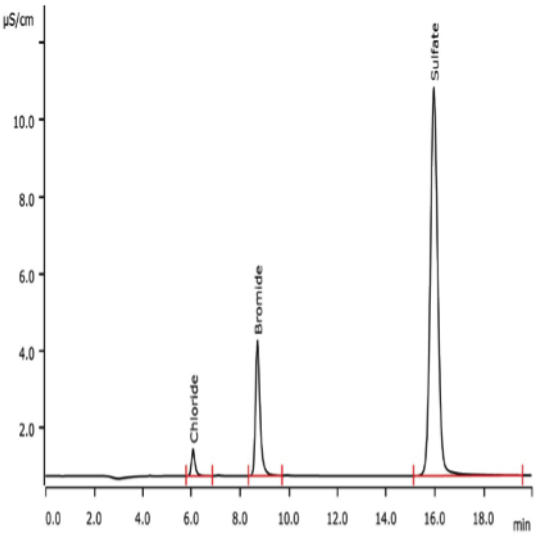
Water is often added during the combustion process at the combustion oven entrance to minimize the corrosion of glass by hydrogen fluoride and reduce chemisorption effects. Since water is continuously added during the process, determining the final volume of the absorption solution is difficult but critical. Some systems use internal standards to account for the dilution effect and others use a level sensor to stop the water addition at a fixed volume. In systems with Dosino technology, the software keeps track of the precise volume of water delivered for use in the final calculations.

CIC for Composition Analysis in the Polymer Industry

Combustion ion chromatography has found application in the analysis of both raw materials and finished components in the polymer industry, as illustrated by the examples below.

Halogens in polymer samples using Metrohm Combustion IC according to RoHS (AN-CIC-010)

Compliance with RoHS requires that the halogen content in various organic materials is drastically reduced. This has created a great demand for halogen-free polymers for various manufacturing operations. The chromatogram here is an example of halogen analysis in polymer using CIC for RoHS compliance.

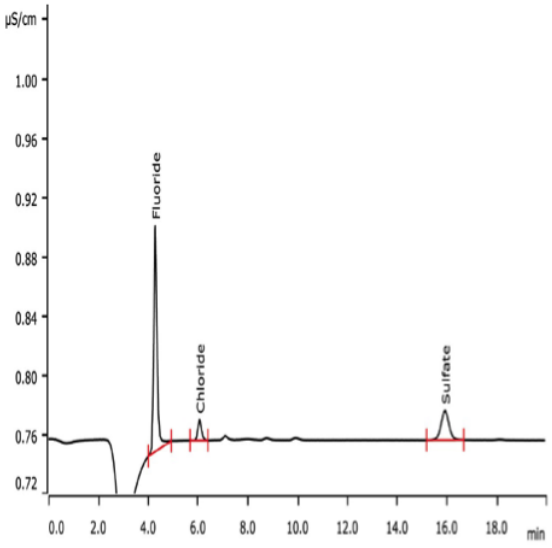


Halogens in polymer sample

Metrosep A Supp 5 - 150/4.0	6.1006.520
Metrosep A Supp 4/5 Guard/4.0	6.1006.500
Metrosep A PCC 1 HC/4.0	6.1006.310
	3.2 mmol/L sodium carbonate
Eluent	1.0 mmol/L sodium hydrogen carbonate
Suppressor regenerant	100 mmol/L sulfuric acid
Rinsing solution	Ultrapure water
Absorption solution	100 mg/L hydrogen peroxide
Flow rate	0.7 mL/min
Injection volume	4 µL
Pmax	15 MPa
Recording time	20 min
Column temperature	30 °C
Argon	100 mL/min
Oxygen	300 mL/min
Oven temperature	1050 °C
Post-combustion time	120 s
Initial volume of absorption solution	2.0 mL
Water inlet	0.2 mL/min

Fluoride in polyisobutene using Metrohm Combustion IC (AN-CIC-008)

Polyisobutene (PIB) is an important raw material for the manufacturing of fuel and lubricant additives to control corrosion. Monitoring of halogens is important when trying to manufacture additives for corrosion control. PIBs are also used in the manufacture of synthetic rubber and as a base material for the manufacture of chewing gum.

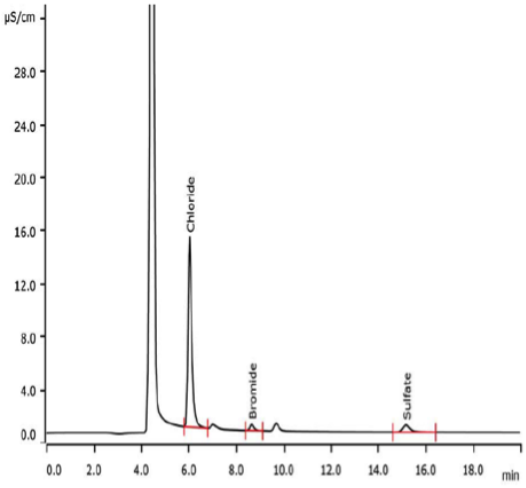


Fluoride in polyisobutene

Metrosep A Supp 5 - 150/4.0	6.1006.520
Metrosep A Supp 4/5 Guard/4.0	6.1006.500
Metrosep A PCC 1 HC/4.0	6.1006.310
	3.2 mmol/L sodium carbonate
Eluent	1.0 mmol/L sodium hydrogen carbonate
Suppressor regenerant	100 mmol/L sulfuric acid
Rinsing solution	Ultrapure water
Absorption solution	100 mg/L hydrogen peroxide
Flow rate	0.7 mL/min
Injection volume	4 µL
Pmax	15 MPa
Recording time	20 min
Column temperature	30 °C
Argon	100 mL/min
Oxygen	300 mL/min
Oven temperature	1050 °C
Post-combustion time	120 s
Initial volume of absorption solution	2.0 mL
Water inlet	0.2 mL/min

Analysis of basic material for printed circuit boards for halogens using Metrohm Combustion IC (AN-CIC015)

The EU Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment and the IEC 61249-2-21 define maximum values for halogen content in materials that are used in electronics. The Metrohm Combustion IC system with ion chromatographic determination permits precise, rapid and automated halogen determination in raw materials that are used in printed circuit boards.



Halogens in printed circuit boards

Metrosep A Supp 5 - 150/4.0	6.1006.520
Metrosep A Supp 4/5 Guard/4.0	6.1006.500
Metrosep A PCC 1 HC/4.0	6.1006.310
	3.2 mmol/L sodium carbonate

Eluent	1.0 mmol/L sodium hydrogen carbonate
Suppressor regenerant	100 mmol/L sulfuric acid
Rinsing solution	Ultrapure water
Absorption solution	100 mg/L hydrogen peroxide
Flow rate	0.7 mL/min
Injection volume	4 µL
Pmax	15 MPa
Recording time	20 min
Column temperature	30 °C
Argon	100 mL/min
Oxygen	300 mL/min
Oven temperature	1050 °C
Post-combustion time	120 s
Initial volume of absorption solution	2.0 mL
Water inlet	0.2 mL/min

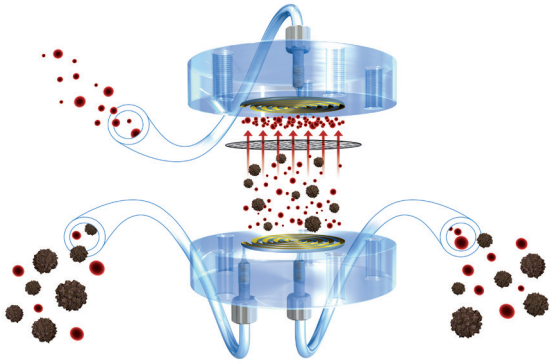
Applications of Standard IC in Environmental Monitoring

In addition to the CIC methods described above, regular IC has many environmental applications – including effluent monitoring, cation determination, and amine analysis. New technologies like ultrafiltration, automatic mulit-point calibration and specialized cation analysis monitor the safety of effluent streams more easily and accurately than ever. This ensures that the byproducts of polymer manufacturing processes meet regulatory standards for release into the environment.

Effluent Monitoring: EPA 300/ASTM 6919-09

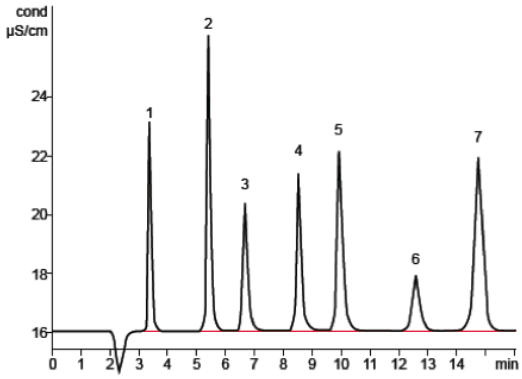
With the wealth of research directly linking contaminants in our water, air and soil to illness and disease, efforts have increased to reduce the amount of waste and chemical by-products we add to our surroundings. In the United States, the Environmental Protection Agency (EPA) is the governing body that sets limits on the amount of chemicals that can be discharged into to the environment. They implement it based on the Clean Water Act and through the National Pollutant Discharge Elimination System (NPDES) permitting process. For many years Metrohm has worked closely with the EPA on methods that determine these limits—and our instruments are highly valued for their precision and adaptability as the applications are refined and improved.

The aqueous effluent samples for IC analysis often require filtration through a 0.45 micron filter. Syringe filters can accomplish this, but are very expensive and time consuming. Technologies such as ultrafiltration, which work on the cross-sectional flow principle, can provide filtration down to 0.2 micron. Ultrafiltration extends the operational life for the analytical column. Depending on the matrix, the filter can last anywhere from 100 to 300 samples before being changed.



http://misp.metrohm.com/methods/Ultrafiltration/animation.html

Automatic multi-point calibration from a single high standard saves countless hours of manual preparation, as the system can precisely measure the correct amount of standard and perform all the tasks up to and including the calibration calculations. The same technique can be used to perform automated intelligent dilution, in which the system identifies samples over the calibration range, dilutes and re-measures the samples. Systems are available which combine ultrafiltration with the dilution set up, thus automating calibration, filtration and dilutions in a single high-performance instrument.



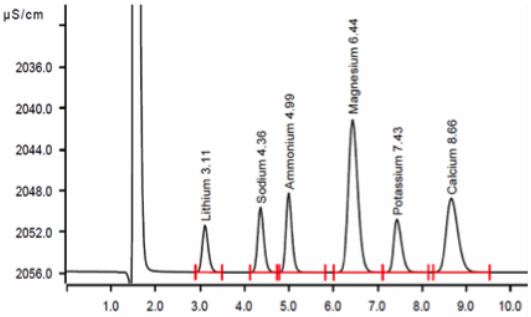
Column: A Supp 5-150
Eluent: 3.2mM Na_2CO_3/1.0mM $NaHCO_3$
Flow Rate: 0.7mL/min
Temperature: 25°C
Injection Volume: 20µL
Detection: Suppressed conductivity

Peak	RT	Component	Concentration
1	3.4 min	Fluoride	2 mg/L
2	5.4 min	Chloride	5 mg/L
3	6.6 min	Nitrite	5 mg/L
4	8.5 min	Bromide	10 mg/L
5	9.9 min	Nitrate	10 mg/L
6	12.5 min	Phosphate	10 mg/L
7	14.7 min	Sulfate	10 mg/L

Standard Anions by 300.0

Cation Determination: ASTM D6919-09

Polymer manufacturing facilities are often required to monitor alkali, alkaline earth metals and ammonium in the effluent discharge water. Non-suppressed cation analysis provides an inexpensive, easy to use configuration for this application with excellent dynamic calibration range and sensitivity.



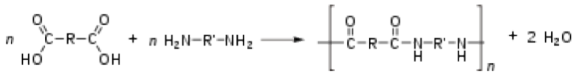
Column: Metrosep C 6-150
Eluent: 6.0mM HNO_3
Flow Rate: 0.9mL/min
Temperature: 30°C
Injection Volume: 20µL
Detection: Non suppressed conductivity

Peak	RT	Component	Concentration
1	3.1 min	Lithium	1 mg/L
2	4.7 min	Sodium	5 mg/L
3	5.0 min	Ammonium	5 mg/L
4	6.4 min	Potassium	10 mg/L
5	7.4 min	Magnesium	10 mg/L
6	8.7 min	Calcium	10 mg/L

Cation Determination: ASTM D6919-09

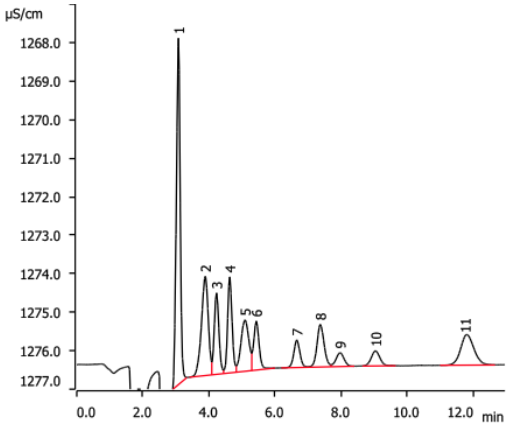
Amine Analysis

Amines are commonly used in the production of various polymers. For example, nylon is a common condensation polymer which is manufactured by reacting di-amines with carboxyl derivatives. In this example the derivative is a di-carboxylic acid, but di-acyl chlorides can also be used. Another approach often used is to react di-functional monomers with one amine and one carboxylic acid group on the same molecule:



General chemical structure of one type of condensation polymer

A general problem in suppressed conductivity detection is the fact that sensitivity will be poor when the product from suppression exhibits a small degree of dissociation. In the case of cation exchange chromatography with suppressed conductivity detection, common cations such as sodium or potassium form strong bases in the eluent suppressor. These strong bases are fully dissociated and therefore give a linear response over a wide concentration range. On the other hand, weak bases such as ammonium and amines form the respective hydroxides are partially dissociated and yield nonlinear response. In non-suppressed conductivity detection, ammonia or amines are detected in their cationic salt form and are thus fully dissociated, extending the linear response range. A linear response increases the accuracy at higher concentrations, requiring fewer calibration check standards over the calibration curve.



Column: Metrosep C6-150
Eluent: 6mM HNO_3/25% Acetone
Flow Rate: 0.9mL/Min
Temperature: 30°C
Injection Volume: 20µL
Detection: Conductivity

Peak	RT	Component	Concent
1	3.1 min	Lithium	2 mg/L
2	3.9 min	Sodium	5 mg/L
3	4.2 min	Ammonium	5 mg/L
4	4.6 min	Potassium	10 mg/L
5	5.1 min	Magnesium	10 mg/L
6	5.4 min	Methyl amine	10 mg/L
7	6.7 min	Calcium	10 mg/L
8	7.4 min	Dimethyl amine	10 mg/L
9	8.0 min	Trimethyl amine N-oxide	10 mg/L
10	9.0 min	Trimethyl amine	10 mg/L
11	11.8 min	Triethyl amine	10mg/L

Cations and amines combined

The detection limit using non-suppressed conductivity detection depends on several factors, the baseline noise being most important. The observed baseline noise in non-suppressed IC chromatograms is the aggregate effect of several components, including the detector block, high pressure pumps, column chemistry, eluent and the chemical purity. The ideal configuration would use a highly temperature-controlled conductivity detector that is stable to within ± 0.00010 °C, where the signals are pre-amplified in the detector block before digital signals are transmitted. By using these two techniques in combination, a significant reduction in the base line noise can be achieved

Combined Analysis Systems

Automated systems have become so sophisticated that a single system can perform combustion IC analysis as well as analysis of anions, cations and amines. Upgrading the anion IC portion of a system to a dual channel anion/cation system and adding an autosampler can enable the system to perform all of these analyses while maintaining the capability to do multipoint calibration and filtration.

Summary

The fields of ion chromatography and combustion ion chromatography have advanced technologically to become efficient and precise methods of quantifying constituents of environmental significance in the polymer industry from raw materials to finished consumer materials and components in effluent streams. It may also be used for other analyses, such as anions in perfluoro carbon (AN-S-228), anions in PVC (AN-S-130), sodium, ammonium, and potassium in polyethers (AN-C-059), and phosphate and sulfate in polymer samples after inline dilution & inline dialysis (AN-S-230).

The technologies for sample handling, calibration automation, and automated sample preparation have become more sophisticated in recent years, keeping pace with the growing demand for rapid and accurate measurement of hazardous materials. As environmental regulations increase around the world, measurement techniques like IC and CIC are our best safeguard to ensure compliance.

References

1. Municipal Solid Waste Generation, Recycling and Disposal in the United States, Tables and Figures for 2012 , US EPA, February 2014 http://www.epa.gov/epawaste/nonhaz/municipal/pubs/2012_msw_dat_tbls.pdf
2. IEC 62321 -3-2 Determination of certain substances in electrotechnical products Part 3-2: Screening total bromine in polymers and electronics by Combustion Ion Chromatography
3. AW IC AE6-0026-092013 Bromide Determination in Polymer samples using Metrohm Combustion IC
4. AW IC CH6-1122-092012 Analysis of polyethylene pellets as certified reference material with Metrohm Combustion IC
5. AW US6-0185-012014 Percentage Level Halides and Sulfur in Plastics using MiPCT with Metrohm combustion IC
6. AWCH6-1123-092012 Polymer samples with Metrohm Combustion IC
7. AWCH6-1130-102012 Analysis of an ion exchange resin with Metrohm Combustion IC
8. AN-S-228 Anions in perfluoro carbon
9. AN-S-130 Anions in PVC
10. AN-S-230 Phosphalic and sulfate in polymer samples after inline dilution and inline dialysis
11. AN-C-059 Sodium ammonium and potasium in polyethers

US & Canada, toll-free: 866-METROHM (638-7646)
www.metrohmusa.com • www.metrohmca.com

Metrohm USA Inc.