Advances in Capillary Ion Chromatography Systems Using On-Line Electrolytic Eluent Generation and Suppressed Conductivity Detection

Yan Liu, Victor Barreto, and Chris Pohl
Thermo Fisher Scientific, Sunnyvale, CA, USA

White Paper 70460

Executive Summary

Capillary-scale IC systems offer substantial benefits over conventional-scale IC systems, including higher mass sensitivity, improved separation efficiency and/or speed, smaller sample volumes, improved MS compatibility, and continuous system operation. Thermo Scientific™ Dionex™ ICS-5000 Capillary Reagent-Free™ IC (RFIC™) systems utilize on-line electrolytic eluent generation and post-column electrolytic suppression to maximize the performance and robustness of both conventional and capillary IC methods. Convenient and cost-effective, these systems are well suited for determination of trace levels of ionic analytes in matrix-rich and volume-limited samples.

Key Words

ICS-5000, Reagent-Free IC, RFIC, Capillary IC, Electrolytic eluent generation

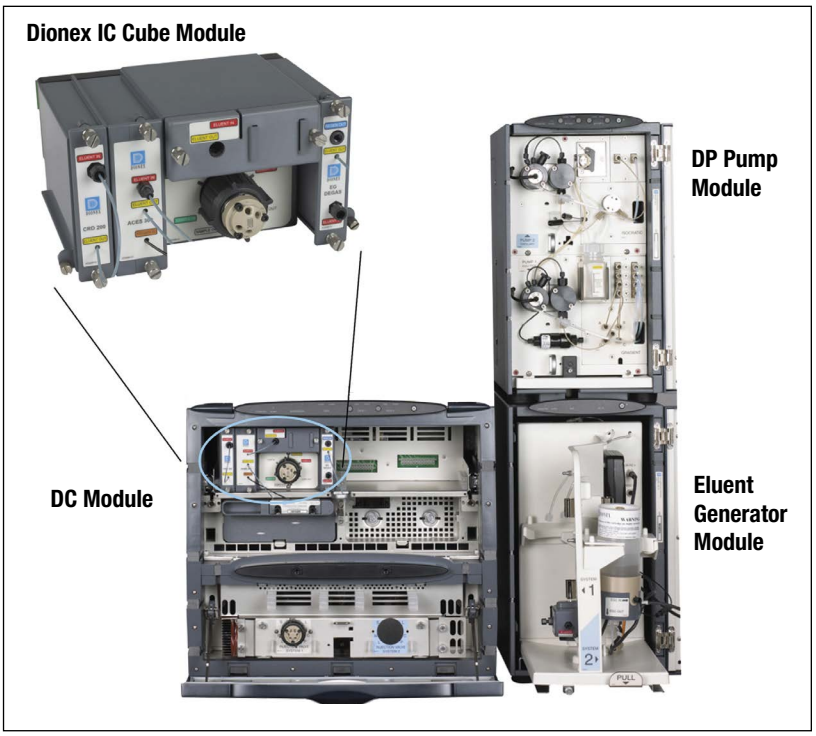

Figure 1. A Dionex ICS-5000 Capillary RFIC system.

Introduction

There has been increasing interest in the development of capillary IC systems and methods for determination of ionic species. The practice of ion chromatography in capillary format offers a number of advantages. Because the eluent consumption is very low, capillary IC systems can be operated continuously and thus are always on and always ready for analysis. Capillary IC systems offer improved compatibility with applications where amount of sample is limited. Capillary IC systems provide improved performance for determination of target analytes at trace levels. The use of capillary columns can improve separation efficiency and/or speed. The operation of capillary IC systems at low flow rates improves the system compatibility with a mass spectrometer. In addition, the use of capillary separation columns opens the door for the possibility of offering new selectivity for difficult applications using new columns packed with stationary phases which are more costly and difficult to prepare.

This white paper describes the efforts in the development of capillary Reagent-Free IC (RFIC) systems with on-line electrolytic eluent generation and suppressed conductivity detection for determination of target ionic analytes. The key components of new Dionex ICS-5000 capillary RFIC systems are discussed, highlighting the analytical capabilities of Dionex ICS-5000 capillary RFIC systems in the determination of target ionic analytes.

Thermo SCIENTIFIC

Experimental

Figure 1 shows the Dionex ICS-5000 RFIC system, the first IC system on the market capable of performing both conventional and capillary-scale IC separations. A typical Dionex ICS-5000 system consists of a Dual-Pump module (DP), an Eluent Generator module (EG), and a Detector/Chromatography module (DC). The Dionex ICS-5000 systems support RFIC technologies including eluent generation as well as manually prepared eluents for both conventional- and capillary-scale separations.The modular design of the Dionex ICS-5000 systems allows users to quickly configure and customize components for a wide range of applications. For example, a Dionex ICS-5000 RFIC system can be configured as a dual-channel capillary RFIC system, a dual-channel conventional RFIC system, or a dual-channel RFIC system supporting both conventional- and capillary-scale IC separations.

One novel feature of the Dionex ICS-5000 RFIC system is the Thermo Scientific™ Dionex™ IC Cube™ module. The Dionex IC Cube module is a small housing that resides in the DC. This module houses an EG degasser cartridge, a capillary column cartridge, an injection valve, a capillary suppressor cartridge, and an optional carbonate removal device (CRD) cartridge. The unique designs of the Dionex IC Cube module and associated cartridges simplify the plumbing of a capillary IC system by reducing the number of operator-made fluidic connections by 50%. The Dionex ICS-5000 RFIC systems are fully supported by Thermo Scientific™ Dionex™ Chromeleon™ 6.8 and 7.0 Chromatography Data System software.

Figure 2 illustrates the key components of a Dionex ICS-5000 capillary RFIC system. The capillary pump is used to deliver a stream of deionized water into the capillary KOH eluent generator which consists of a high-pressure generation chamber containing Pt cathode and a low pressure electrolyte reservoir containing Pt anode. Under the applied electrical field, the potassium ions migrate across the ion exchange connector to combine with hydroxide ions to form a KOH eluent. The downstream system components including the miniaturized degas unit, sample injector, separation column, electrolytic suppressor, and conductivity detector have been optimized for operation under capillary flow conditions. Table 1 summarizes the typical conventional and capillary RFIC system operating parameters.

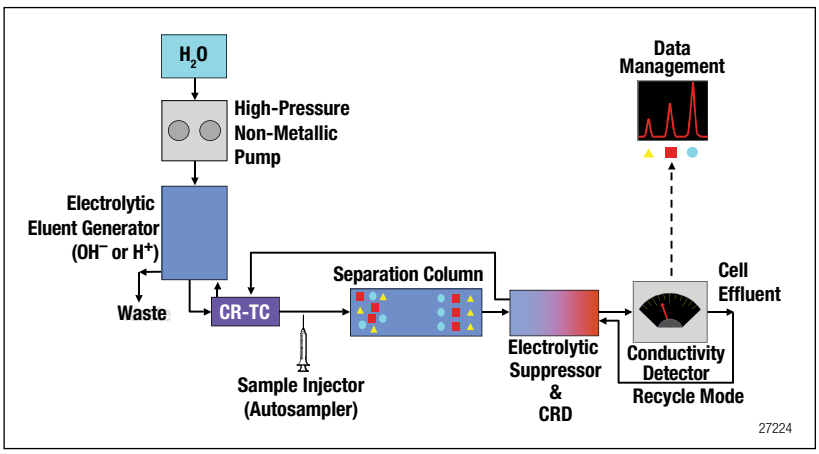

Figure 2. Block diagram of a capillary RFIC system.

Table 1. Typical conventional and capillary RFIC system operating parameters.

	Conventional IC	Capillary IC
Column i.d.	4 mm	0.40 mm
Flow Rate	1.0 mL/min	10 µL/min
Injection Loop	25 µL	0.4 µL
Suppressor Dead Volume	60 µL	0.6 µL
EG Current (50 mM KOH)	80.4 mA	0.804 mA
K^+ Consumption/Year	26.3 mol (50 mM KOH)	0.263 mol (50 mM KOH)
H_2O Consumption/Year	525.6 L	5.256 L

Results and Discussion

The Dionex ICS-5000 capillary RFIC systems use capillary electrolytic eluent generator cartridges (EGC) to generate potassium hydroxide (KOH) or methanesulfonic acid (MSA) eluents on-line using deionized water as the carrier stream. The electrolytic eluent generator in the capillary format provides an ideal eluent generation and delivery platform for both isocratic and gradient capillary separations for several reasons. 1) Electrolytic eluent generators with small dead volumes can be prepared. 2) Electrolytic eluent generators are capable of providing high-fidelity gradient profiles at low µL/min flow rates through precise current and flow rate controls. 3) It is much more practical and cost-effective to generate higher concentrations of eluents at low µL/min flow rates.

The electrolytic suppressor is another key component of a capillary RFIC system. The desired characteristics of capillary IC suppressors include low dead volume, high suppression capacity, and low baseline noise. The capillary IC suppressors should be capable of continuous operation, easy to operate without the need to have external acid or base regenerant solution, as well as rugged and reliable. It is desirable that the capillary IC suppressors are compatibile with mass spectrometry detection. The capillary-scale suppressors developed in this study offer these desired characteristics.

The Dionex ICS-5000 capillary RFIC systems with suppressed conductivity detector are capable of providing performance equivalent to those used in the conventional-scale RFIC systems. Figure 3 shows the isocratic separation of common anions obtained using a capillary Thermo Scientific™ Dionex™ IonPac™AS19 column. For 30 consecutive injections performed, the retention time relative standard deviation (RSD) ranges from 0.060% (bromide) to 0.091% (fluoride), and the peak area RSD ranges from 0.24% (sulfate) to 0.50% (fluoride).

Figure 4 shows the gradient separation of a complex mixture of 22 anions on a capillary Dionex IonPac AS19 column at 10 µL/min.The results demonstrate that the Dionex ICS-5000 capillary RFIC system provides highly reproducible separation of target analytes under gradient elution conditions with retention time %RSD ranging from 0.09% (arsenate) to 0.18% (fluoride).

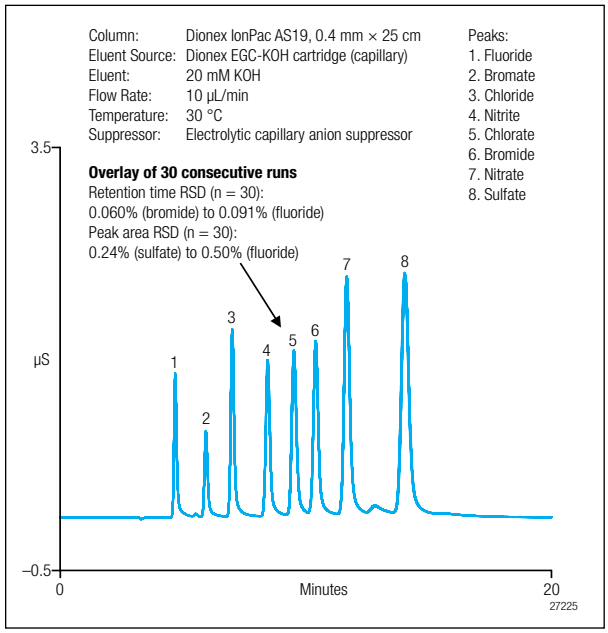

Figure 3. Isocratic separation of common anions obtained using a capillary Dionex IonPac AS19 column.

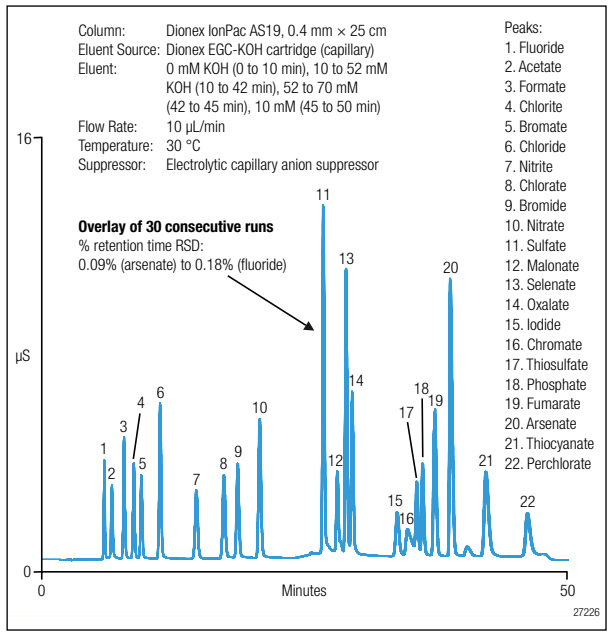

Figure 4. Gradient separation of 22 anions on a capillary Dionex IonPac AS19 column.

Figure 5 shows isocratic separation of common cations obtained using a capillary Dionex IonPac CS16 column. For 30 consecutive injections, the retention time RSD ranges from 0.052% (magnesium) to 0.092% (ammonium), and the peak area RSD ranges from 0.30% (potassium) to 0.46% (magnesium).

Figure 6 illustrates the determination of common anions in a treated wastewater sample using a Dionex ICS-5000 capillary RFIC system. In this study, a Dionex ICS-2000 conventional-scale RFIC system was used to analyze the same sample. The results demonstrate the Dionex ICS-5000 capillary RFIC system provides analytical results equivalent to those used in the conventional-scale RFIC systems.

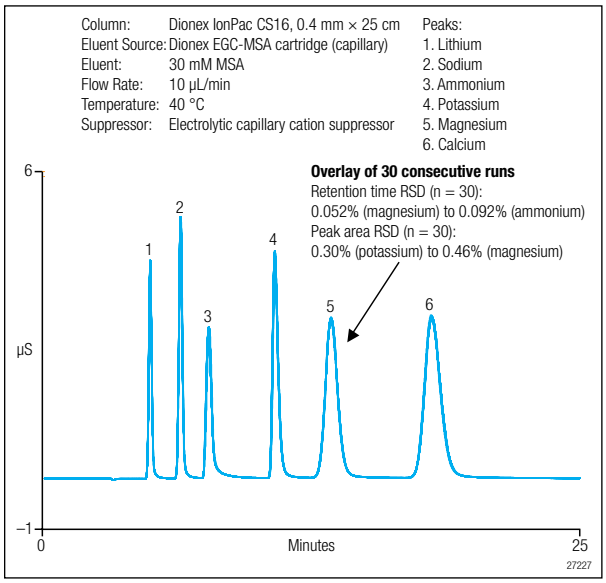

Figure 5. Separation of common cations obtained using a capillary Dionex IonPac CS16 column.

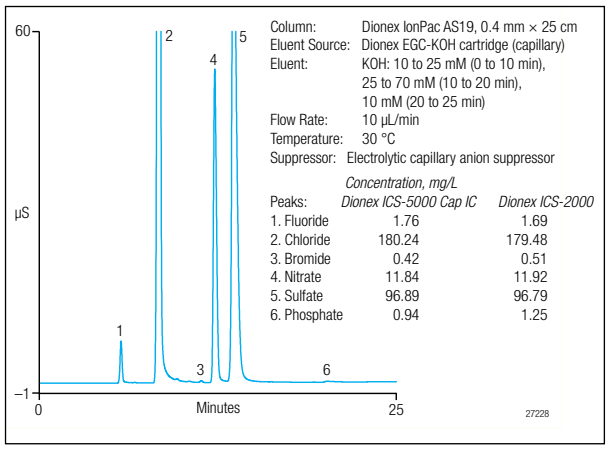

Figure 6. Determination of common anions in a treated wastewater sample.

Capillary RFIC systems provide improved determination of target analytes at trace levels since such measurements can be accomplished using relatively small volumes. One approach is to perform large-volume direct injection. This approach is suitable for samples with low levels of matrix ions. It should be pointed out that a 10 µL injection onto a 0.4 mm i.d. column in a capillary IC system is equivalent to a 1000 µL injection onto a 4 mm i.d. column. Loading a 250 uL sample onto a capillary concentrator can be much more conveniently accomplished than loading a 25 mL sample onto a conventional concentrator. Therefore, capillary IC systems can offer significant benefits in trace analysis, especially in applications where sample volumes are limited.

Figure 7 shows the separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS19 column. With a 10 µL injection, the Dionex ICS-5000 capillary RFIC system is capable of determining the target anions at concentrations ranging from 0.2 µg/L to 1.0 µg/L with excellent signal-to-noise ratios.

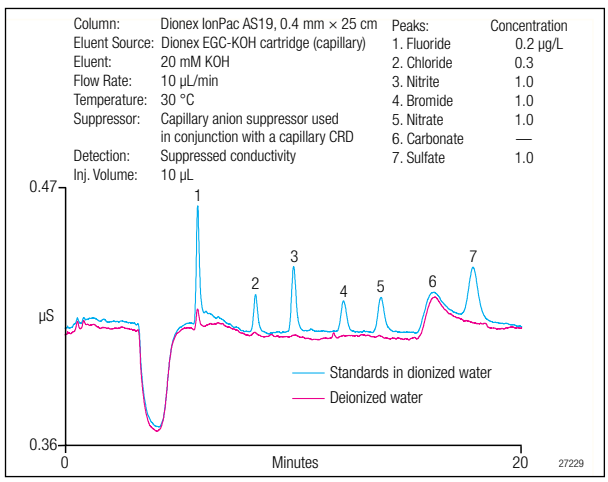

Figure 7. Separation of inorganic anions at trace concentrations on a capillary Dionex IonPac AS19 column with 10 µL injection.

Figure 8 shows the determination of trace bromate in drinking water samples using a capillary Dionex IonPac AS19 column. The results demonstrate the Dionex ICS-5000 capillary RFIC system is able to determine bromate at low µg/L levels using only 10 µL of samples.

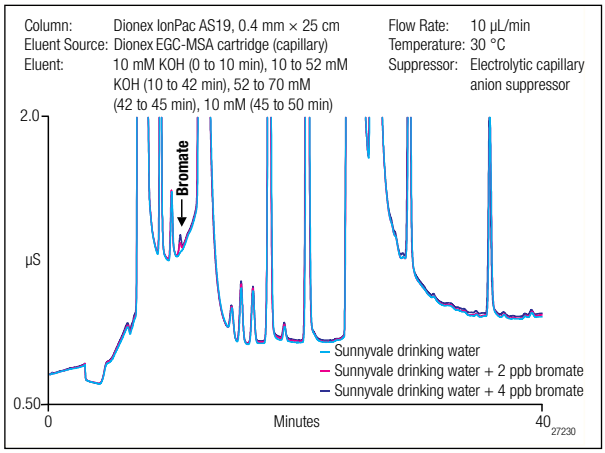

Figure 8. Determination of trace bromate in drinking water samples using a capillary Dionex IonPac AS19 column and large loop (10 µL) injections.

The Dionex ICS-5000 RFIC systems can be conveniently configured to perform two-dimensional IC (2D-IC) separations to improve the determination of target analytes at trace levels in complex sample matrices. Figure 9 illustrates a 2D-IC system constructed using Dionex ICS-5000 system modules. In this system, analyte ions are partially resolved from matrix ions on a conventional IC column (e.g., 4 mm i.d.) in the first dimension, collected onto a capillary concentrator column, then resolved from residual matrix ions on a capillary IC column (e.g., 0.4 mm i.d.) in the second dimension. Because the suppressed effluent from the hydroxide eluent in the first dimension is water, it provides the ideal environment for ion-exchange retention and concentration before the target analyte is transferred to the second dimension. Because the second dimension column has one-hundredth the cross-sectional area relative to the first dimension column, detection sensitivity is theoretically enhanced by a factor of 100. It is important to determine the optimum cut time from the first dimension to ensure the target analyte is quantitatively retained on the capillary concentrator column.

Figure 10 shows the determination of bromate in bottled water samples using the Dionex ICS-5000 two-dimensional RFIC (2D-RFIC) system with a second-dimension capillary column. For determination of bromate, 4 mm Dionex IonPac AG19/AS19 columns were used in the first dimension, a prototype Dionex IonPac AS20 column was used in the second dimension, and the cut time window of 19 to 24 min was used to load 2500 µL of the first dimension effluent onto the capillary concentrator column. The results indicate the Dionex ICS-5000 system is capable of determining bromate at parts-per-billion levels in drinking water samples.

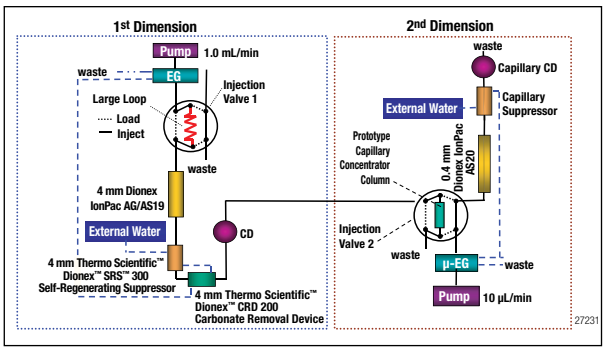

Figure 9. 2D-RFIC system using a capillary column in the second separation dimension.

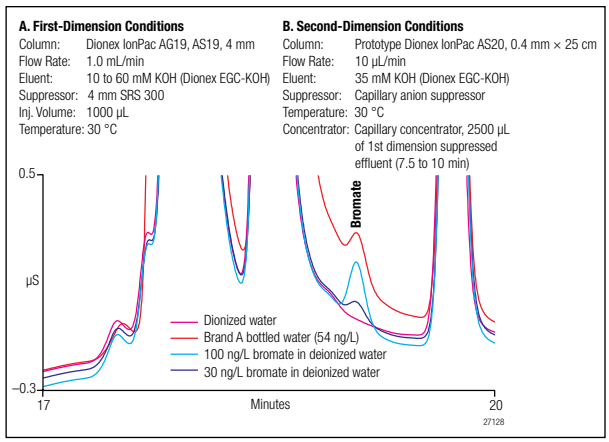

Figure 10. Determination of trace bromate in a bottled water sample using a 2D-RFIC system.

The Dionex ICS-5000 capillary RFIC systems can be used to achieve fast separation of target analytes. Figure 11 shows the fast separation of seven common anions on a capillary Dionex IonPac AS18 column. By increasing the separation flow rate to 20 µL/min, the separation of seven common anions was obtained using 33 mM KOH as the eluent in less than 5 min. Figure 12 shows the fast separation of six common cations on a capillary Dionex IonPac CS12A column. In this example, the separation of cations was performed using 20 mM MSA and the separation flow rate was varied from 12 to 18 uL/min. At 18 uL/min, the separation of six common cations was achieved in less than 6 min.

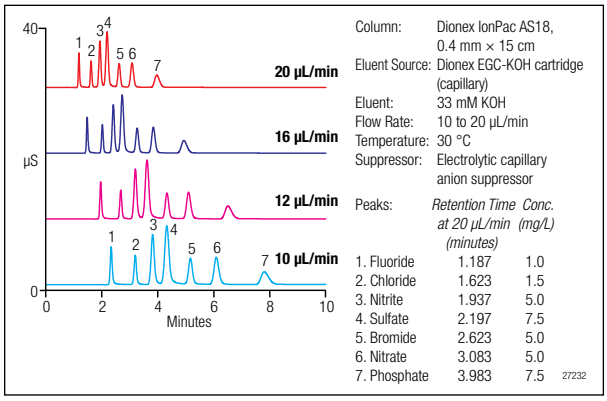

Figure 11. Fast separation of seven common anions on a capillary Dionex IonPac AS18 column.

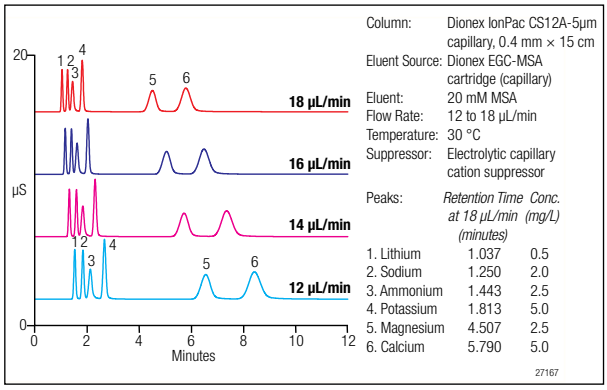

Figure 12. Fast separation of six common cations on a capillary Dionex IonPac CS12A column.

Conclusion

Dionex ICS-5000 RFIC systems with on-line electrolytic eluent generation enable fast, highly reproducible isocratic and gradient IC separations. Suppressed conductivity detection allows determination of trace levels of ionic analytes in complex samples. Both conventional- and capillary-scale IC methods are supported on these flexible, convenient, and cost-effective systems.

www.thermofisher.com/dionex

Australia +61 3 9757 4486
Austria +43 1 616 51 25
Benelux +31 20 683 9768
+32 3 353 42 94
Brazil +55 11 3731 5140
China +852 2428 3282
Denmark +45 36 36 90 90
France +33 1 39 30 01 10
Germany +49 6126 991 0
India +91 22 2764 2735
Ireland +353 1 644 0064
Italy +39 02 51 62 1267
Japan +81 6 6885 1213
Korea +82 2 3420 8600
Singapore +65 6289 1190
Sweden +46 8 473 3380
Switzerland +41 62 205 9966
Taiwan +886 2 8751 6655
UK +44 1276 691722
USA and Canada +847 295 7500

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

WP70460_E 08/16S