Thermal Analysis Techniques Applied to Solar Energy and PV Materials

Recent research efforts have focused on the development of a sustainable global energy policy. With the goal of minimizing carbon footprint and increasing sustainable or "green" energy, industry is aggressively pursuing solar energy and photovoltaic (PV) materials development. As production volumes are expected to increase substantially every year, the PV industry is more and more interested in optimizing both the performance of PV devices and the production efficiency of solar panel technology. Specific targeted areas include improvements such as increasing solar cell efficiency, as well as improving quality control in PV manufacturing.

Thermal analysis provides powerful tools to address these challenges. Thermal analysis techniques measure a specific thermophysical property as a function of time and/or temperature. The most common thermal analysis technique is Differential Scanning Calorimetry (DSC). DSC is widely used in materials research, analytical and quality control applications. DSC measures the rate of heat flow into or out of a sample, and is used as both a thermometric (temperature of a transition) and calorimetric (enthalpy of a transition) tool. DSC is sensitive to many of the critical transitions and processes which define ultimate performance in PV materials. As such, it is an important tool in the development and quality control applications typical in the production of solar energy technology.

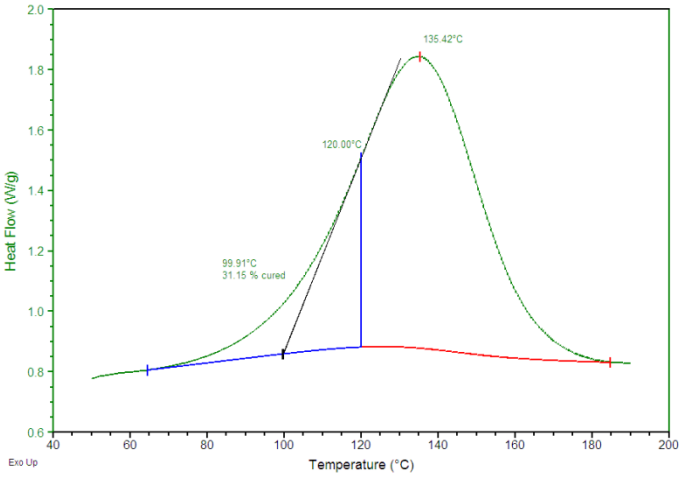

Figure 1: Typical DSC Result From a Crosslinking Material

Is There a Faster and More Accurate Test to Replace Standard Gel Content Analysis?

Solar panels employ crosslinking resins such as ethylene vinyl acetate (EVA) as encapsulation materials. The primary purpose of the encapsulant is to bond, or laminate, the multiple layers of a module together. Encapsulant characteristics must include high optical transmittance, good adhesion to different module materials, adequate mechanical compliance to accommodate stresses induced by

differences in thermal expansion coefficients between glass and cells, and good dielectric properties[1]. The gel content of the crosslinked EVA is a direct indicator of the material's end use properties, and as such it is often used as a quality control metric. The classical method for determining gel content of a material such as EVA involves dissolving away the additives and non-crosslinked resin from the cured material. The solvent-treated films are usually dried in a vacuum oven at room temperature for at least 24 hours. The gel content is then determined from the weight difference before and after solvent extraction. The main disadvantages of chemically determining the degree of crosslinking are the long duration of the test and high variability of the data. Furthermore, the chemicals used in the process such as xylene, THF and toluene are toxic to humans and environment.

DSC can solve this problem

The crosslinking reaction produces heat, the amount of which is quantitatively proportional to the degree of cure. This heat (enthalpy) can easily be accurately and precisely measured by DSC. The calculation of degree of curing requires accurate measurements of enthalpies of raw materials and cured product, with the latter known as the "residual curing heat." A higher the degree of curing results in a smaller residual curing enthalpy as measured by DSC[2]. Figure 2 shows a comparison of EVA samples with different degrees of curing.

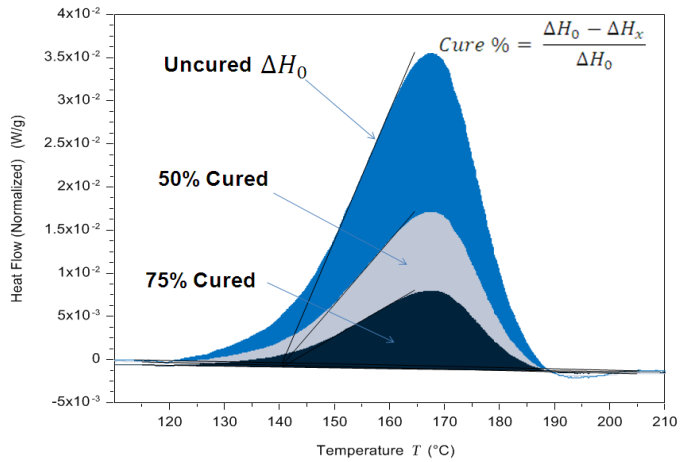

Figure 2: Method of Using DSC to Determine EVA Degree of Curing

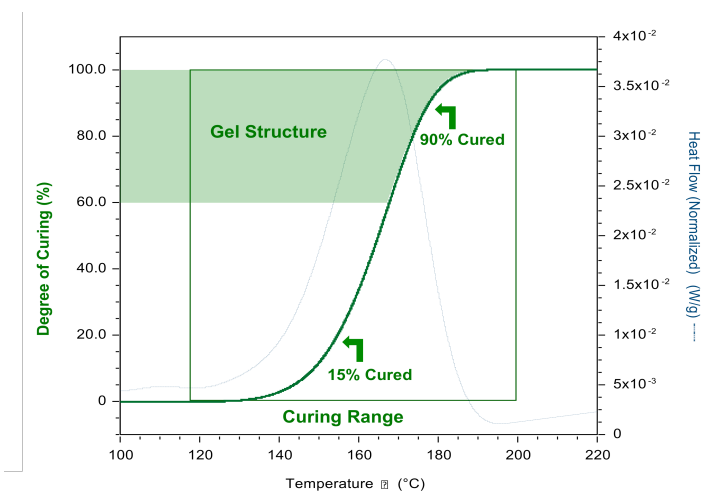

Figure 3: The Correlation of Gel Content Determination and Degree of Curing Using DSC

Curing degree can be obtained by comparing the enthalpy of the raw material and curing product. A higher degree of curing represents a higher cross-linking density of EVA, and a corresponding higher density of the structure. In addition, DSC accurately tracks conversion through the all stages of curing (induction, growth and maturation) as shown in Figure 3, while gel content determination only analyzes the final growth and maturation stages. A comparison of the resolution of the techniques is illustrated later in Figure 5.

[1] K. Agroui et al., *Desalination,* 209,(2007) 1–9

[2] Z. Xia, D. W. Cunningham & J. H. Wohlgemuth, *PVI Lite,* Vol 05 (2009) http://legacy.pv-tech.org/technical_papers/_a/a_new_method_for_measuring_cross-link_density_in_ethylene_vinyl_acetate-bas/

The table below lists the significant advantages of the DSC method, compared to the solvent extraction analysis.

	Solvent Extraction	DSC Method
Time Required	12~24 hr	15~30 min
Quantitative Accuracy	Low	High
Precision	≥ ±10%	< ±2%
Hazard	High	Negligible
Consumables	Solvent	DSC pan

Why Instrument Performance Matters

Critical to the success of the degree of curing measurement using DSC is the flatness and accuracy of the baseline. Flat baselines are necessary for accurate peak integration, resulting in a more precise determination of the degree of curing. Therefore, DSC instruments which produce a baseline which is flat, quantitatively accurate, and highly reproducible provide the best result for this analysis.

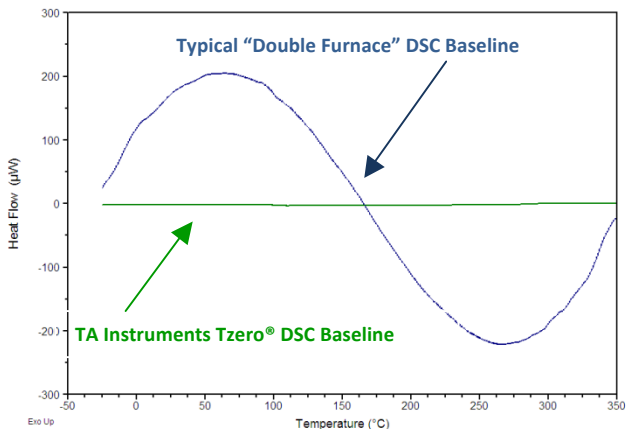

Figure 4: DSC Baseline Curvature Comparison

TA Instruments differential scanning calorimeters include a unique and proprietary technology known as Tzero® DSC[3]. This patented approach to measuring heat flow results in the industry's flattest baselines, free from artifactual components typical in competitive technology which can distort the baseline shape and compromise the quantitative measurement of curing enthalpy. Figure 4 compares the curvature of a Tzero DSC baseline with a typical response of a competitive "double furnace" DSC.

Only a DSC with the flattest and most reproducible baseline is capable of replacing the solvent extraction method for gel content analysis.

The data in the Figure 5 below demonstrates how DSC accurately and precisely follows the real chemical reaction while xylene extraction produced noisy, unreliable data.

[3] US Patents: 6,488,406, 6,431,747 and 6,561,692; Additional Patent Nos. EP 1136802, JP 4074441, 3936846, 3,936,847

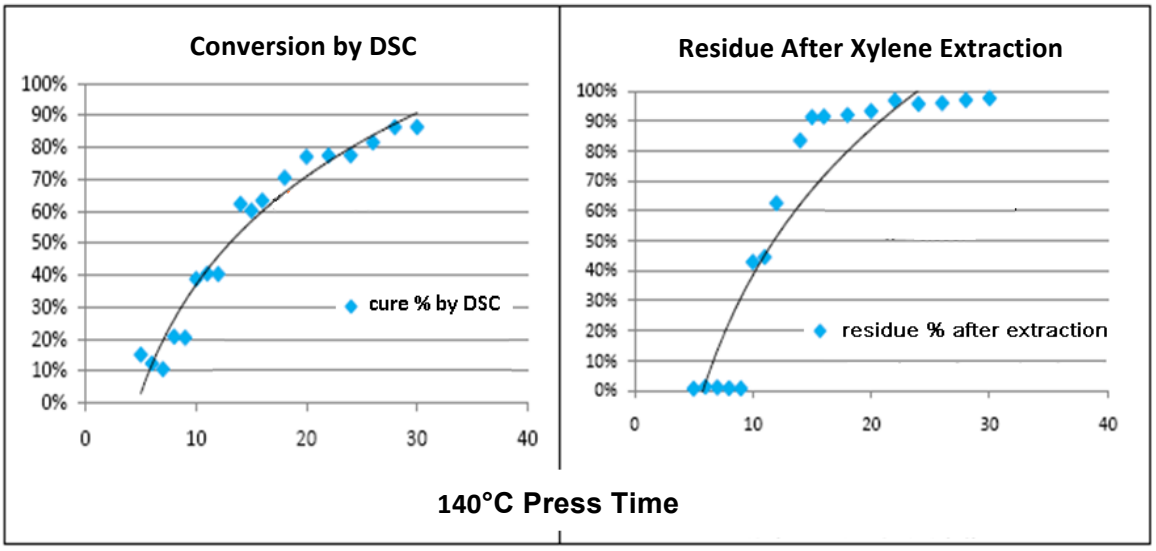

Figure 5: Comparison of Crosslinking Data from DSC Method and Solvent Extraction Technique

Optimization of the EVA Encapsulation Process

EVA encapsulation films have a very simple function; to protect the solar panel electrode. This is accomplished by encapsulating the fragile electrode with a film that is fused with heat and pressure. The traditional solar panel is a sandwich made of glass/EVA/electrode/EVA/back panel (Figure 6). To be effective, the encapsulant must satisfy the following requirements:

- It must efficiently flow into every contour (no voids)
- It must be as clear as possible (no yellowing)
- It must be sufficiently flexible to handle daily thermal expansion/contraction
- It must be pliable to act as a shock absorber between the glass front panel and the supporting back panel
- It must do all of these for a minimum of 25 years.

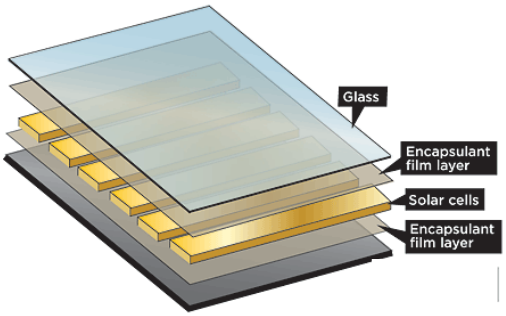

Figure 6: Typical Solar Cell Construction

The quality of the PV module encapsulation is the key point to ensure these criteria are met. To initially optimize the encapsulation process, it is important to use an appropriate EVA material which can optimize the luminous flux and increase power generation efficiency. In addition, during the design and manufacturing process one should measure the characteristics of materials and equipment to determine the optimal production parameters. This is accomplished through a series of thermal analysis techniques and methods.

Thermal Analysis is Crucial for Optimizing the Encapsulation of a PV Module

As shown in the previous section, DSC is a fundamental instrument for monitoring the curing of EVA. However, it can also measure the glass transition (Tg), melting temperature (Tm) and crystallization temperature (Tc) of EVA materials. Figure 7 shows a common DSC heat-cool-heat test result. In this experiment, the sample was from cycled from -90˚C to 250˚C at a ramp rate of 10˚C/min. The information one can obtain from this result includes:

- Is there a shift in Tg before and after curing?
- How much does the Tm change before and after the cure?
- Is the amount of heat released during curing stable?
- Is there any trace amount of gas released during curing?
- During cooling, what was the crystallization rate and percentage of crystallinity?

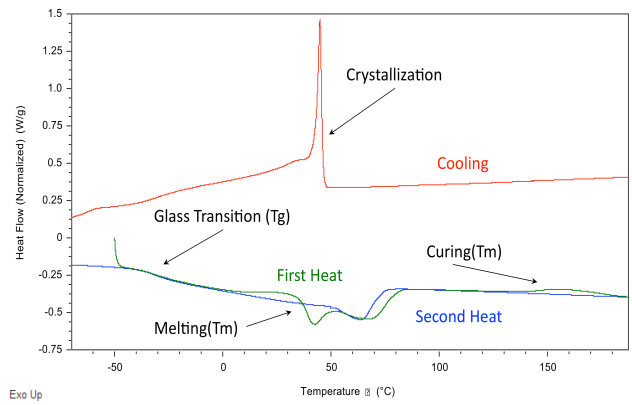

Figure 7. DSC Heat-Cool-Heat Result for EVA

The answers to these questions determine the characteristics of the EVA encapsulation material.

The amount of vinyl acetate in EVA affects its physical properties. Thermogravimetric Analysis (TGA) is a thermal analysis technique which can quantify compositional information by measuring weight loss during decomposition. When EVA is heated in an inert atmosphere, it undergoes a two-step thermal decomposition with concurrent elimination of the vinyl acetate component as acetic acid (Figure 8). Figure 8 also contains a TGA analysis of EVA. From the quantitative TGA result, the vinyl acetate content can be quickly and accurately calculated. The test accuracy of the TGA method is generally considered better than FTIR techniques for determining quantitative analysis of copolymer content.

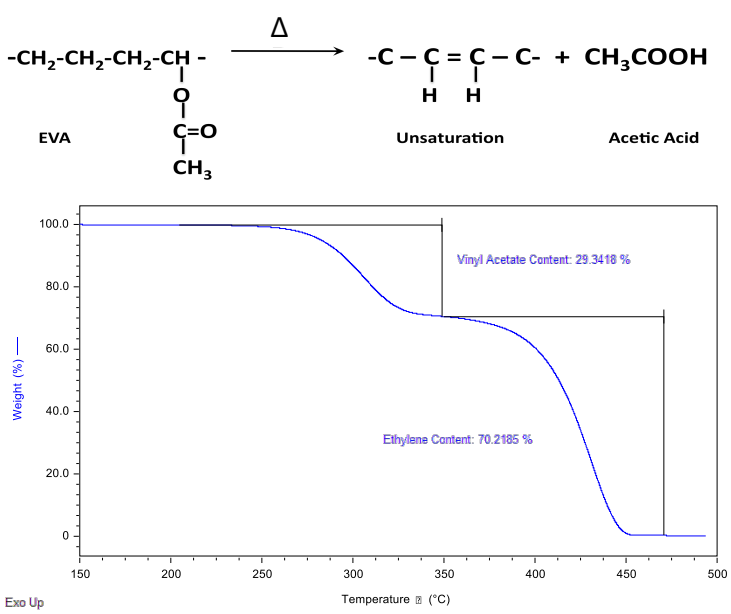

Figure 8: Decomposition Mechanism and TGA Analysis of EVA

Determining the Potential for Back-Sheet Deformation (Warping)

In a solar panel structure, the main function of the back sheet is to protect the battery from the surrounding environment, and especially to block the moisture. As the back sheet itself has a multi-layer laminate structure, it must also adhere to the EVA encapsulant. However, under the typical vacuum hot pressing process it is very easy to deform this laminate structure which can lead to poor adhesion. Therefore, it is critical that a back sheet material have dimensional and thermal stability.

Thermomechanical Analysis (TMA) is a thermal analysis technique which measures the change in the dimension of a materials as a function of temperature. It can be used to evaluate and compare the dimension thermal stability of different back-sheets. Figure 9 contains the TMA test results of two different back-sheet materials, A and B. In this test, the sample was heated at 10˚C/min from ambient to 150˚C, held isothermally for 30 minutes, followed by a 10°C/min cooling ramp back to ambient. The TMA results demonstrate that the initial expansion of Back-Sheet B is ca. 25% higher than that of Back-Sheet A. In addition, the ultimate deformation of Back-Sheet B is considerably higher than that of Back-Sheet A (which recovers back to its original dimension). This suggests that Back-Sheet B has more potential to cause adhesion defects during the encapsulation process.

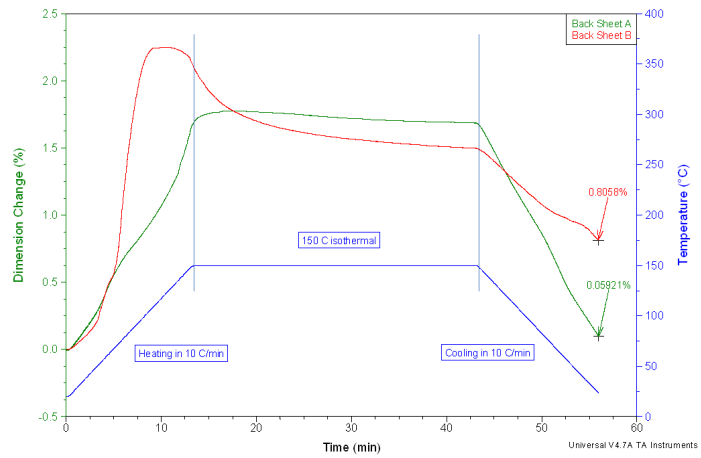

Figure 9: TMA Analysis of Two Different Back-Sheet Materials

Predicting Product Stability and Lifetime

Photovoltaic modules are designed to remain efficient for at least 25 years. A standard requirement is that a PV module must exhibit a decline in efficiency of no more than 20% during its lifetime. The efficiency is highly depending on the quality of the materials of construction, especially the EVA. To evaluate the lifetime, accelerated aging tests employing high temperature and high humidity in combination are often employed. However, these tests can still be time-consuming and imprecise. Thermo-gravimetric Analysis (TGA) can be used in combination with well-known kinetic models to predict the lifetime of materials at a variety of temperatures. This data can then be used to compare candidate resins.

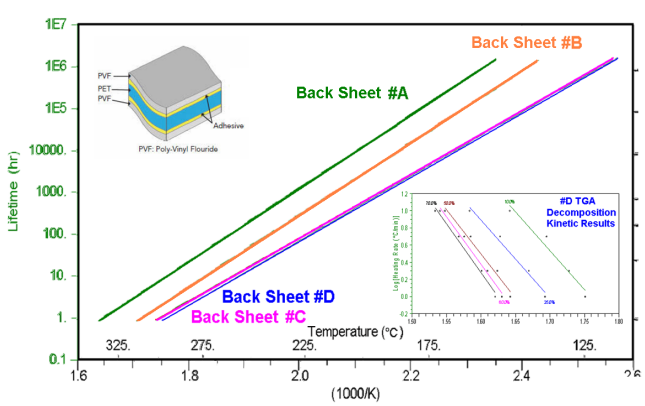

Figure 10: Lifetime Comparison of Back-Sheet Materials

PVF/PET/PVF is a common back-sheet material. The thermal decomposition of this

composite is initially measured by TGA, and the resulting data is evaluated using the protocol defined in ASTM Standard E1641 Decomposition Kinetics by TGA.[4] The kinetic evaluation can produce a lifetime plot as shown in Figure 10. This figure contains the TGA lifetime analysis results of 4 candidate back-sheet samples (A, B, C, D) provided by 4 different vendors. The results demonstrate that Sample A shows the best lifetime performance, while Samples C and D will exhibit similar diminished performance under identical conditions. Through further investigation, it was determined that Samples C and D used poorer quality adhesive materials.

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TA Instruments is the recognized world leader in Thermal Analysis technology, and offers a wide range of products with the advanced technology required for accurate determinations on photovoltaic materials.

Discovery DSC

The Discovery DSC™ represents the latest innovation from TA Instruments in the field of Differential Scanning Calorimetry and redefines the standard in performance, quality, and usability. The Discovery DSC features our innovative new Diffusion-Bonded Thermocouple technology which provides unmatched baseline flatness and repeatability, as well as improvement in measurement sensitivity, resolution, and precision. Modulated DSC® and a reliable 50-position autosampler are included as standard features.

DSC Q2000

The Q2000 is a research-grade DSC with superior performance in baseline flatness, precision, sensitivity, and resolution. Advanced Tzero technology and multiple new hardware and software features make the Q2000 powerful, flexible, and easy-to-use. Modulated DSC and a reliable 50-position autosampler are available as options.

[4] For more information go to http://www.astm.org or write to ASTM, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, +1 (610) 832-9500

	Discovery DSC	Q2000
Baseline Flatness (-50 to 300°C)	≤5 µW	≤10 µW
Baseline Accuracy	≤20µW	≤100µW
Baseline Repeatability	±5 µW	±50 µW
Temperature Accuracy	±0.025°C	±0.1°C
Temperature Precision	±0.005°C	±0.01°C
Enthalpy Precision	±0.04%	±0.05%
Tzero® Technology	Included	Included
Modulated DSC®	Included	Optional
50-Position Autosampler	Included	Optional

TGA Q5000IR

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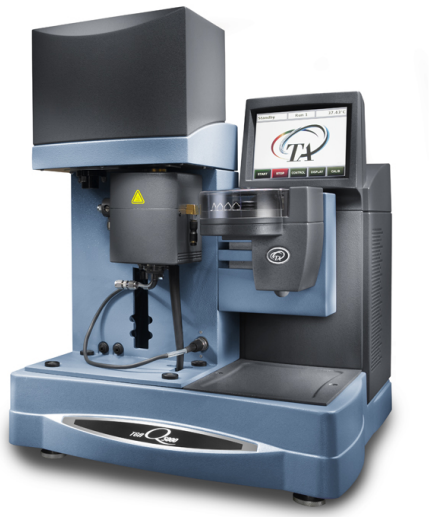

TMA Q400

The Q400 is the industry's leading research-grade thermo-mechanical analyzer with unmatched flexibility in operating modes, test probes, and available signals. The Q400 allows for additional transient (stress / strain), dynamic and Modulated TMA™ experiments that provide for more complete viscoelastic materials characterization plus a way to resolve overlapping thermal events (MTMA). The Q400 offers all the major TMA deformation modes necessary to characterize a wide range of materials.

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Headquartered in New Castle, DE (USA), TA Instruments prides ourselves in the technical competence and professionalism that our sales force offers. We are the only thermal analysis, rheology, and micro-calorimetry supplier recognized worldwide for our prompt, courteous and knowledgeable service staff, the hallmark of our company. Our technical support group is committed to handling all of your thermal analysis and rheology needs, and is available by phone, email and through the internet.

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TA Instruments

159 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • E-mail: info@tainstruments.com

Canada

Phone: 1-905-309-5387 • E-mail: shunt@tainstruments.com

Mexico

Phone: 52-55-5200-1860 • E-mail: mdominguez@tainstruments.com

Spain

Phone: 34-902-254-254• E-mail: spain@tainstruments.com

United Kingdom

Phone: 44-1-293-658-900 • E-mail: uk@tainstruments.com

Belgium/Luxembourg

Phone: 32-2-706-0080 • E-mail: belgium@tainstruments.com

Netherlands

Phone: 31-76-508-7270 • E-mail: netherlands@tainstruments.com

Germany

Phone: 49-6196-400-600 • E-mail: germany@tainstruments.com

France

Phone: 33-1-304-89460 • E-mail: france@tainstruments.com

Italy

Phone: 39-02-2650-983 • E-mail: italia@tainstruments.com

Sweden/Norway

Phone: 46-8-555-11-521 • E-mail: sweden@tainstruments.com

Japan

Phone: 813-5759-8500 • E-mail: japan2@tainstruments.com

Australia

Phone: 613-9553-0813 • E-mail: sshamis@tainstruments.com

India

Phone: 91-80-2319-4177 • E-mail: india@tainstruments.com

China

Phone: 86-21-64956999 • E-mail: info@tainstruments.com.cn

Taiwan

Phone: 886-2-2563-8880 • E-mail: info@tainstruments.com.tw

Korea

Phone: 82.2.3415.1500 • E-mail: ykson@tainstruments.com

To contact your local TA Instruments representative visit our website at www.tainstruments.com