Advances in chemical sensitivity and robust, solid-state designs for microwave/millimeter-wave instrumentation compel the expansion of molecular rotational spectroscopy as research tool into applied science. It is familiar to consider molecular rotational spectroscopy for air analysis. Those techniques for molecular rotational spectroscopy are included in our presentation of a more broad application space for materials analysis using Fourier Transform Molecular Rotational Resonance (FT-MRR) spectrometers. There are potentially transformative advantages for direct gas analysis of complex mixtures, determination of unknown evolved gases with parts per trillion detection limits in solid materials, and unambiguous chiral determination. The introduction of FT-MRR as an alternative detection principle for analytical chemistry has created a ripe research space for the development of new analytical methods and sampling equipment to fully enable FT-MRR. We present the current state of purpose-built FT-MRR instrumentation and the latest application measurements that make use of new sampling methods.