In forensic casework, non-invasive methods for postmortem examinations are extremely valuable because they allow medicolegal investigation of the body in its original state. For this reason, whole body postmortem multi-detector computed tomography (MDCT) is often used to provide visualization of the internal characteristics of a body prior to further invasive procedures. Postmortem MDCT scanning has also been used to locate gas reservoirs inside the body to assist in documenting the circumstances surrounding death and potential causes of death. Preliminary studies have demonstrated that analyzing the volatile organic compounds (VOCs) located in these gas reservoirs by comprehensive two-dimensional gas chromatography – high-resolution time-of-flight mass spectrometry (GC×GC-HRTOF-MS) may assist in providing information regarding the state of decomposition. The aim of the current study was to optimize procedures related to solid-phase microextraction (SPME) and GC×GC-HRTOF-MS analysis of gas reservoirs collected from deceased individuals. Postmortem MDCT scanning is becoming more widespread amongst medicolegal centers; therefore, a long-term objective would be to implement a total gas analysis screening method that would be non-destructive in nature and may assist pathologists in understanding body taphonomy in casework scenarios. SPME fiber extraction and quantification procedures were optimized in this study in order to make progress towards a method that could be applied in routine analyses in the future.