A22 In-House Production of a Metrologically Sound Traceable Ethyl Centralite Reference Material for Smokeless Powder Analysis

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After this presentation, attendees will be able to rationalize the in-house production of a metrologically sound, traceable, high purity Ethyl Centralite (EC) reference material for smokeless powder analysis and extend this knowledge to other compounds.

This presentation will impact the forensic science community by providing a method for analysts to make their own reference materials required in their routine analyses in a metrologically sound, traceable manner in order to compensate for the lack of available forensic reference materials. The chemical compound chosen to demonstrate this approach was EC, a common organic stabilizer of smokeless powders.

The analysis of organic compounds present in smokeless powder from ammunition and improvised explosive devices is important in crime elucidation, especially after the advent of "environmentally friendly" ammunition, free of barium, lead, and antimony. The most common organic additive in Brazilian ammunition is EC, in which its function is to stabilize the smokeless powder by delaying degradation of nitrocellulose. Both qualitative and quantitative analysis of additives and propellants in smokeless powder are important for forensic scientists. By qualitatively identifying and quantitatively determining the additives in smokeless powder it is possible to calculate a numerical propellant to stabilizer ratio which allows the association of handgun-fired organic gunshot residues with unfired powder. To perform quantitative analysis of most Brazilian ammunitions, the use of a smokeless powder certified reference material (CRM) containing EC is recommended for calibration, method validation, and quality control. Workers at the Brazilian National Institute of Metrology, Quality and Technology - INMETRO are working to produce a smokeless powder CRM containing EC as additive. However, to quantify EC in smokeless powder for the production of such a CRM, or even to quantify EC in common routine analysis, a high purity EC CRM is required for calibration. Because such a commercial CRM is also not yet available worldwide, in-house production of a metrologically sound, traceable EC reference material for smokeless powder analysis is necessary. The objective of this research was to assess the purity of a commercial EC in a metrologically sound, traceable manner.

High purity EC was purchased and the identity of EC was confirmed by determination of melting point, Mass Spectrometry (MS), Fourier Transform Infrared spectroscopy (FTIR), and 1H and 13C Nuclear Magnetic Resonance (NMR). The purity was assessed by three independent methods: Differential Scanning Calorimetry (DSC), quantitative 1H NMR (using benzoic acid NIST 650b SRM as internal standard), and mass balance. The latter consisted of a broad investigation of the impurities, which included identification and quantification of non-volatile organic impurities (by gas chromatography coupled to flame ionization detector – GC-FID), volatile organic impurities (by headspace GC-FID), water content (by coulometric Karl Fischer titration), and inorganic impurities (by ashing).

EC melting point was 72.57 ± 0.03°C. Mass spectra of sample showed m/z = 268, 164, 148, 120, and 77, which is consistent with EC structure. FTIR and 1H and 13C NMR spectra were consistent with EC structure. All these data confirmed the identity of the commercial product as EC.

EC purity by DSC was 99.83 ± 0.05 mol % (average and standard deviation). EC purity (m/m) by quantitative 1H NMR was 99.89 ± 0.7% (average and measurement uncertainty – 95% CI; k = 1.98). EC purity (m/m) by mass balance was 99.86 ± 0.02% (average and measurement uncertainty – 95% CI; k = 2). The mass balance is also called 100% - impurities % method and the individual impurities found were (m/m): (1) non-volatile organic impurities: methyl-ethyl centralite (0.0762%); (2) volatile organic impurities: m/p-xylene (0.0263%), ethyl benzene (0.0079%) and dimethylchloramine (0.013%); (3) water content: 0.0083%; and, (4) inorganic impurities: 0.0025%.

EC purity results by three independent methods are in agreement with one another. It was decided to consider the mass balance result (99.86 ± 0.02% m/m) because of the reduced measurement uncertainty valor. Metrological traceability came by the use of a primary method (DSC), by the use of a certified reference material in quantitative NMR, and by a detailed investigation of impurities, which provided an indirect purity assessment (mass balance). This approach can be used for the production of in-house reference materials suitable for calibration, quality control (after spiking a blank matrix), and method validation involving forensic analysis.

Reference Material, Smokeless Powder, Ethyl Centralite

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