

Development of High Accuracy Hazardous Air Pollutants Primary Standard Gas Mixtures

ABSTARCT

Volatile organic compounds also classified as hazardous air pollutants (HAPs) such as benzene, chloroform, dichloromethane, 1,2-dichloroethane, tetrachloroethylene, trichloroethylene, vinyl chloride and 1,3-butadiene. have been identified to be potential carcinogens and travel longer distances from their point sources from one environmental compartment to the other. Monitoring of HAPs in ambient air has been receiving great attention across the world due to its contribution to emission studies of air pollution. However, to accurately measure these contaminants in the atmosphere standards of high accuracy are needed to ensure good air quality monitoring. Measurements which are accurate have traceability to SI unit because they are comparable internationally and are associated with low uncertainty.

In this study the development of gaseous standard gas mixtures was carried following gravimetric method. The preparation of gaseous mixture is difficult due to the nature and properties of gas. To accurately follow gravimetric preparation, purity analysis of high pure starting materials was performed to obtain the precise composition of the final mixture. Various techniques such as gas chromatography coupled to mass-spectroscopy, thermal conductivity detector and pulsed charged ionisation detector were used.

The development of gases was carried out following direct-step dilution for pure liquid samples using syringe method and multiple-step dilution for pressurized liquid. To carefully understand the behaviour of gases, binary gas mixtures were prepared in nitrogen at 10 $\mu\text{mol/mol}$, followed by 10 $\mu\text{mol/mol}$ multicomponent of six gas component and 100 nmol/mol eight components to check for matrix interference.

Gas chromatography coupled to flame ionisation detector was used to verify gravimetric concentration and following ABA sequence using one-point calibration. The sequence was used to monitor instrumental drift, affecting analysis results. No impurities were detected in benzene, chloroform, tetrachloroethylene,

trichloroethylene, dichloromethane and 1,2-dichloroethane. Nitrogen impurities were detected in vinyl chloride at $681 \pm 4.4 \text{ } \mu\text{mol/mol}$ and 1,3-butadiene at $254 \pm 2.1 \text{ } \mu\text{mol/mol}$.

The method of analyses obtained good results with instrumental drift of less than 1.0. Good accuracy of less than 3 % was obtained between the gravimetric and analytical results. Relative expanded uncertainty was different for the binary gas mixtures, benzene was obtained within 3.2 %, tetrachloroethylene 1.9 %, chloroform 2.5 %, vinyl chloride 0.15 %, trichloroethylene 2.3 %, dichloromethane 2.7 %, 1,2-dichloroethane 2.5 % and 1,3 butadiene 0.15 % at coverage factor of $K=2$ at 95 % confidence level. Multicomponent development showed no interferences within the mixture during analyses for determining of accuracy of mole-fraction gravimetrically prepared. Percentage difference between the gravimetric and analytical values were within 2.03 % with relative expanded uncertainty ranging between 3.1 to 9.8 % at $K=2$ at 95 % confidence level.

The developed multicomponent was successfully used to identify and quantify HAPs found in air sample.

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