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Project Summary

Direct Calibration of GC/MS Systems Using SRM Gas Cylinders

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A cryogenic trapping system has been developed for use in calibrating GC/MS systems for the analysis of volatile organic compounds. This system provides for direct Standard Reference Material (SRM) traceability on data generated on gaseous samples. The cryogenic trap is a coil of stainless steel tubing immersed in a cryogen to trap and preconcentrate organic species present in a gaseous sample. The trap also contains a heated injection port for the addition of isotopically labeled compounds for use in isotope dilution measurements. The first part of this research is concerned with the development of isotope dilution mass spectrometry (IDMS) as an independent method for the quantification of analytes in gaseous samples to be used as standards. Results are presented for the determination of bromobenzene in nitrogen at nominal concentrations of 1 and 25 ppb. In the second part of the research, a calibration curve method was developed for using these standards in auditing the performance of GC/MS systems. This method is demonstrated on multicomponent aromatic mixtures in the 10 to 200 ppb concentration range. The system using the calibration curve method was evaluated at an independent laboratory and compared with a static dilution bottle calibration curve method.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Summary

The goal of this project was to develop a trapping system that can be used to introduce volatile organic compounds (VOCs) at low concentrations (ppb) from a gas cylinder into a combined gas chromatograph/mass spectrometer (GC/MS) instrument. A trap has been constructed that condenses the gaseous sample from the cylinder using a small coil immersed in a dry ice-ethanol bath. The coil is then electrically heated to revolatize the sample. The gas is introduced into the GC/MS with a syringe needle that is silver soldered to the coil tubing so that the effluent can be injected directly into the instrument. A heated injection port also allows introduction of liquid solutions into the GC/MS. The performance of the trap was evaluated using isotope dilution mass spectrometer (IDMS) measurements on samples that had been well characterized by other methods. Response factor determinations were made using isotopically labeled analytes.

A GC/MS method based on establishing a calibration curve was developed that permits a direct comparison of the concentrations of trace components from two gas sources. This provided a means of linking data from different laboratories to a common SRM. The cryogenic trap was used for this method, since it can be employed with any GC system that contains a septum inlet. The principle of the calibration curve is to establish a plot of response versus amount for a particular analyte. From a measured volume of a sample with an unknown concentration of the analyte and its response, the concentration can be calculated. SRM gas cylinders containing the analytes of interest are well suited as calibrant

samples because of their certified values for analytes. In order for this method to work properly, a known relationship, preferably linear, must be established over the desired concentration range. This, in turn, requires that reproducible amounts of the sample be trapped and delivered to the GC/MS for analysis. The procedure was validated by measurements at an independent laboratory on two cylinders containing "unknown" concentrations of benzene, chlorobenzene, and bromobenzene. A cylinder containing known concentrations of the same compounds was used for calibration. All of the cylinders had been previously prepared and analyzed at the National Bureau of Standards (NBS) using the trapping system. The combined average values for all the measurements made on these cylinders at both laboratories were within two standard deviations of the prepared value for all analytes except bromobenzene in one cylinder. This value was slightly more than three standard deviations outside of the prepared concentration.

The components of the gas cylinders were also analyzed by GC/MS using a calibration curve generated by injections of pure gaseous compounds from static dilution flasks. This was the usual method of calibration of the independent laboratory and afforded a way to compare the results of the two ways to calibrate the analytical system. The differences in the relative standard deviations for the two sets of measurements were not significant, indicating similar precision for both laboratories. The average percent difference between delivered and measured amounts for the analytes was biased on all cases with 11% to 35% more of the compounds detected than was delivered.

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The complete report, entitled "Direct Calibration of GC/MS Systems Using SRM Gas Cylinders," (Order No. PB 86-110715/AS; Cost: $9.95, subject to change) will be available only from:
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