



Project Summary

Investigation of Selected Detectors for Application on Hydrocarbons Continuous Emissions Monitoring Systems

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The development of a prototype emissions monitoring instrument to provide continuous or semi-continuous quantitative measurement of total gaseous nonmethane organic carbon (TGNMOC) emissions from stationary sources will provide better characterization and control of compounds listed in Title III of the Clean Air Act Amendments of 1990. To meet this goal a search was initiated to identify detection systems for TGNMOC that are both simple to use and accurate for a wide range of organic compounds. The measurement of oxygenated compounds is of particular interest since many emission sources emit a considerable volume of these compounds.

Detection systems were identified by searching detector manufacturers' literature and talking with manufacturers' technical personnel. Several detector systems are marketed as capable of measuring TGNMOC. In this report, data are presented on the laboratory evaluation of a Catalyzed Flame Ionization Detector, a Thermionic Ionization Detector, an Oxygen-Flame Ionization Detector, and an Elemental Analyzer for TGNMOC measurement. Fourier Transform Infrared Spectroscopy was also evaluated as a candidate detector. The primary performance requirement was that the detectors produce equal response for all organic compounds in a mixture, including oxygenated compounds, based on the number of carbon atoms in the compound. None of the detection systems evaluated met the primary performance goal of uniformly measuring organic carbon regardless of the chemical structure. Some detectors were successful for

many classes of organic compounds, but oxygenated compounds presented a challenge that none of the detection systems could master.

This Project Summary was developed by EPA's National Exposure Research 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).

Introduction

The objective of this project was to identify an appropriate detection system for incorporation into a prototype total gaseous nonmethane organic carbon (TGNMOC) emissions monitoring instrument. The accurate measurement of TGNMOC is critical to total VOC measurement required at many industrial processes. The measurement of oxygenated compounds is of particular interest since many emission sources emit a considerable volume of these compounds. The primary performance requirement was that the detectors produce equal response for all organic compounds in a mixture, including oxygenated compounds, based on the number of carbon atoms in the compound.

Although the flame ionization detector (FID) has been used as a universal detector for complex mixtures of organic compounds, compounds containing heteroatoms have been shown to yield lower response than straight chain aliphatic hydrocarbons¹, producing an underestimate

¹ Skoog, D. A. *Principles of Instrumental Analysis*. Third Edition, Saunders College Publishing, New York, 1985. p. 767.

of organic carbon. The following manufacturers of instruments indicated in their literature that they should be successful in determining TGNMOC including oxygenated organic compounds. These instruments were evaluated in this study.

The Catalytic Flame Ionization Detector (CFID) manufactured by DETector Engineering and Technology, Inc, (Walnut Creek, CA) is marketed as a detection system that provides enhanced responses for organic compounds containing heteroatoms. The Thermionic Flame Ionization Detector (TID), also manufactured by DETector Engineering and Technology, is marketed as an oxygen-selective detector when operated in a nitrogen (N_2) environment. The Oxygen-Flame Ionization Detector (O-FID) manufactured by Fisons Instruments (Danvers, MA) is marketed as the recommended detection system of the European Economic Community and the U.S. Environmental Protection Agency for analysis of oxygenated compounds in gasoline.

The Elemental Analyzer (EA) also manufactured by Fisons, is marketed as a detection system for simultaneous carbon, H_2 , N_2 , and O_2 determinations from solid, liquid, or gas samples. High detection limits and detection of methane and carbon

dioxide interfere with the application of this detection system to TGNMOC measurement.

A Fourier Transform Infrared (FTIR) optical detection system was investigated. The FTIR technique allows the collection of the entire IR spectrum from about 4000 to 200 wave numbers within a few seconds. The molecular signature is obtained over a broad spectral range; accurate identification of the species can be made from this signature. The advantage of taking the entire IR spectrum is that if interfering species are present they will almost certainly not be present at all of the same frequencies, and judicious selection of analysis regions will produce interference-free detection.

Laboratory Procedures

The FID, CFID and TID were evaluated with liquid standards containing the oxygenated and non-oxygenated compounds. The compounds were acetaldehyde, methanol, acetone, 2-butanone, benzene, butyl cellosolve®, benzaldehyde, hexane, heptane, iso-octane, nonane, methylene chloride, and triethylamine. The FTIR spectrometer was evaluated using a synthetic mixture of standards prepared in SUMMA® canisters.

Conclusions

None of the detectors evaluated met the performance goal of universal, linear, organic carbon response. While some success was realized for many classes of organic compounds, oxygenated compounds presented the strongest challenge to the detection systems evaluated. Within an individual chemical class, a 1:1 linear carbon response relationship was achieved, but a linear carbon response relationship was not achieved when comparing one chemical class to another. These detectors are useful for selective applications, but they do not meet the needs of an universal detector for total carbon in a sample containing a mixture of compounds from various chemical classes.

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The complete report, entitled "Investigation of Selected Detectors for Application on Hydrocarbons Continuous Emissions Monitoring Systems," (Order No. PB97-143168; Cost: \$21.50, subject to change) will be available only from:

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