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# Project Summary

# Investigation of Analyzer Problems in the Measurement of $NO_X$ from Methanol Vehicles

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The rapid development of vehicles designed to operate on methanol fuel has prompted development and evaluation of methods for measuring their emissions. Classical measurement methods prescribed for gasoline cars are not always applicable to methanol cars because of the inherently high concentrations of methanol and formaldehyde in their emissions. One such exception applies to the FID (flame ionization detector) measurement of hydrocarbons in the presence of methanol. Another less publicized exception and the subject of this report pertains to the chemiluminescent method of measuring nitrogen oxides ($NO_X$) from methanol cars.

The chemiluminescent method is based upon the principle that nitric oxide (NO) can be reacted with ozone ($0_3$) to give about 10 percent electronically excited $NO_2^*$. When the electronically excited $NO_2^*$ transits to its normal state, a detectable light emission is given off. The intensity of this emission is directly proportional to the mass flow rate of NO into the reaction chamber. The light emission is detected and measured by a photomultiplier tube and the associated electronics process a voltage response which is proportional to the intensity of light being emitted. To make this method applicable to $NO_X$ (NO + $NO_2$) emissions, the $NO_2$ in the sample is changed to NO in an $NO_2$ converter.

Problems with chemiluminescent $NO_X$ measurement from methanol cars were first reported as large variations in $NO_X$ data and large values of $NO_2$. Later descriptions identified a sort of residual response which occurred immediately following sample analysis while the analyzer was being zeroed. These symptoms tried but found to be impractical because of resultant zero/span difficulties. The interference was finally cleared by cleaning the analyzer's reaction chamber. Isolation of the reaction chamber as the source of contamination was attained by systematically exchanging parts between the old and new analyzers until the interference went away.

$NO_X$ measurements were made on tailpipe emissions from a Methanol Escort with the older Beckman 951A before and after its reaction chamber was cleaned. The measurements were compared with those from a TECO chemiluminescent NOx analyzer which had demonstrated no response to either methanol or formaldehyde. Before cleaning, the Beckman measurement was about 35 percent higher than the measurement from the TECO. After cleaning, the difference between measurements was reduced to about 3 percent.

Toward the conclusion of the study, the new Beckman 951A began responding to formaldehyde. A

**response between 4 and 7 ppm was obtained with a 100 ppm formaldehyde sample. No response to methanol occurred. It is estimated that this first observed response to formaldehyde occurred after subjecting the new analyzer to three or four 60 liter bags of 100 ppm formaldehyde and two or three bags of 250 ppm methanol.**

***This Project Summary was developed by EPA's Atmospheric Sciences 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).***

## Conclusions and Recommendations

A study was carried out to investigate the extent and source of irregularities related to the measurement of $NO_x$ emissions from methanol cars. Corrective measures were also explored. Because the results in this study were obtained in tests using Beckman 951A Chemiluminescent Analyzers, some of the conclusions based on those results are relative to the experience with that particular analyzer. However, there is evidence which suggests that other types of chemiluminescent analyzers could be similarly affected.

The conclusions of the study are as follow:

1. $NO_x$ chemiluminescent analyzers respond to formaldehyde and methanol gases when exposed to high concentrations of these gases over extended time periods.
2. The response to formaldehyde and methanol can be severe enough to cause significant errors in the measurement of $NO_x$ emissions from methanol cars.
3. Analyzer response to methanol accounts for most of the error when measuring $NO_x$ emissions from methanol cars.
4. Reactions involving formaldehyde in the reaction chamber are the principal cause of spurious analyzer response with samples containing either methanol or formaldehyde.
5. The most effective way of eliminating the spurious response is to clean the reaction chamber inaccordance with the manufacturer's instructions.

Further research is recommended t definitively identify the wavelengths c light emission associated with th interference. Bracketing the range c those wavelengths might b accomplished through an examination c the effect of different cut-off filters o response to formaldehyde. Such a approach might lead to the selection c an improved filter which could eliminat the interference altogether.

It is also recommended that a study b carried out on other chemiluminescer analyzers to determine the effect of lor term exposure to high concentrations c methanol and formaldehyde. Thus f only the Beckman 951A models hav been so exposed as a result of emissic tests on malfunctioning methanol car Until such studies are completed, or must assume that all NC chemiluminescent analyzers cou develop problems associated wi extended testing on methanol car Therefore, when testing methanol car more than the usual care should be take by instrument operators to assure th their instruments are clean and w maintained.

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*The complete report, entitled "Investigation of Analyzer Problems in the Measurement of $NO_x$ from Methanol Vehicles," (Order No. PB 89-124 374/AS; Cost: $13.95, subject to change) will be available only from:*

*National Technical Information Service*
*5285 Port Royal Road*
*Springfield, VA 22161*
*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

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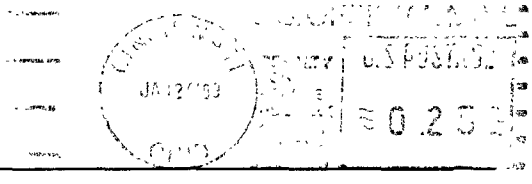

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