



Project Summary

Development and Validation of a Method for Measuring Exempt Volatile Organic Compounds and Carbon Dioxide in Consumer Products

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Ground-level ozone can cause a variety of adverse health effects as well as agricultural and ecological damage. Controlling emissions of volatile organic compounds (VOCs) is important to reducing ground-level ozone; however, not all VOCs are photochemically reactive and several have been exempted from control regulations. Currently, there is no standard method for measuring the exempt VOC content of consumer products. This report describes the development of such a method. The new method involves heating a sample in an oven at 110°C for 1 hour while purging the sample container with nitrogen gas. The resultant mixture of nitrogen and volatile compounds from the sample is then collected in a Tedlar™ bag and analyzed by gas chromatography with mass selective detection (GC/MSD). An internal standard is added to the sample container to permit quantitation without measurement of the purge gas volume. The method was evaluated by analyzing samples that were spiked with known amounts of the exempt compounds. Recoveries of spiked compounds were excellent, ranging from 86% to 107% for the compounds and products tested. This method should be applicable to other volatile compounds that might be present in consumer products and could be useful in evaluating the risk that these products pose to the environment.

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Research Laboratory's Air Pollution Prevention and Control Division, 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).

Ground-level ozone can cause a variety of adverse health effects as well as agricultural and ecological damage. To control the levels of ozone in the environment, the U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for ozone. In 1990, 98 areas in the country did not meet the NAAQS for ozone, with over 150 million Americans living in these areas. VOCs are important contributors to the formation of ozone in photochemical smog. Control of VOC emissions is an important strategy for controlling ozone levels. The 1990 Amendments to the Clean Air Act (CAAA) require EPA to conduct a study of VOC emissions from consumer products. However, there was no standard method for measuring the VOC content of consumer products. Such measurements are needed to assess the risk to the environment posed by VOCs in consumer products. Such a method will also be needed if EPA determines that the risk associated with VOCs in consumer products is sufficient to require control regulations.

To address the need for measurement of VOCs in consumer products, EPA has established a research program. This program has already produced results in four previous phases:

- Phase I - Preliminary studies were performed on two candidate methods for VOC measurement (EPA Reference Method 24 and Gravimetric Purge and Trap Gas Chromatography).
- Phase II - A Consumer Products Test Methods Work Group was established with participation from a number of state and federal agencies. This Work Group, after consideration of an initial list of 10 candidate methods, reached a consensus that further research should be concentrated on two methods: EPA Reference Method 24 and Gravimetric Purge and Trap Gas Chromatography.
- Phase III - A test method was developed to determine the total VOC content of consumer products. This method was based on EPA Reference Method 24, with added modifications for sampling and analysis of consumer products.
- Phase IV - The test method developed in Phase III was validated in an interlaboratory study.

The validated total VOC method (Phase IV) for consumer products gravimetrically measures the total volatile content and determines the amount of water by gas chromatography with thermal conductivity detection (GC/TCD). The water content is then subtracted from the total volatile content to calculate the total VOC content; however, many VOCs have been exempted from the list of regulated VOCs (40 CFR 51.100) due to their low photochemical reactivity and thus low ozone formation potential. Measurement of these exempt VOCs in consumer products would allow EPA to correct the total VOC measurements to better reflect the total ozone formation risk that consumer products pose to the environment.

Upon examination of the exempt VOC compounds, only 12 compounds are relevant to consumer products. Carbon dioxide, which is measured by the total VOC method, is also exempt and therefore is added to the target list shown in Table 1.

Since it is anticipated that determining the exempt compound content will be considerably more expensive and time consuming than measurement of total VOC content, a two-step approach to assessing the ozone formation risk posed by

consumer products is envisioned. The first step would involve measurement of total VOC content for the product. Consumer products that might pose significant risks for ozone formation based on their total VOC content would then undergo a second step of having their exempt VOCs measured to provide a better assessment of their ozone formation risk. This report describes the development and validation of an exempt VOC measurement method that would be used as the second step of the VOC risk assessment process. The measurement method involves heating a sample in an oven at 110°C for 1 hour while purging the sample container with nitrogen gas. The resultant mixture of nitrogen and volatile compounds from the sample is then collected in a Tedlar™ bag and analyzed by gas chromatography with mass selective detection (GC/MSD). An internal standard is added to the sample container to permit quantitation without measurement of the purge gas volume. The method was evaluated by analyzing samples that were spiked with known amounts of the exempt compounds. Recoveries of spiked compounds were excellent, ranging from 86% to 107% for the compounds and products tested.

Table 1. Exempt VOC Method Target List

Compound Name	Class II Ozone Depleting Chemicals ^c
carbon dioxide ^a	chlorodifluoromethane (HCFC-22)
methylene chloride (dichloromethane)	1,1,1-trifluoro 2,2-dichloroethane (HCFC-123)
1,1,1,2-tetrafluoroethane (HFC-134a)	1,1-dichloro 1-fluoroethane (HCFC-141b)
pentafluoroethane (HFC-125)	1-chloro 1,1-difluoroethane (HCFC-142b)
1,1,1,2-tetrafluoroethane (HFC-134)	
1,1,1-trifluoroethane (HFC-143a)	
1,1-difluoroethane (HFC-152a)	
acetone	
tetrachloroethylene (perchloroethylene or perc) ^b	

^aCarbon dioxide is not a VOC, but is measured by the total volatiles method and has been added to the target list to permit correction of measured total volatiles.

^bTetrachloroethylene was added to the exempt list during the course of this work (61 FR 4588, February 7, 1996).

^cUse of class II ozone-depleting chemicals (58 FR 65018, December 10, 1993) is currently restricted. These chemicals may be phased out in the future.

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J. Kaye Whitfield is the EPA Project Officer (see below).

The complete report, entitled "Development and Validation of a Method for Measuring Exempt Volatile Organic Compounds and Carbon Dioxide in Consumer Products," (Order No. PB97-143143; Cost: \$21.50, subject to change) will be available only from:

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