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Laboratory and Field Evaluation of Crystallized DOW 704 Oil on the Performance of the Well Impactor Ninety-Six Fine Particulate Matter Fractionator

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ABSTRACT

Subsequent to the 1997 promulgation of the Federal Reference Method (FRM) for monitoring fine particulate matter ($PM_{2.5}$) in ambient air, U.S. Environmental Protection Agency (EPA) received reports that the DOW 704 diffusion oil used in the method's Well Impactor Ninety-Six (WINS) fractionator would occasionally crystallize during field use, particularly under wintertime conditions. Although the frequency of occurrence on a nationwide basis was low, uncertainties existed as to whether crystallization of the DOW 704 oil may adversely affect a sampling event's data quality. In response to these concerns, EPA and the State of Connecticut Department of Environmental Protection jointly conducted a series of specialized tests to determine whether crystallized oil adversely affected the performance of the WINS fractionator. In the laboratory, an experimental setup used dry ice to artificially induce crystallization of the diffusion oil under controlled conditions. Using primary polystyrene latex calibration aerosols, standard size-selective performance tests of the WINS fractionator showed that neither the position nor the shape of the WINS particle size fractionation curve was substantially influenced by the crystallization of the DOW 704 oil. No large particle bounce from the crystallized impaction surface was observed. During wintertime field tests, crystallization of the DOW 704 oil did not adversely affect measured $PM_{2.5}$ concentrations. Regression of measurements with crystallized DOW 704 versus liquid dioctyl sebacate (DOS) oil produced slope, intercept, and R^2 values of 0.98, 0.1, and 0.997 $\mu g/m^3$, respectively. Additional field tests validated the use of DOS as an effective impaction substrate. As a result of these laboratory and field tests, DOS oil has been approved by EPA as a substitute for DOW 704 oil. Since the field deployment of DOS oil in 2001, users of this alternative oil have not reported any operational problems associated with its use in the $PM_{2.5}$ FRM. Limited field evaluation of the BGI very sharp cut cyclone indicates that it provides a viable alternative to the WINS fractionator.

IMPLICATIONS

By providing sharp fractionation of aspirated ambient aerosols, EPA WINS fractionator is an integral part of the FRM for $PM_{2.5}$. Results of laboratory and field investigations showed that occasional crystallization of the DOW 704 oil used in the WINS does not change the cut point nor slope of the WINS fractionation curve. $PM_{2.5}$ measurements obtained during periods of crystallized oil, therefore, can be considered as valid for purposes of making National Ambient Air Quality Standards compliance decisions. An alternative impaction oil has been approved for use by EPA, and no problems have been experienced with its widespread use.

INTRODUCTION

In response to growing health concerns associated with atmospheric fine particles, U.S. Environmental Protection Agency (EPA) promulgated in 1997 a new particulate matter (PM) standard accompanied by a new sampling methodology.[1,2] Based on a review of pertinent literature, a new metric (fine PM [$PM_{2.5}$]) was adopted, and its measurement method was specified as a 24-hr, integrated sample of which the mass concentration was to be determined gravimetrically.

Accurate $PM_{2.5}$ fractionation of aspirated atmospheric aerosol is a critical feature of the measurement method. In the Federal Reference Method (FRM) sampler, this fractionation is provided by a single-stage, single-jet impactor known as the WINS (Well Impactor Ninety-Six). Particles >2.5 μm in aerodynamic diameter are efficiently collected on a glass fiber filter immersed in a low-volatility diffusion oil. Particles <2.5 μm in aerodynamic diameter are transported to a Teflon afterfilter for subsequent gravimetric measurement.

Critical to the successful development of the WINS separator was the selection of the impaction substrate needed to ensure complete sticking efficiency of impacting particles to the impaction surface. After a review of available substrates, a single component diffusion oil, tetramethyltetraphenyltrisiloxane, CAS 3982-82-9 (herein referred to as DOW 704), was selected as the substrate that possessed the most favorable properties for field operation. Commercially available from a variety of sources, DOW 704 had been used previously in inertial impactors with favorable results.[3] Moreover, extensive laboratory and preliminary field evaluation of the DOW 704 oil demonstrated that it met the method's performance specifications well. Although manufacturers of this oil cautioned that it can occasionally "crystallize under rare and undefined conditions below 21 °C," EPA's laboratory (Research Triangle Park, NC) and field evaluation (Denver, CO) of prototype $PM_{2.5}$ FRM samplers during the winter and spring of 1996 revealed no field-related problems associated with the selected DOW 704 oil.

Following the $PM_{2.5}$ method's promulgation, EPA received reports that the DOW 704 diffusion oil used in the method's WINS separator had been occasionally observed to crystallize during field use. Reports first originated in 1999 from the State of Connecticut Department of Environmental Protection (CT DEP) and prompted EPA to request that FRM site operators throughout the country regularly inspect WINS wells for oil crystallization and report their observations to the agency. States that have subsequently reported that crystallization has occurred on an occasional basis include Connecticut, Maine, Michigan, New York, North Dakota, Pennsylvania, and Wisconsin. However, site operators in Alaska, California, Colorado, Illinois, Iowa, Minnesota, Montana, Utah, Vermont, and Edmonton (Alberta, Canada) have not observed oil crystallization at their $PM_{2.5}$ monitoring sites.

Factors that contribute to the crystallization events are not currently well understood. Very cold sampling conditions appear to increase the probability of DOW 704 crystallization, although no particular temperature has been documented to initiate the process. As illustrated by the list of sampling sites that have not experienced oil crystallization, low temperature is certainly not the sole causative agent. In conjunction with reduced ambient temperatures, the crystallization process may be affected by oil contaminants, relative humidity (RH), site operator procedures, oil storage and handling procedures, collected aerosol properties, gaseous copollutants, and impaction filter properties.

Although the frequency of occurrence and the conditions under which crystallization occurs had not yet been determined, uncertainties existed as to whether the crystallization of the DOW 704 oil during a given sampling event adversely affected the data quality of the event. In particular, concerns were expressed that the measured $PM_{2.5}$ concentration may be artificially high during a crystallization event because of possible particle bounce from the crystallized impaction surface onto the $PM_{2.5}$ collection filter of the sampler.

In direct response to these concerns, EPA and the CT DEP conducted a series of laboratory and field tests to characterize the size-selective behavior of the WINS separator in conjunction with crystallized DOW 704 oil. Laboratory tests were conducted under carefully controlled conditions using hard, spherical calibration aerosols to maximize any bounce from the crystallized surface. In addition to the laboratory tests, wintertime field tests were conducted in Windsor, CT, using collocated FRMs equipped with both crystallized and noncrystallized oil.

This paper describes the WINS separator in detail, describes the procedures used to characterize the effect of crystallized DOW 704 oil on WINS performance, and presents the results of these tests. This paper also documents the results of laboratory and field tests of an alternative impaction substrate, dioctyl sebacate (DOS) oil, of which the documented fp is −48 °C (−54 °F) and, thus, represents an alternative oil for sampling sites that periodically experience crystallization of the DOW 704 oil. Last, field test results are presented of the BGI very sharp cut (VSC) cyclone, which was designed as a possible alternative fractionator to the WINS for use in the $PM_{2.5}$ FRM.

EXPERIMENTAL WORK

Description of the WINS Separator

Figure 1 is a schematic drawing of the WINS separator for $PM_{2.5}$ measurement. The unit consists of three primary components: upper housing, impaction well, and lower housing. The upper housing of the WINS is located downstream of the sampler coarse PM (PM_{10}) size-selective inlet and receives the <10-μm fraction of the aspirated ambient aerosol. For purposes of cost and fabrication simplicity, aerosol size fractionation in the WINS is provided by a single jet, single stage impactor of which the nozzle is an integral part of the upper housing.

Regardless of the inertial fractionation mechanism (conventional impaction, virtual impaction, or cyclonic separation) and the separator design, all of the separators overload to some degree if continuously exposed to particle-laden airstreams. The magnitude of the performance change versus loading is a complex function of separator design, aerosol concentration, particle size distribution, particle type, sampling flow rate, sampling time, and separator maintenance schedules and procedures. In recognition that overloading ultimately occurs in all separators, the impaction well of the WINS was designed to be easily accessible, removable, and replaceable. In effect, the overloaded surface is designed to be replaced periodically with a clean unit. The dirty well can then be taken back to the laboratory, cleaned, and prepared for subsequent reuse. A previously used WINS filter is not intended to be cleaned but simply discarded and replaced with a new filter.

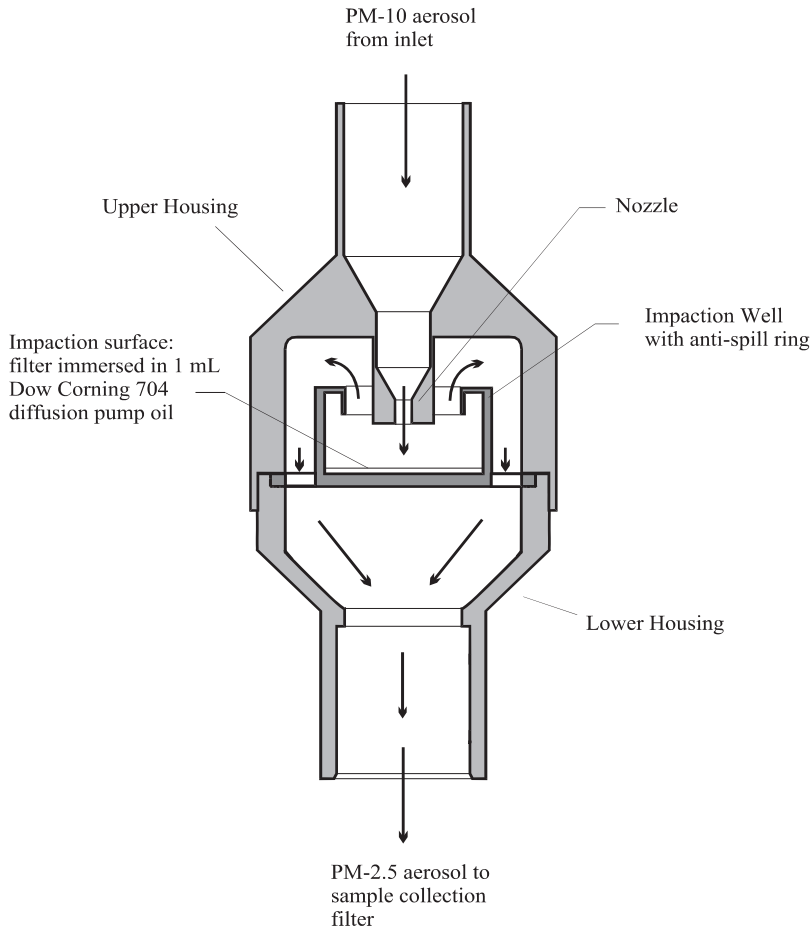

Figure 1. Schematic of WINS separator showing location of major components.

The impaction surface of the WINS well consists of a 37-mm diameter glass fiber filter saturated with 1 mL of a single component diffusion oil (tetramethyltetraphenyltrisiloxane, DOW 704) to assure retention of impacted particles. The inherently low vapor pressure of the oil (maximum 2×10^{-8} Torr at 25 °C) ensures that the oil does not readily volatilize and, thus, does not adversely affect the downstream $PM_{2.5}$ measurement. The low kinematic viscosity of the oil (39 cSt at 25 °C) ensures that the oil effectively wicks up by capillary action through previously deposited particles.[3] The novel geometry of the well's antispill configuration prevents loss of oil should the well become inadvertently turned over or on its side.

The size-selective performance of the WINS separator had been carefully calibrated in the laboratory[4] using spherical, monodisperse calibration aerosols. The calibration was conducted at nominal test conditions (Q = 16.67 actual L/min; T = 25 °C; p = 760 Torr; 1 mL of oil). As depicted in Figure 2, results showed that the WINS possessed a cut point of 2.48 μm aerodynamic diameter and had a fairly sharp particle size separation curve. Test results conducted with primary calibration aerosols composed of ammonium fluorescein aerosols (detected fluorometrically) agreed well with results obtained using polystyrene latex (PSL) calibration aerosols detected using a time-of-flight particle spectrometer (Model Aerosizer-LD, TSI Inc.).

Study Design

The primary data quality issue associated with WINS oil crystallization during a given sampling event is as follows: does the presence and nature of the crystallized oil adversely affect the quality of the measured $PM_{2.5}$ mass concentration? This, in turn, leads to the more fundamental question: does the presence and nature of the crystallized oil adversely affect the performance of the WINS separator?

As described previously, the primary purpose of the DOW 704 diffusion oil in the WINS separator is to ensure complete retention of particles that strike the glass-fiber filter. As was demonstrated during the WINS calibration, the physical properties of liquid DOW 704 are such that completely inelastic particle-substrate collisions occur, which prevents particle bounce from the surface. Regarding crystallized DOW 704 during a given sampling event, the issue is whether or not the crystallized oil's mechanical properties are such that partially elastic collisions occur, resulting in the possibility of particle bounce from the surface.

Although there exists a fundamental understanding of the factors that influence particle bounce,[5] actual collection mechanics are strongly influenced by particle size, particle shape, particle density, particle mechanical properties, jet velocity, and the local mechanical properties of the impaction substrate and/or its adhesive coating. Because these parameters are typically unknown and their

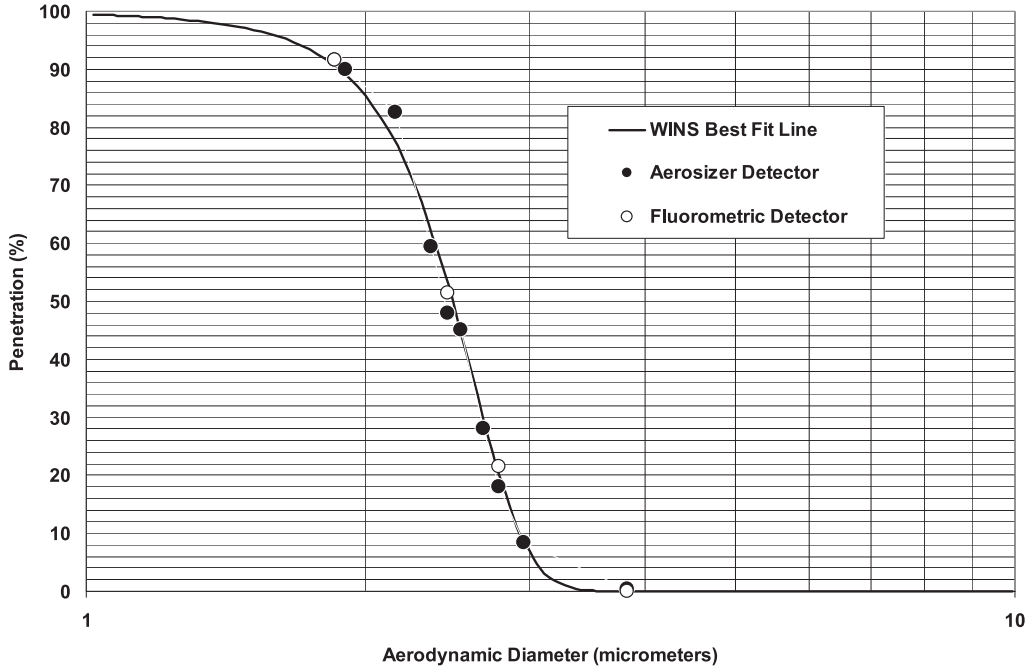

Figure 2. Laboratory calibration curve of the WINS separator as a function of quantitation method and particle type. ○ and ● represent calibration aerosols composed of PSL and ammonium fluorescein, respectively.

interactions complex, particle bounce characteristics in inertial impactors are typically determined experimentally under controlled conditions.[6]

Although results of laboratory tests can be extrapolated to predict the field performance of the fractionator, field tests under actual conditions are always of value to ensure that these extrapolations are correct. In the case of the DOW 704 crystallization phenomenon, field tests were necessary, in addition to the laboratory tests, to ensure that any associated change in overall performance of the FRM sampler $PM_{2.5}$ did not adversely compromise the quality of collected compliance data.

In addition to the primary goal of understanding how DOW 704 crystallization might affect $PM_{2.5}$ measurement quality, a secondary goal of this study was to identify alternative impaction oils that might prove to be more robust during field use. Selection of an alternative oil to the FRM DOW 704 impaction oil was based on careful consideration of the factors that affect the field performance of the WINS separator. First, the mechanical properties of the oil must enable it to fully absorb the kinetic energy of the impacting particle and, thus, prevent particle bounce. Second, the vapor pressure of the oil must be sufficiently low to minimize excessive volatilization of the oil during sampling and, thus, potentially bias measured downstream $PM_{2.5}$ mass concentrations. Third, the kinematic viscosity of the oil must be in the correct range[3] to allow it to wick up through layers of previously deposited particles by capillary action. This property of the oil is important to minimize the effect of substrate overloading during extended sampling of coarse particle concentrations. Because the kinematic viscosity of the oil during field use inherently changes with ambient temperature, the temperature response curve of the oil must allow operation at a wide range of operating temperatures. Last, the oil must be commercially available and pose no special health hazards during its intended use.

After a review of available oils that met these restrictive criteria, DOS (CAS 122-62-3) was selected, purchased, and evaluated. Figure 3 presents the viscosity versus temperature relationships for DOW 704 and DOS diffusion oils based on American Society for Testing and Materials Method D341-93 Standard Viscosity Temperature Charts for Liquid Petroleum Products. Both DOW 704 and DOS oils display acceptable viscosity ranges recommended previously.[3] In conjunction with its −48 °C (−54 °F) fp, however, the DOS oil viscosity/temperature slope makes it the better WINS oil choice during low-temperature sampling of ambient aerosols.

It should be noted that the proposed use of DOS as an alternative WINS oil does not present any significant safety concerns. It is commercially available from several vendors, and its cost is similar to that of DOW 704. DOS has historically been used as a diffusion fluid and valued for its low temperature properties as a plasticizer. It is also used as an ingredient in cosmetics and skin care products. DOS is neither a skin irritant nor absorbed through the skin,[7] and an animal toxicity study concluded that DOS lacked carcinogenic action.[8] Results of the systematic laboratory and field evaluations of this alternative impaction oil will be described.

Laboratory Tests

To address the issue of bounce in the WINS separator, a specialized experimental setup was designed, constructed, and validated to enable characterization of WINS performance as a function of the physical state of the DOW 704 oil. Figure 4 is a schematic diagram showing the apparatus used for generation of primary calibration aerosols, their transport to the WINS separator, and the means by which

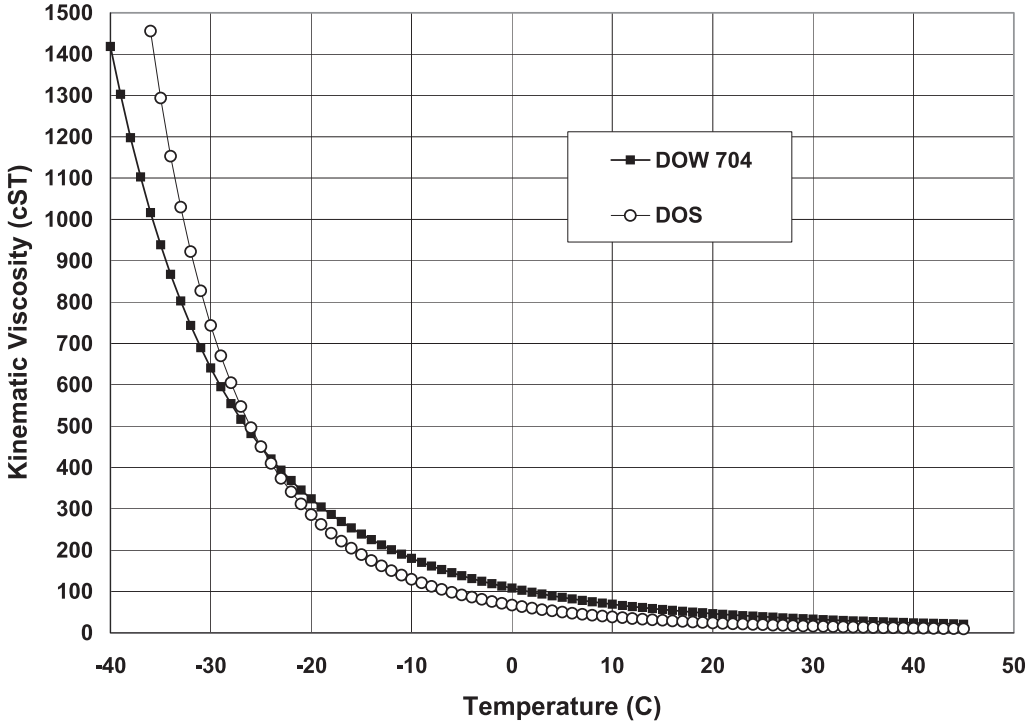

Figure 3. Kinematic viscosity vs. temperature relationships for DOS and DOW 704 diffusion oils.

the size of the calibration aerosols was continuously validated and their concentration measured. The system was based on the WINS calibration system developed previously[4] and includes modifications to enable cold temperature evaluation of the WINS separator.

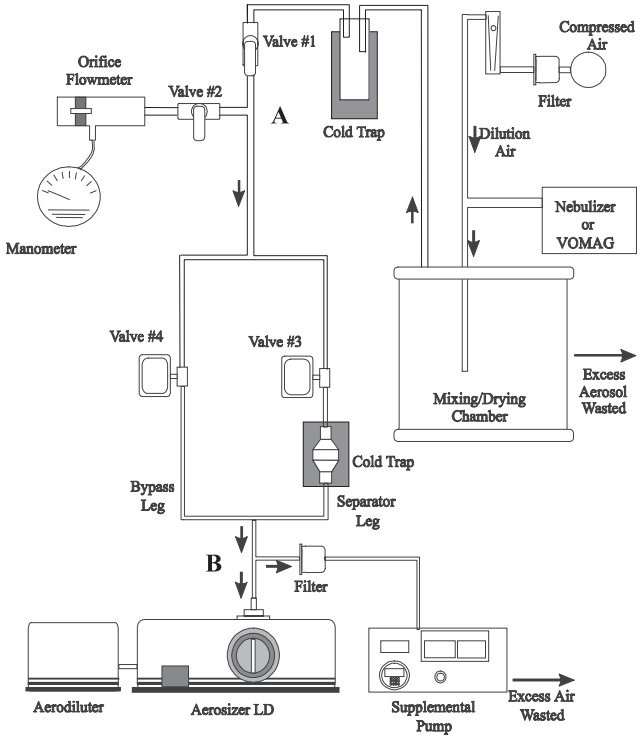

Figure 4. Schematic of experimental setup used for cold temperature WINS evaluation.

Primary calibration aerosols were generated using a pneumatic nebulizer (Professional Medical Products, Inc.), which nebulized liquid suspensions containing deionized water and National Institute for Standards and Technology-traceable PSL spheres (Duke Scientific Corp., Polysciences, Inc.). The pneumatic nebulizer was fed filtered compressed air at operating pressures of ~15 pounds per square inch gauge (103 kPa). The nebulized aerosol stream was then dried by introducing it into a 10-L capacity metal chamber and diluted with dry, filtered compressed air. The bottom of the metal chamber was filled with 500 g of silica gel to facilitate drying of the aerosol. The aerosol exiting the drying chamber was then passed through a dry ice-based cold trap. The purpose of the cold trap was to ensure complete drying of the aerosol and to remove excess water vapor, which would otherwise condense in the WINS separator at reduced temperatures.

The volumetric flow rate of the air downstream of the cold trap (Figure 4, point A) was then periodically measured using the calibrated orifice meter accessed through use of valves 1 and 2. If necessary, adjustments were made to the experimental system supplemental pump to ensure that the volumetric flow rate at point A was maintained at the $PM_{2.5}$ FRM 16.7 actual L/min specification.

Downstream of point A, the aerosol stream was then alternately split into one of two flow channels using computer-controlled switching valves (valves 3 and 4). One flow channel (separator leg) housed the WINS separator, whereas the other channel (bypass leg) was used to divert the aerosol flow around the WINS separator. The entire apparatus was carefully designed and symmetrically constructed to ensure that equal particle losses were experienced when an aerosol passes through either the bypass leg or the separator leg. Tests conducted with the WINS

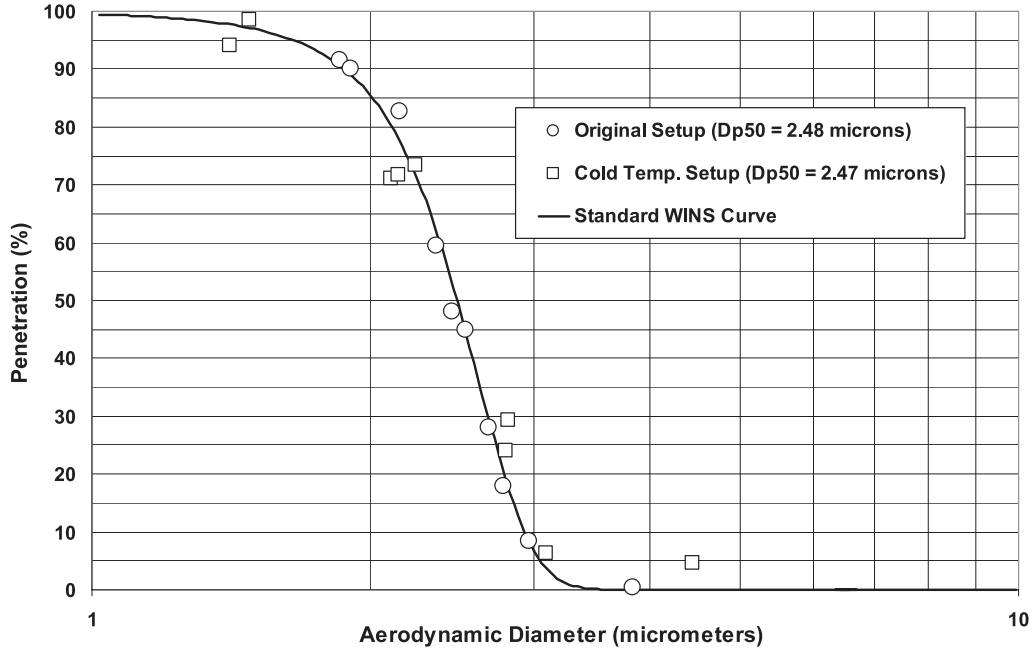

Figure 5. Results of the experimental system's validation.

replaced with a straight tube verified that particle losses were equivalent in both legs.

The physical state of the WINS diffusion oil was controlled through use of a custom-built polypropylene container designed to be filled with dry ice. At the dry ice mp of −78 °C, heat transfer through the WINS and the surrounding container was sufficient to routinely induce crystallization the DOW 704 oil, as verified by visual and tactile inspection. At steady-state conditions, the temperature of the WINS components was measured to be approximately −25 °C.

The separator and bypass legs of the apparatus joined at a tee fitting (point B) and a fraction of the aerosol flow was sampled by the aerosizer. As depicted in the Figure 4 schematic, the aerosizer was accompanied by an aerodiluter (Model Aerodiluter, TSI Inc.). The aerodiluter provided particle-free air to elevate the total flow rate into the aerosizer to its design flow rate of ~5 actual L/min. The aerodiluter also ensures a constant flow rate into the aerosizer regardless of pressure drop differences in the legs of the experimental apparatus. A supplemental pump withdrew the balance of the flow through a high-efficiency particulate filter. The aerosizer, aerodiluter, and supplemental air pumps were allowed sufficient warm-up time before each test series to provide steady-state responses.

The aerosol number concentrations penetrating through the bypass leg and through the separator leg of the system were then alternately measured with 5-min aerosizer runs. Three sets of bypass and separator measurements were then completed to yield three replicate measurements of sampler penetration. The penetration, $P(D_{ae})$, for a given particle size was then calculated as:

$$P(D_{\mathrm{ae}}) = \frac{C_{\mathrm{separator}}}{C_{\mathrm{bypass}}} \qquad (1)$$

where $C_{\mathrm{separator}}$ and C_{bypass} represent the measured number concentrations for the separator leg and bypass leg, respectively. Per standard procedures,[4] if the coefficient of variation of the three replicate measurements was >10%, then the original data were discarded, and the measurements were repeated for that specific particle size. Typical values of coefficient of variation during these tests were <2%. An entire penetration curve was then developed by stepping through the discrete particle sizes until an adequate number of sizes was evaluated to fully describe the position and shape of the performance curve under those test conditions.

RESULTS

System Validation and Characterization

Before conducting the cold temperature tests, validation tests were first conducted at room temperature to ensure that the cold temperature modifications of the setup did not adversely influence the measured performance of the WINS. As depicted in Figure 5, the resulting 2.47-μm cut point of the modified setup agreed closely with the 2.48-μm value measured during the development of the WINS separator.[4]

The experimental system was characterized once the dry ice was added to the setup and the system achieved thermal equilibrium. As indicated by a thermocouple mounted in the WINS housing, thermal equilibrium was typically achieved within ~15 min. Although the exact temperature of the airstream impinging on the impactor plate could not be accurately measured without altering the thermal properties of the flow stream and without adversely affecting the impaction dynamics, the temperature of the WINS components was measured to be ~248 °K (−25 °C). Under these conditions, the surface of the DOW 704 oil was determined to be crystallized as observed by visual and tactile inspection. Measurements also showed that the air temperature entering the aerosizer

was identical regardless of which leg of the testing apparatus was currently the active leg. Cold air exiting the WINS separator, therefore, reached thermal equilibrium with the room air by the time its particle number concentration was measured by the aerosizer. This allowed direct calculation of WINS penetration (eq 1) without the need to compensate volumetric flow rate and reported number concentrations for temperature differences between the two legs.

Prediction of WINS Cut Point

Before interpreting test results of the WINS separator under cold conditions, it was first necessary to predict the WINS cut point under the cold temperature conditions. In general, there were two factors that needed to be considered for this calculation. First, the reduction in air temperature in the separator leg naturally reduced the volumetric flow rate through the WINS nozzle. The corresponding reduction in jet velocity inherently reduced each particle's inertia and resulted in higher WINS cut points. The second effect of cold temperature evaluation of the WINS was to modify the fluid properties of the airstream (e.g., fluid viscosity, density, and mean free path). These factors had to be properly accounted for to enable estimation of WINS cut point during the cold temperature tests. In the following paragraphs, the factors governing impactor performance will be reviewed as they relate to these cold temperature tests.

For a round jet impactor, the cut point (Dp_{50}) can be predicted[9] based on the impactor's critical dimensions and the properties of the airstream:

$$\sqrt{C}\ Dp_{50} = \sqrt{\frac{9\mu W}{\rho_p V}}\ \sqrt{STK_{50}} = \sqrt{\frac{9\pi n\mu W^3}{4\rho_p Q}}\ \sqrt{STK_{50}} \tag{2}$$

where C is the particle slip correction factor, μ is the dynamic viscosity of the airstream, W is the impactor jet width, ρ_p is the particle density, V is the mean fluid velocity through the jet, STK_{50} is the dimensionless impaction parameter, n is the number of jets, and Q is the volumetric flow rate through the impactor. The slip correction factor, C, is itself a function of particle physical diameter and the air properties and can be estimated based on empirical studies[10]:

$$C = 1 + 1.246 * Kn = 0.42 * Kn * \exp(-0.87/Kn) \tag{3}$$

where Kn is the Knudsen number and is defined as the mean free path of air divided by the particle radius. Because the mean free path of air is a function of both temperature and pressure, the Knudsen number must be calculated at actual sampling conditions:

$$Kn = 0.0653\left(\frac{2}{P\ Dp}\right)\left(\frac{T}{296}\right)\left(\frac{1.3716}{1 + 110/T}\right) \tag{4}$$

where P is the ambient pressure (atm), Dp is the particle diameter (μm), and T is the ambient temperature (°K).

The dynamic viscosity of a gas is virtually independent of pressure from 0.01 to 100 atm and depends only on the composition of the gas and its temperature.[11] For air:

$$\mu = 1.81 \times 10^{-4}\left(\frac{T}{293}\right)^{0.74}\ \text{g/(}cm\ sec\text{)} \tag{5}$$

where the temperature has units of Kelvin.

The Stokes number, *STK*, is defined as the ratio of the particle's stopping distance to the radius of the impactor jet width. Studies of impactor flow fields and the trajectories of particles within those flow fields have shown that the Stokes number for a given impactor stage is a function of particle aerodynamic diameter, jet Reynolds number, jet-to-plate distance, and nozzle throat length.[12,13] Published Stokes numbers as a function of these parameters allows one to design an impactor's dimensions and operating flow rate. Once a prototype stage is constructed, its laboratory calibration under carefully controlled conditions allows the user to determine the cut point of the stage accurately. Once the cut point is known, changes in the performance of the stage versus various operating parameters can be predicted through consideration of eq 2.

Proper consideration of eqs 2–5 allowed estimation of the WINS cut point as a function of temperature. As has been mentioned, however, the exact temperature of the airstream impinging on the impaction plate could not be accurately determined. Fortunately, the predicted WINS cut point in this experimental setup is relatively insensitive to actual jet temperature. Recalling that the setup's mass flow rate is maintained regardless of WINS temperature, inspection of eq 2 reveals that jet velocity (V) will decrease as predicted by the ideal gas law. For example, at a jet temperature of −25 °C, ideal gas considerations predict that the 16.7 actual L/min flow rate at the inlet of the setup would be reduced by ~17%. However, eq 5 predicts a 12% decrease in the viscosity of the fluid at this temperature. Because the gas viscosity is in the numerator of eq 2 and jet velocity is in the denominator of the equation, the decrease in the two values approximately cancel each other out. Further accounting for temperature-specific changes in Stokes numbers and slip correction factors, only slight increases in WINS cut point are expected at extremely low setup temperatures. At an impaction jet temperature of −25 °C, for example, the predicted cut point of the WINS fractionator was ~2.54 μm. Figure 6 demonstrates the near linear relationship between the expected WINS cut point and the impaction jet temperature.

Because the actual jet temperature for a given test is unknown, it is reasonable to expect greater uncertainty in actual WINS cutpoints during the cold temperature tests than can be achieved at near standard conditions. For these tests, cut point uncertainties are estimated to be approximately ±0.05 μm. It is also reasonable to expect some daily variability in WINS cut point during the cold temperature tests because of variations in final system equilibrium temperatures from one test to another. This variability naturally resulted in performance curves,

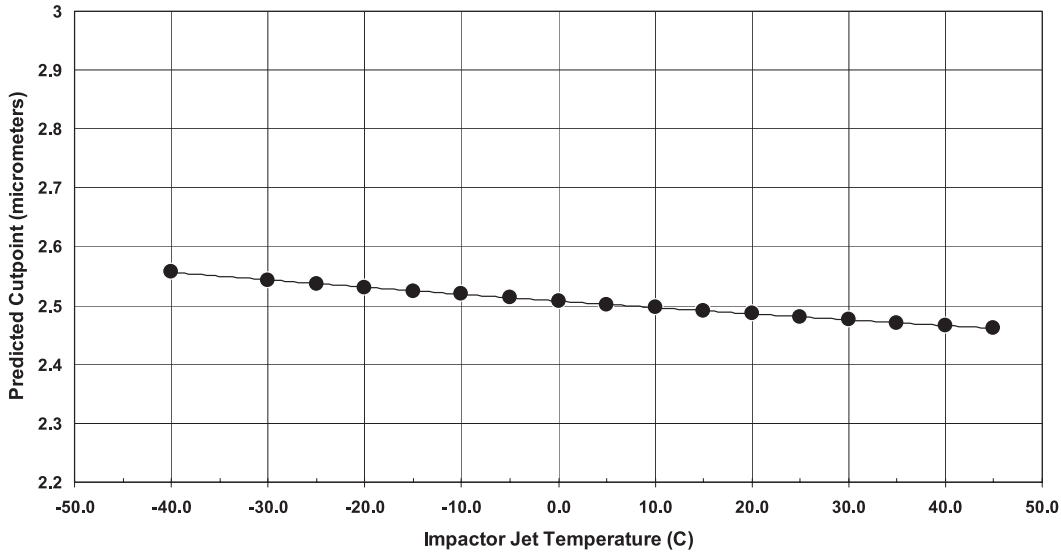

Figure 6. Predicted WINS cut point vs. assumed jet temperature during the cold tests.

which were not as smooth as observed during room temperature testing conditions.

Test Results. After successful validation of the cold temperature test apparatus, a series of tests was conducted using both the DOW 704 diffusion oil, as well as the DOS oil that was being considered as an alternative oil. Before each experiment was conducted, a new 37-mm glass-fiber filter (Whatman, Type 934-AH, catalog No. 1827-037) was placed in the bottom of the WINS well, and 1 mL of DOW 704 oil was dispensed to the filter surface. The WINS impactor was then assembled and placed in the experimental setup. The entire system was turned on, and flow rates and temperatures were allowed to fully stabilize before conducting the WINS penetration tests.

Results of the crystallized DOW 704 performance tests are presented in Figure 7 along with tests conducted using DOW 704 in its liquid state at room temperature. For comparison purposes, data are also presented from the WINS standard calibration and calibration tests performed using an uncoated, bare aluminum well.[4] Results show that neither the position nor the shape of the WINS performance curve is adversely affected by the crystallized state of the DOW 704 oil. Most importantly, no bounce of particles from the crystallized oil surface was observed even using these hard, spherical test aerosols. In sharp contrast, the curve measured for an uncoated aluminum WINS well displayed a noticeable increase in cut point and appreciable bounce of particles from the hard metal

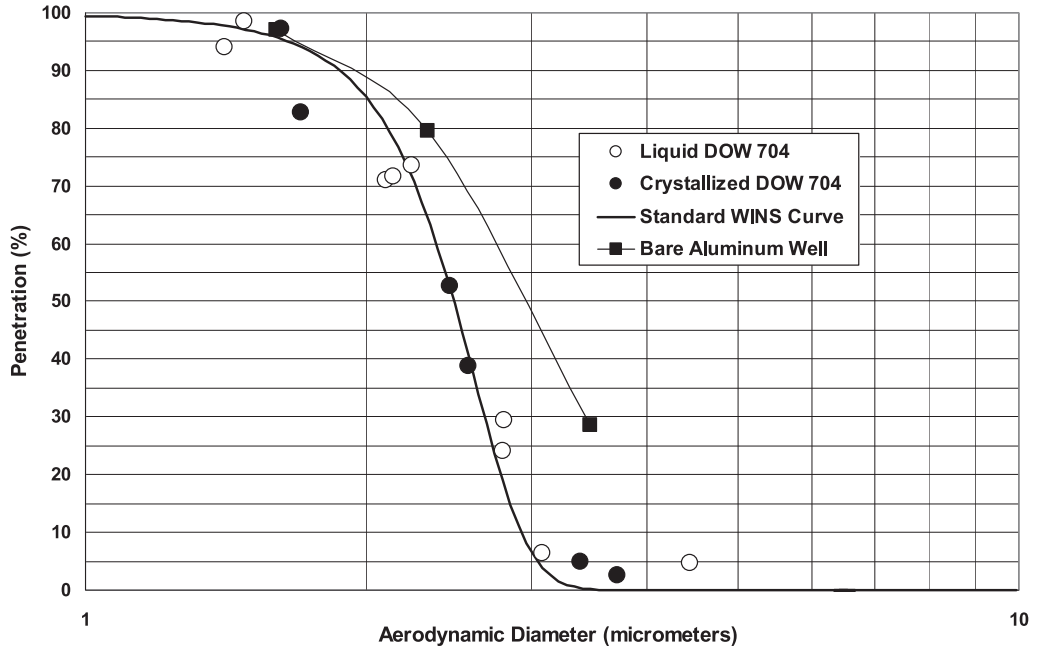

Figure 7. WINS performance curves obtained using various impaction substrates.

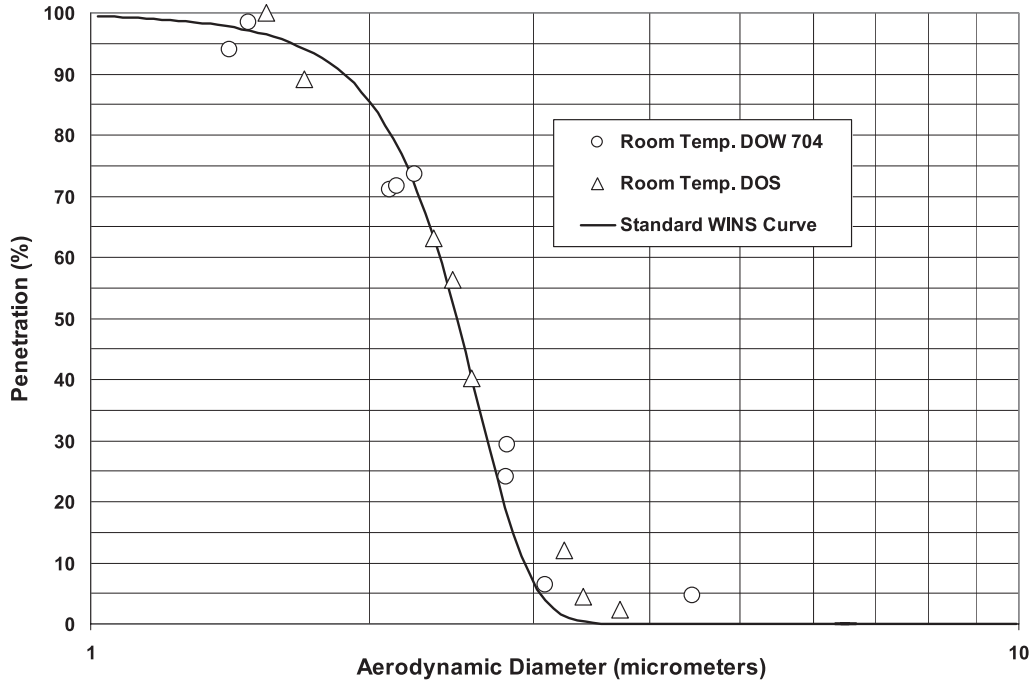

Figure 8. Size-selective performance of the WINS using DOS diffusion oil.

surface. The high observed penetration of particles from the metal surface also demonstrates that any condensed water vapor on the surface of the crystallized DOW 704 does not account for its efficient particle collection characteristics.

Although the crystallized DOW surface is certainly hard to the touch, its mechanical properties are apparently such that it is capable of fully absorbing the kinetic energy of the impacting particles. As a result, there appears to be no adverse effect of crystallized oil on the overall size-selective performance of the WINS or on the predicted $PM_{2.5}$ mass concentration associated with its use.

As presented in Figure 8, the laboratory use of DOS oil in the WINS separator produced size-selective performance virtually identical to that measured during use of liquid DOW 704 oil. Unlike the DOW 704 oil, however, the DOS diffusion oil has a documented fp of −48 °C, which is sufficiently low to enable it to remain in its liquid state in virtually all field sampling situations. During all of the laboratory tests, the DOS was observed to remain in its liquid state regardless of temperature.

Field Tests

Although results of the laboratory evaluation of crystallized DOW 704 were very favorable, field tests were necessary to ensure that laboratory tests results accurately predicted the overall sampler's performance under conditions of actual field use. Specific objectives of the field study included the following: (1) to conduct warm weather and cold weather tests to evaluate DOS as an alternative impaction oil for the WINS separator; (2) to conduct cold weather tests to determine the frequency, nature, and effect of the crystallized DOW 704 oil; and (3) to evaluate the BGI VSC cyclone as a possible alternative to the WINS fractionator for use in FRM samplers.

Site Setup and Operating Procedures. Under warm weather conditions, extensive field evaluations of the DOS oil were conducted at field sites in Research Triangle Park; Rubidoux, CA; and Phoenix, AZ. The purpose of these tests was to ensure that use of liquid DOS oil provided the same test results as those provided by use of liquid DOW 704 oil. In these tests conducted in 1999 and 2000, 15 daily 22-hr sampling events were conducted at each of the three sampling sites. During each test, three $PM_{2.5}$ reference method samplers (manufactured by Thermo-Andersen [AND], Rupprecht and Patashnick [R&P], and BGI) were collocated with a comparable set of three reference method samplers. The WINS wells of the first set of samplers were equipped with DOS oil, whereas the other set was equipped with the DOW 704 oil prescribed in the method regulations. Other than differences in the impaction oil, each set of samplers was set up, calibrated, operated, and maintained in an identical manner. It should be noted that these tests were conducted under warm weather conditions and, thus, no crystallization of the DOW 704 oil was observed.

Before conducting the field tests, all of the samplers were shipped to the field site, unpacked, and thoroughly cleaned. Each sampler was then leak checked and calibrated for accurate measurement of volumetric flow rate, ambient temperature, filter temperature, and ambient pressure using appropriate transfer standards. Performance audits of each sampler were then conducted before the first sampling test and after every 15 sampling runs. A final performance audit was conducted at the completion of the field study. Field blank tests for each sampler were conducted at the same time and frequency as the performance audits.

Conditioning and weighing of all of the filters were conducted by the same technician during the study and took place in the environmentally controlled chamber

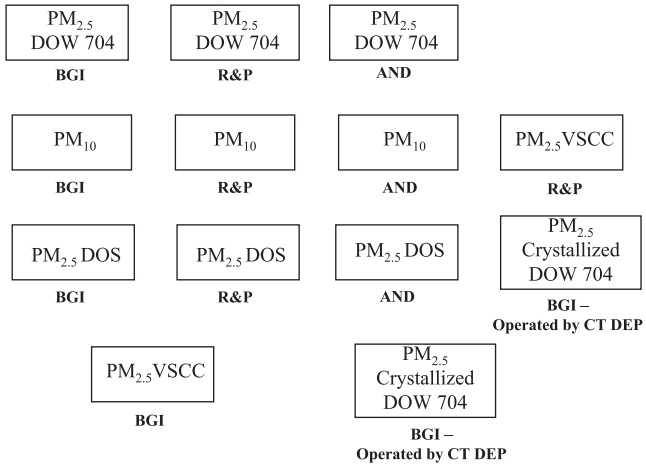

Figure 9. Schematic of sampler configurations at the Windsor sampling site.

that had been designed, constructed, and operated to comply with federal regulations for $PM_{2.5}$ filter weighing. Temperature and RH set points for the environmental chamber were 22 °C and 35% RH, respectively.

During December 2000 and January 2001, cold weather field tests were conducted in Windsor, CT, as a collaborative effort between EPA and the CT DEP. Based on EPA's previous survey of sampling sites throughout the country, Windsor was selected for the field tests because it represented the geographic region of highest reported frequency of DOW 704 crystallization. All of the winter field tests during this study were conducted in a large, asphalt-paved parking lot immediately adjacent to the CT DEP Field Operations Facility in Windsor. The ground level sampling platform itself was surfaced with large, loose stones, and the platform area was free from immediate flow obstructions, such as trees or buildings. The site was secure with a chain link fence surrounding the parking lot, and site access was provided to field personnel 7 days a week. Parking activities in the area were limited to a few cars a day, and these were located downwind of the sampling location.

Figure 9 is a schematic diagram showing the relative horizontal position of the tested samplers. Per EPA monitoring network testing regulations, samplers were installed such that their inlets were spaced horizontally with a minimum separation distance of 1 m. The samplers were also installed such their inlet heights were 2 ± 0.2 m. The nine FRM samplers involved in the study included three EPA-designated FRM samplers from each of three different sampler manufacturers: AND, R&P, and BGI. In the first set of FRM samplers, each sampler's WINS fractionator was equipped with 1 mL of DOW 704 oil in accordance with standard $PM_{2.5}$ testing procedures. In the second set of FRM samplers, each sampler's WINS fractionator was equipped with 1 mL of DOS oil. Per standard $PM_{2.5}$ FRM operating procedures, WINS oil in each fractionator was replaced after every 5 days of sampling. In the final set of samplers, the WINS fractionator was removed and replaced with a straight downtube. This modification converted the $PM_{2.5}$ samplers into reference method PM_{10} samplers, thus providing information regarding the size distribution of ambient aerosols encountered during sampling.

The two VSC cyclones were installed and operated by RTI on a designated BGI FRM sampler and a designated R&P FRM sampler. The VSC cyclones were cleaned after every 14 days of operation per recommendations provided by BGI before the tests.

In addition to the samplers operated by RTI, two additional samplers were operated by CT DEP personnel. These samplers were designated BGI $PM_{2.5}$ FRM samplers of which the WINS wells contained crystallized DOW 704 during all of the field tests. These crystallized DOW 704 wells were typically collected a few days before use in this study and were stored in a freezer until needed. For these two samplers, CT DEP was responsible for all phases of the testing, including sampler setup, calibration, and operation, as well as subsequent shipment and gravimetric analysis of collected filters.

Despite the low ambient temperatures encountered during the wintertime test period, field audits showed that the samplers were able to maintain their initial flow rate, temperature, and pressure measurement calibrations throughout the 48 days of study. As a result, no midstudy calibrations of the various samplers were required. For the designated FRM samplers, the maximum flow bias encountered was +2.6%, which is well within the ±4% allowed. The maximum ambient pressure bias of 8 Torr was within the ±10 Torr allowed. A maximum ambient temperature measurement bias of +1 °C was encountered, which was within the ±2 °C allowed.

Warm Weather Field Test Results. As presented in Figure 10, excellent agreement between the two sets of samplers was observed at all three of the warm weather sites irrespective of concentration. $PM_{2.5}$ particle concentrations during the 45 discrete sampling events ranged from a low of 5 $\mu g/m^3$ (measured in Research Triangle Park) to a high of 54 $\mu g/m^3$ (measured in Rubidoux). Statistical correlation between the DOS-based samplers and the DOW-based samplers was extremely high, as indicated by the measured R^2 value of 0.999. Slope and intercept for the DOS versus DOW $PM_{2.5}$ concentrations was 0.995 and -0.006 $\mu g/m^3$, respectively. Although DOS has an inherently higher vapor pressure than DOW 704 at the same temperature, field evaluation of the DOS oil showed no adverse effect on measured $PM_{2.5}$ mass concentrations even during extended sampling periods at ambient temperatures of 46 °C (115 °F) experienced during testing June 2000 in Phoenix.

Cold Weather Field Test Results. During the cold weather tests, 15 daily tests were conducted in December 2000, and 33 daily tests were conducted in January through February 2001. The cold temperatures encountered at the Windsor sampling site during December through February met the study's objectives well. As depicted in Figure 11, mean daily temperatures were quite variable, ranging from −9.1 °C to +4.4 °C and averaging −1.8 °C. The highest temperature measured during the 48 days study was +12.5 °C, whereas the lowest temperature encountered was −16.6 °C. In conjunction

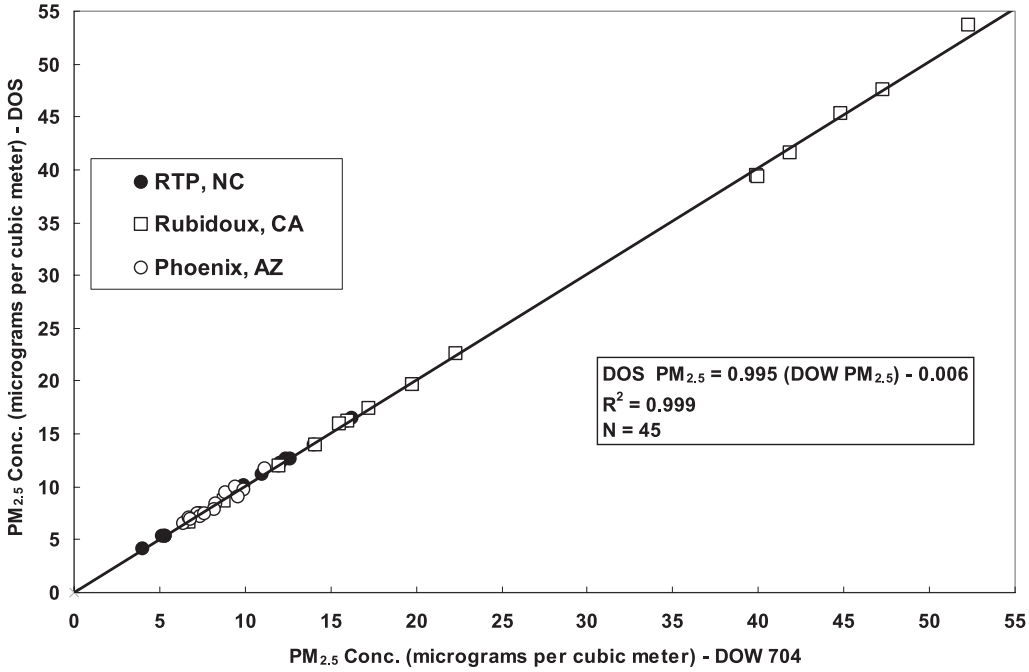

Figure 10. Results of collocated DOS vs. DOW 704 during the warm weather field tests.

with other factors in the Windsor airshed, these temperatures were sufficiently low to induce crystallization of the DOW 704 oil and, thus, enabled field personnel to measure any effect of the oil's crystallization on measured $PM_{2.5}$ concentrations.

Once the field tests began, daily observations were carefully made regarding the nature of each FRM sampler WINS well. Although no crystallization of the DOW 704 oil was observed during the first 3 days of testing, crystallization of the oil was observed during day 4 and was regularly observed for the duration of the study. On average, approximately two of every three sampling events involved a crystallized DOW 704 substrate. Typically, a newly changed WINS well would require a day or 2 for crystallization of the DOW 704 to occur. The crystallized DOW 704 oil would remain solidified until the well was scheduled to be replaced with a newly prepared one. Crystallization events did not appear to be a function of sampler manufacturer. Despite careful observations and records of each sampling event, it remains unclear why this region of the country experienced a higher frequency of DOW 704 crystallization than any other area.

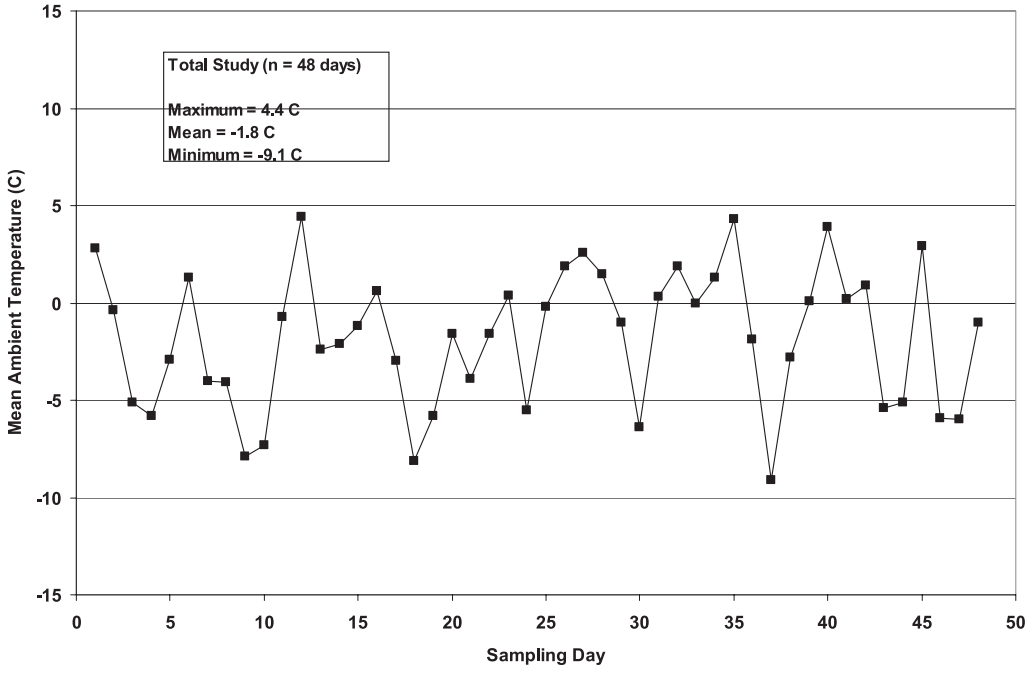

Figure 11. Timeline of mean daily ambient temperatures at the Windsor sampling site.

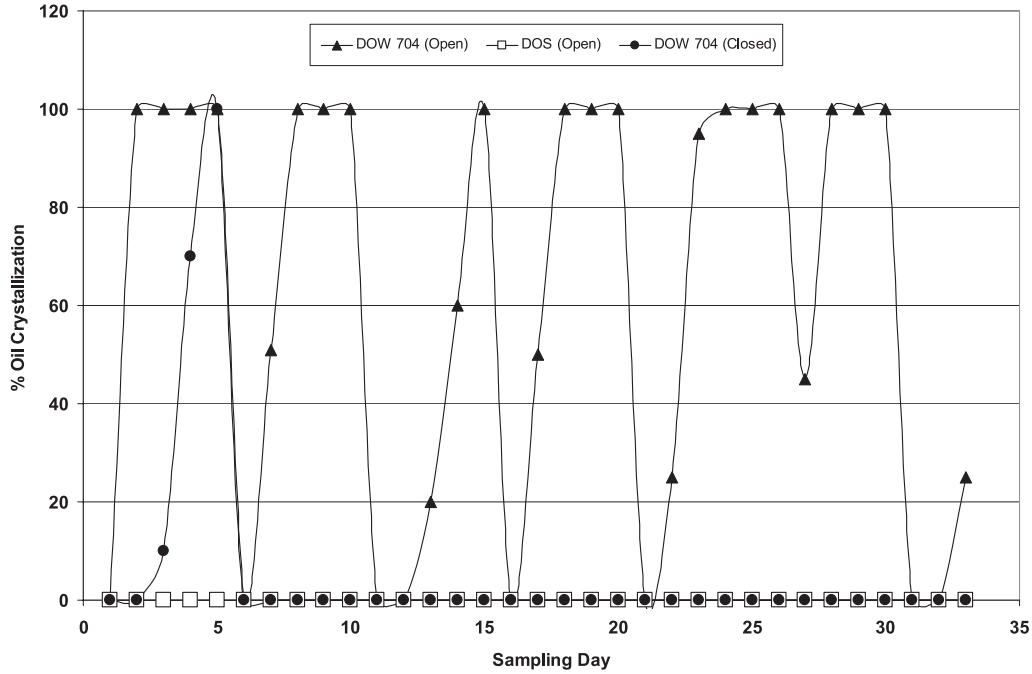

Figure 12. Effect of oil exposure to ambient air in Windsor. The term "open" refers to nonsampling WINS wells exposed to ambient air, whereas "closed" refers to nonsampling WINS wells in closed containers. WINS wells were regenerated every fifth sampling event.

During the course of the field study, special nonsampling tests of the oils were conducted. Two separate WINS wells were prepared with DOW 704, one of which was left open to the atmosphere, whereas the other remained sealed within a zip-lock style freezer bag. A third well was prepared using the DOS oil. All three of the WINS wells were placed outdoors, and observations were made regarding the oil's properties. As illustrated in Figure 12, none of the DOS oil was observed to crystallize during these tests. However, the DOW 704 left open to the atmosphere typically required a day or two to crystallize and would remain in that state until it was exchanged with new fluid following day 5. This behavior was similar to that observed when DOW 704 was used in the wells of the $PM_{2.5}$ sampler. On only one occasion did the sealed DOW 704 oil undergo crystallization despite its being subjected to the same ambient temperature as the exposed WINS well. Ambient temperature, therefore, is clearly not the sole causative agent in inducing crystallization of the DOW 704 oil in this region of the country. Although unknown, other properties of the ambient air in this airshed are apparently responsible for inducing the crystallization of the oil.

Figure 13 is a timeline of the $PM_{2.5}$ and PM_{10} concentrations measured using three FRM samplers equipped with DOS oil. During these 48 days of tests, the mean $PM_{2.5}$ concentration measured during the study was 14.1 $\mu g/m^3$, with minimum and maximum concentrations of 2.5 $\mu g/m^3$ and 41.3 $\mu g/m^3$, respectively. Intermanufacturer agreement among the three $PM_{2.5}$ FRM samplers was typically quite strong as evidenced by the 2.6% mean daily coefficient of variation. The highest intermanufacturer variabilities typically occurred during low $PM_{2.5}$ concentration events. It is conjectured that uncertainties in the aerosol mass measurement primarily accounted for most of the overall measurement uncertainty at these low concentrations.

PM_{10} concentrations averaged 20.5 $\mu g/m^3$ during the 48 days of testing, with measured minimum and maximum concentrations of 3.9 $\mu g/m^3$ and 54.3 $\mu g/m^3$, respectively. Similar to that for the $PM_{2.5}$ measurements, the intermanufacturer precision for the PM_{10} FRMs was considered to be excellent as evidenced by the 2.9% coefficient of variation. Note from Figure 13 that the $PM_{2.5}$ on any given day never equals or exceeds the measured PM_{10} concentration. The coarse fraction of PM_{10} (calculated as the numerical difference between measured PM_{10} and $PM_{2.5}$ concentrations) would, thus, never be ≤ 0.

The size distribution of the ambient aerosol during the test period was quite variable, as evidenced by the calculated $PM_{2.5}/PM_{10}$ fraction. The mean 0.70 ratio indicates that, on average, approximately two thirds of the PM_{10} fraction were associated with $PM_{2.5}$ aerosols. This ratio varied considerably during the tests, however, as indicated by measured minimum and maximum ratios of 0.14 and 0.89, respectively.

As mentioned, DOW 704 crystallization occurred on approximately two thirds of these wintertime sampling events. For the 16 sampling days when crystallization did not occur, the agreement between samplers equipped with liquid DOW 704 and liquid DOS was quite strong. This relationship is depicted in Figure 14 and shows that the slope, intercept, and R^2 values for these tests were 0.99, 0.0, and 0.999 $\mu g/m^3$, respectively. The favorable agreement provided by these two liquid oils for these tests agrees with the previously discussed test results obtained in Research Triangle Park, Phoenix, and Rubidoux. It also indicates that the various $PM_{2.5}$ samplers are functional and providing

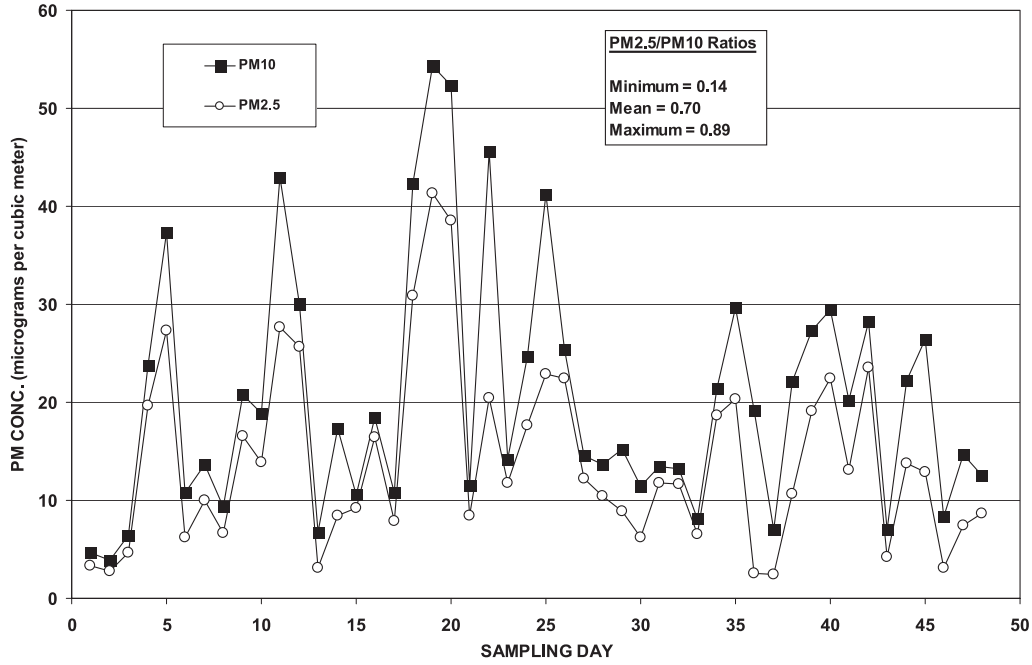

Figure 13. Timeline of mean $PM_{2.5}$ and PM_{10} concentrations at the Windsor site during the 48 sampling events.

valid tests results and validates the DOS oil as an appropriate alternative to the DOW 704 oil.

Figure 15 presents tests results obtained during the 32 sampling events when the DOW 704 was observed to be crystallized. As the figure indicates, samplers equipped with the crystallized DOW 704 oil provided $PM_{2.5}$ concentrations very close to those equipped with the liquid DOS oil. These results were highly correlated ($R^2 = 0.997$), which indicates that this agreement was virtually independent of $PM_{2.5}$ concentration.

Before this study, the CT DEP would occasionally collect crystallized DOW wells and store them in a freezer. This study provided an opportunity to compare the performance of samplers equipped with these archived crystallized wells versus samplers equipped with wells containing liquid impaction oil. Figure 16 plots the test results obtained by CT DEP using these archived crystallized WINS wells versus the test results obtained by RTI using WINS wells equipped with liquid DOS. Although the data shows slightly more scatter than the

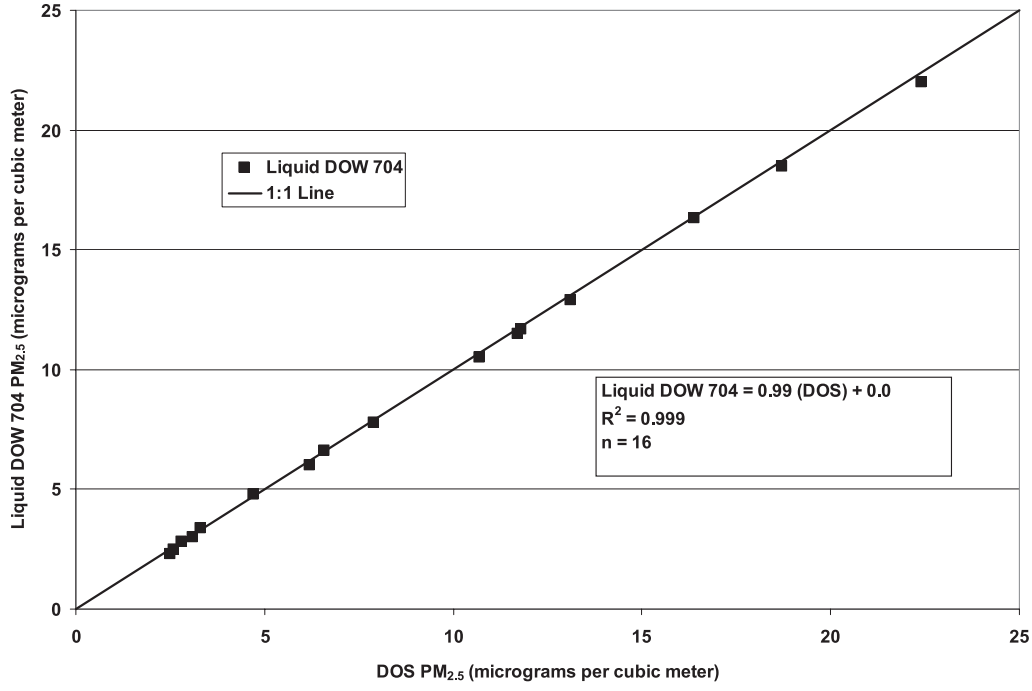

Figure 14. Field test results of liquid DOW 704 vs. liquid DOS at the Windsor site.

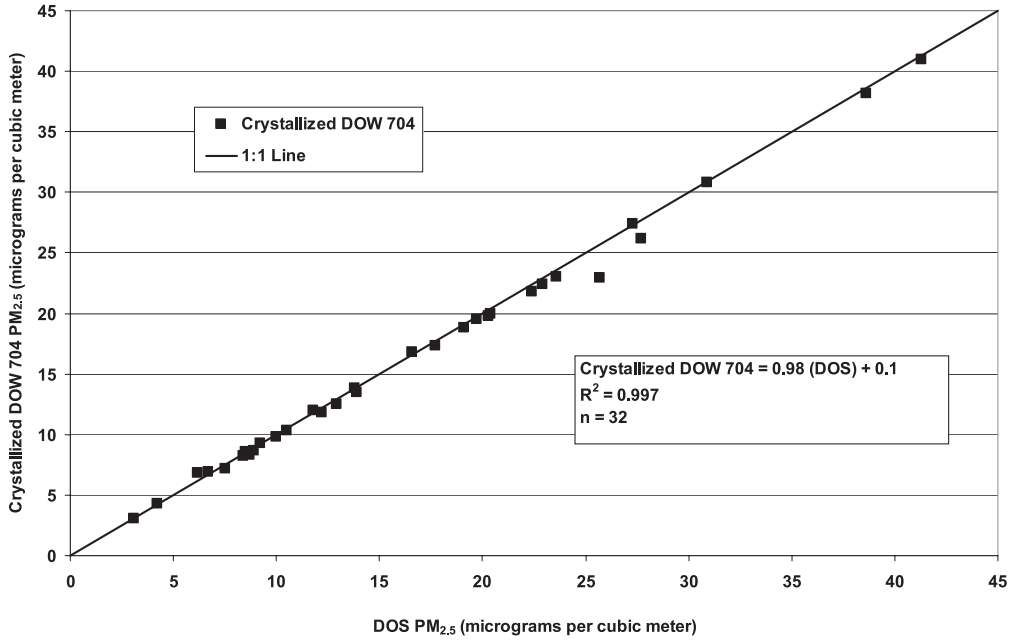

Figure 15. Field test results of crystallized DOW 704 vs. liquid DOS at the Windsor site.

previous plots, the level of agreement is excellent considering that different site operators, shipping protocols, and analytical laboratories were used by the two research groups. Figure 17 shows that excellent interlaboratory agreement was obtained when both research groups operated $PM_{2.5}$ samplers of which the DOW 704 had undergone crystallization. As depicted in these two plots, crystallization of the DOW 704 did not adversely affect the quality of the measured $PM_{2.5}$ concentrations. Although the crystallized DOW 704 is certainly solid to the touch, its mechanical properties are apparently such that it is still capable of fully absorbing the kinetic energy of the impacting particles.

Encompassing a 33-day test period, Figure 18 depicts the mean performance of the two samplers equipped with the BGI VSC cyclones versus FRM samplers equipped with DOS oil. As the figure shows, excellent agreement was obtained between these two systems as evidenced by the slope, intercept, and R^2 of 1.01, 0.1, and 0.999 $\mu g/m^3$, respectively. Subsequent to these tests, BGI applied for, and was granted by EPA, class 1 equivalency approval for use of the VSC cyclone. The VSC cyclone, therefore, represents an approved alternative to the WINS fractionator for use in conducting $PM_{2.5}$ compliance measurements.

Figure 19 depicts the performance of the various sampling configurations over the 48 days of testing. Note that

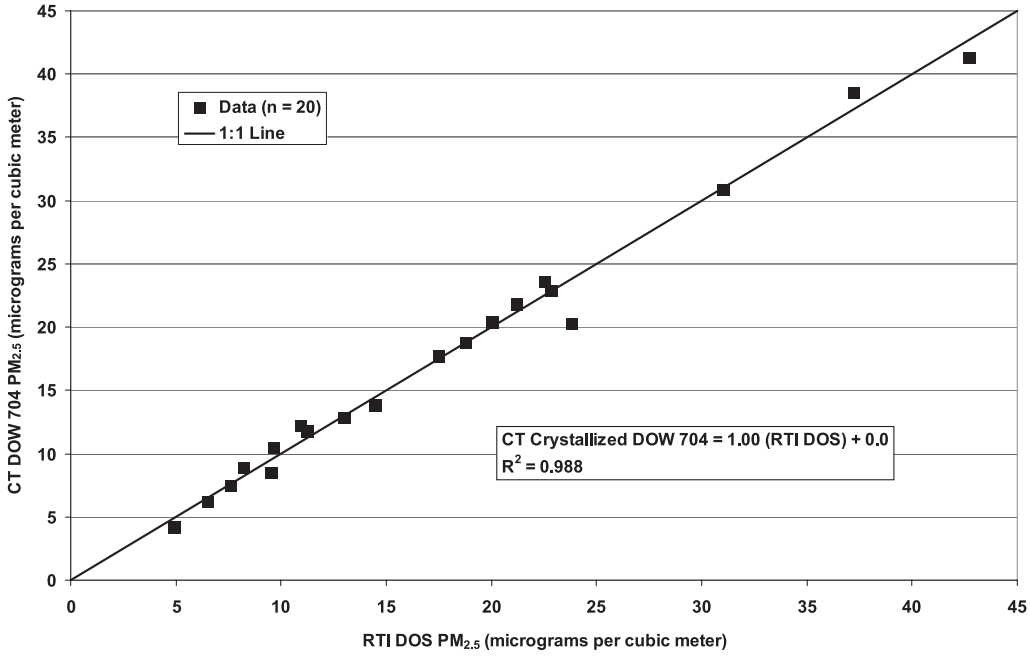

Figure 16. Field comparison of crystallized DOW 704 (CT DEP) vs. liquid DOS (RTI).

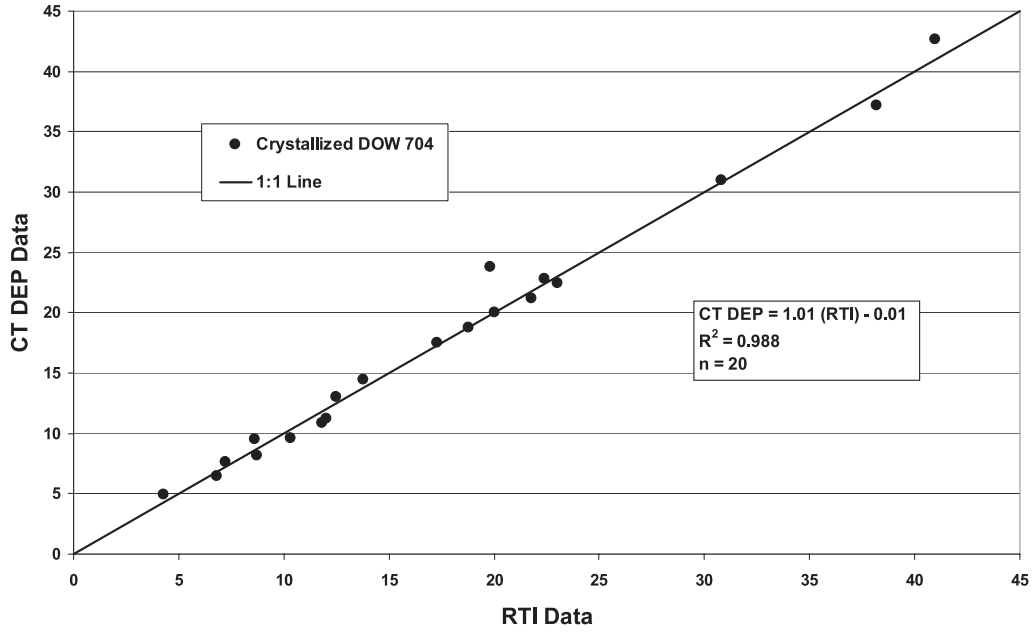

Figure 17. Interlaboratory comparison of Windsor test results using crystallized DOW 704 data.

many of the data points are close enough to obscure each other. Given the harsh sampling conditions under which the samplers were operated and the measurement variability inherent to ambient particulate sampling, the level of agreement depicted in the figure is considered to be very favorable.

SUMMARY AND CONCLUSIONS

Reports of crystallization of the WINS fractionator diffusion oil prompted EPA to conduct a nationwide survey of site operators to determine the nature and frequency of the phenomenon. Although the frequency of crystallization on a nationwide basis was judged to be low, EPA designed a series of laboratory and field tests to evaluate the particle size-selective performance of the WINS fractionator under this condition. Selection of an alternative impaction oil with improved field properties was also a primary goal of this study.

A modified calibration setup using dry ice was designed and constructed to induce crystallization of DOW 704 diffusion oil in the laboratory. The performance of this specialized system was validated before its use. At room temperature conditions, the resulting 2.47-μm cut point agreed well with the 2.48-μm value measured

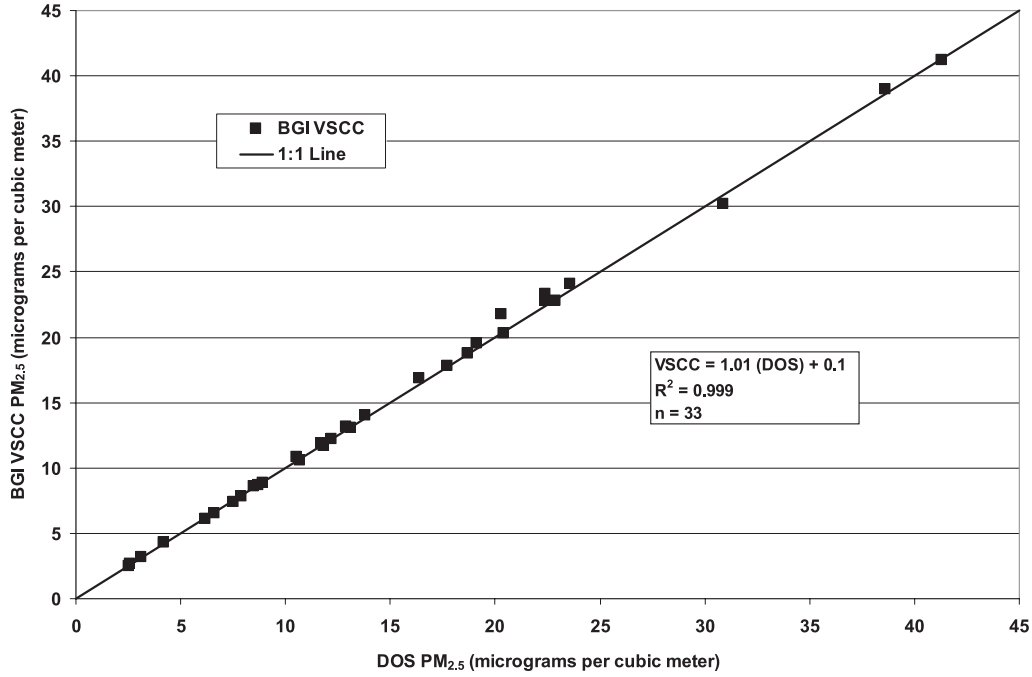

Figure 18. Windsor field performance of the BGI VSC cyclone vs. the WINS fractionator.

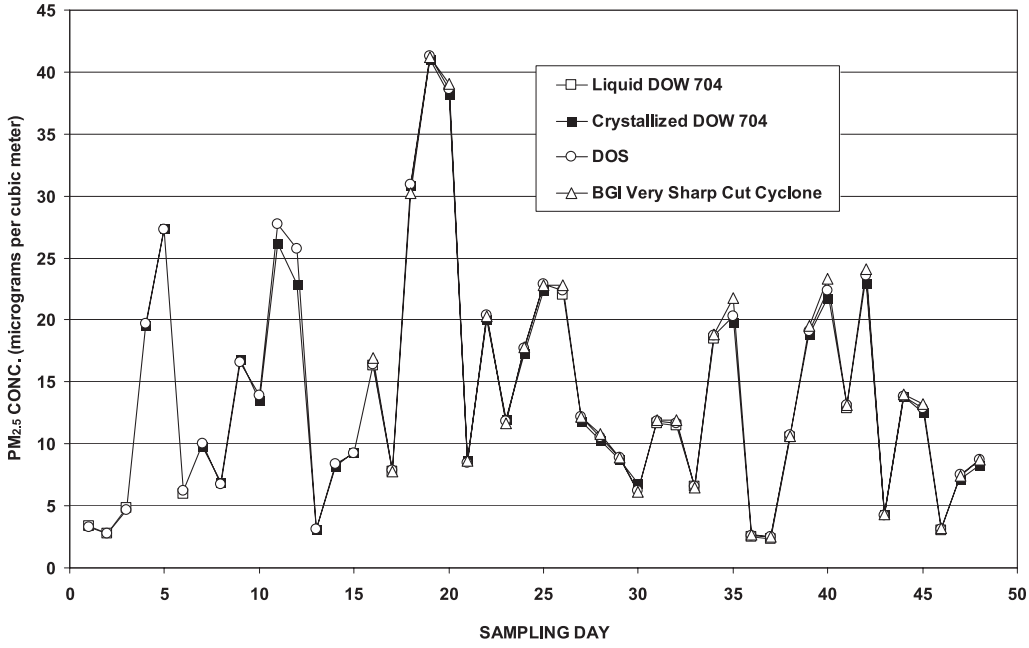

Figure 19. Summary of measured $PM_{2.5}$ concentrations vs. impaction substrate characteristics during the Windsor field tests.

during the development of the WINS.[4] At low temperature operating conditions, the surface of the DOW 704 oil was determined to be crystallized. WINS performance tests were then conducted using hard, spherical PSL calibration aerosols. The resulting position and shape of the WINS penetration curve at the low temperature condition were similar to those measured using liquid diffusion oil at room temperature conditions. As opposed to results obtained using a bare aluminum surface, no large particle bounce from the frozen DOW 704 substrate was observed. As a result of these tests, there appears to be no adverse effect of crystallized oil on the overall performance of the WINS separator or on the predicted $PM_{2.5}$ mass concentration measurement.

A review of suitable, commercially available substrates revealed that DOS represents an advantageous alternative oil for use at sampling sites that experience occasional crystallization of the DOW 704 oil. The DOS oil remains in its liquid state at operating temperatures down to −48 °C (−54 °F) and possesses favorable kinematic viscosity versus temperature relationships for minimizing WINS substrate overloading. Size-selective tests of the WINS separator in the laboratory demonstrated that the DOS oil provides identical performance to that of liquid DOW 704. During warm weather tests conducted at three separate field sites, excellent agreement was observed between reference method $PM_{2.5}$ samplers equipped with DOS oil versus samplers equipped with DOW 704 oil. For the 45 discrete sampling events, the slope and intercept for the DOS versus DOW 704 $PM_{2.5}$ concentrations were 0.995 and −0.006 $\mu g/m^3$, respectively. Over the wide range of coarse particle mass concentrations encountered during these tests, results were highly correlated, as demonstrated by an R^2 value of 0.999. Since the time of EPA's approval and recommendation of the DOS alternative oil in 2001, there have been no reports of problems associated with the field use of the oil.

In collaboration with the CT DEP, EPA conducted systematic field tests to determine whether an oil crystallization event adversely affects the quality of $PM_{2.5}$ compliance measurements. A full evaluation of the performance of the crystallized oil was conducted during wintertime field tests in the geographic region having the highest reported frequency of oil crystallization. During 32 separate crystallization events, no significant adverse effect of the crystallized oil on measured $PM_{2.5}$ concentrations was observed. Results obtained using the DOS oil verified that it represents a viable replacement oil for the DOW 704 oil. All of the test results were highly correlated, and excellent interlaboratory agreement was observed between two separate research organizations that conducted the collocated field tests.

Based on the favorable results obtained both in the laboratory and in the field, it was concluded that a DOW 704 oil crystallization event does not compromise the quality of the measured $PM_{2.5}$ mass concentration of the event. Site operators who do not observe crystallization of the DOW 704 oil are encouraged to use existing reserves, then procure the replacement DOS oil or replace their WINS fractionators with the BGI VSC cyclone. Because the size-selective performance of both of these designs is virtually identical, WINS fractionators equipped with DOS oil provide identical test results to those achieved using the BGI cyclone.

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of trade names or commercial products does not constitute endorsement or recommendation by the agency.

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