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Research and Development Report

A STUDY OF VARIABLES AFFECTING RESULTS IN THE D2274  
ACCELERATED STABILITY TEST  
Part 3 - Effects of Selected Physical Variables

by  
Dr. E.W. White

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Part 3 - Effects of Selected Physical Variables



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There should be a continuing effort to develop a standard bath responsiveness criterion for ASTM D2274 to further define sparger effectiveness and to determine the differences between the chemical nature of the adherent and filterable insolubles.

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## ABBREVIATIONS

°API	Aniline point index
ASTM	American Society for Testing and Materials
°C	Degrees Celsius
cSt	Centistokes
°F	Degrees Fahrenheit
HPLC	High pressure liquid chromatography
Hz	Hertz
ID	Inside diameter
kPa	Kilopascals
LCO	Light cycle oil
L/hr	Liters per hour
µm	Micrometers
mg	Milligrams
mg KOH/g	Milligrams of potassium hydroxide per gram
mL	Milliliters
mm	Millimeters
NDF	Naval Distillate Fuel
OD	Outside diameter
psi	Pounds per square inch
std dev	Standard deviation
wt	Weight

## ABSTRACT

Physical variables were examined to determine their effects on the formation or determination of the insolubles in the ASTM D2274 accelerated stability test. We examined the following physical variables that could affect the aging step: bubbler geometry, the oxygen release depth, the fuel volume, the ratio of wetted surface to fuel volume, the age of the oxidation cell in the temperature bath, and the responsiveness of the bath. We examined the following variables that could affect the results during postaging work-up of the aged fuel: filter porosity, filter type (glass fiber versus membrane), drying time for filterable insolubles, and the use of tri-solvent in adherent insolubles recovery.

Only the bath responsiveness and the time allowed to dry the filterable insolubles affected the total insolubles measurement. The use of a fritted glass sparger would increase adherent and total insolubles. Variables such as the wetted surface and cell age had some effect on the ratio of filterable to adherent insolubles, without affecting the total insolubles. The cellulose ester membrane gave the same results as the glass fiber filters, if both are dried to constant weight.

There should be a continuing effort to develop a standard bath responsiveness criterion for ASTM D2274 to further define sparger effectiveness and to determine the differences between the chemical nature of the adherent and filterable insolubles.

## ADMINISTRATIVE INFORMATION

The work described in this report was conducted over 7 years as part of the Navy Energy Program. Initial block funding was provided by the Naval Material Command (Code 08E) under Program Element 63724N and Task Area Z0838. Dr. C.F. Krolick at this Center (Code 275) was the block program manager, and Mr. Richard Strucko (Code 2759) was the project engineer.

Currently, the work is funded by the Office of Naval Research (Code 123) under Program Element 63724N, Task Area R0838-802; and Program Element 62233N, Task Area RM33A63. Mr. W.H. Stoffel of the Shipboard Energy R&D Office (Code 2759) is the block program manager, Mr. Strucko is the project engineer, and Dr. Edmund W. White of the Fuels and Tribology Branch (Code 2832) is the Technical Manager. Work during Fiscal Year 1989 was conducted under Center Work Units 2759-703 and 2759-707.

## INTRODUCTION

This is the third in a series of reports<sup>1,2</sup> that examine the criticality of the test variables encountered in conducting the ASTM D2274 Test Method for Oxidation Stability of Distillate Fuel Oil (Accelerated Method).<sup>3</sup> In the first report, White<sup>1</sup> discussed the importance of the laboratory, the operator, and the main specified variables (test temperature, test duration, and oxygen flow rate). He found that practitioners of the method frequently introduced their own modifications, producing major variables in the results obtained by different operators within the same laboratory. The major variables were not significant factors in those differences as long as they were controlled within the specified tolerances.

White's second report<sup>2</sup> explored the effects of variables that could affect the chemistry of the instability reactions which lead to the formation of gums (inherent solubles) and sediment (filterable insolubles). He evaluated the results of experiments in which oxygen concentration, fuel acidity, metallic contamination, and ultra-violet radiation were varied and found that:

- The use of air rather than the specified oxygen leads to lower levels of insolubles.
- Residues of acid cleaners in oxidation cells can cause increased insolubles formation.
- Metals, particularly copper, can enhance the formation of insolubles.
- Exposure of fuel to ultraviolet radiation (such as that present in sunlight) can result in increased insolubles formation.
- Higher levels of insolubles may result if a fuel is sparged with air prior to conducting the ASTM D2274 test.

This report examines the effects of various physical factors that could affect the formation of insolubles. Some of the factors would influence results during the 16-hr aging period; others would affect results during the work-up of the fuel following aging.

Variables that could affect insolubles formation during the aging step include:

- Configuration of the bubbler through which oxygen is introduced into the oxidation cell,
- Depth at which oxygen is released into the fuel,
- Volume of fuel used in the test,
- Ratio of wetted surface to fuel volume,
- Number of times the oxygen cell had been used,
- Condenser temperature,
- Location of the oxidation cell in the temperature bath, and
- Temperature responsiveness of the bath.

Variables studied that could affect measurement of the insolubles following aging include:

- Porosity of the filter medium used to separate the filterable insolubles from the aged fuel,
- Nature of the filter medium (glass fiber versus membrane),
- Time allowed to dry the filterable insolubles (i.e., for the adherent hydrocarbon solvent to evaporate), and
- The manner in which the trisolvant is used to removed adherent insolubles from the glassware (volume used and temperature of the solvent).

This report describes the equipment, materials, and test procedures used and interprets the results.

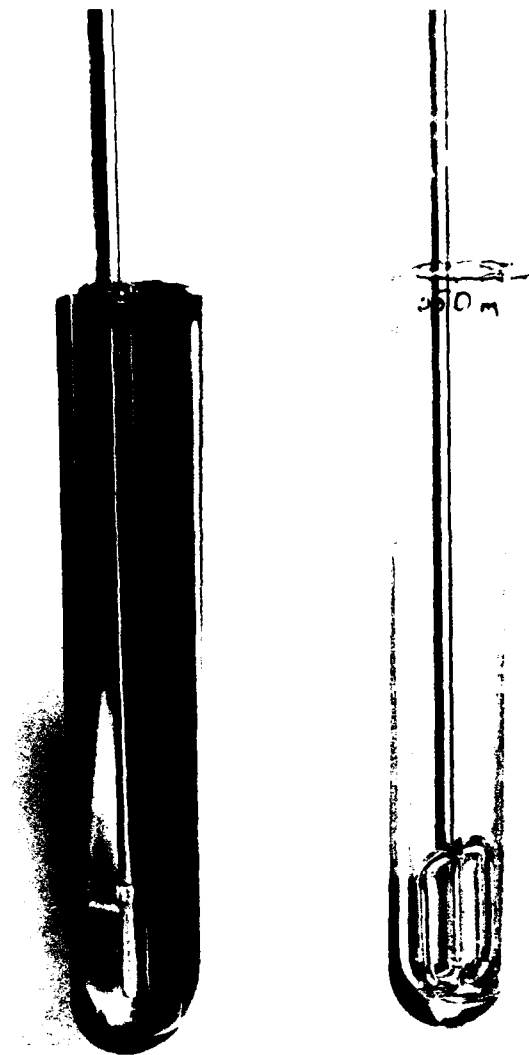
## TECHNICAL BACKGROUND

### ASTM D2274 TEST METHOD

The ASTM D2274 test method<sup>3</sup> consists of aging 350 mL of filtered fuel at 95°C (203°F) for 16 hr while bubbling oxygen through the fuel at a rate of 3 L/hr. Then the fuel is cooled in the dark to the ambient temperature of 22° to 27°C (72° to 80°F) before it is filtered to recover the filterable insolubles. The filterable insolubles are rinsed with isooctane, dried in an oven, and weighed. ASTM D2274-74 specified 1 hr drying at 99°C and glass fiber filter paper. The revised D2274-88 specifies 30 minutes drying at 80°C and a cellulose ester membrane filter. Insolubles adhering to the oxidation cell and the oxygen delivery assembly are recovered by rinsing with trisolvent -- an equal volume of toluene, acetone, and methanol. (Toluene is specified in D2274-88 for safety reasons, to replace the benzene specified in D2274-74.) The trisolvent is evaporated, leaving the adherent insolubles which are weighed. The sum of the filterable and adherent insolubles is reported as the total insolubles expressed as mg/100 mL of fuel.

The aging step occurs in a 600-mm-long, 45-mm outside diameter (OD) borosilicate glass oxidation cell. Oxygen is delivered through a 7-mm borosilicate glass tube to a point 15 mm above the bottom of the oxidation cell. The oxygen delivery tube is kept approximately centered in the oxidation cell by a glass yoke visible in Fig. 1.

The 350 mL of fuel fills the oxidation cell to a point 280 to 290 mm above the bottom. With the fuel at test temperature in the heating bath and the oxygen delivery tube in place, the fuel reaches a height of 320 to 330 mm above the bottom of the oxidation cell. During the aging period, the oxidation cell is surmounted by a condenser that penetrates 100 mm into the oxidation cell to ensure against excessive loss of fuel components to the atmosphere.



Note: The oxygen delivery tube with integral centering yoke is visible in the empty cell to the right.

Fig. 1. Oxidation cells used in the ASTM D2274 procedure.

#### VARIABLES IN THE AGING STEP

An earlier report<sup>2</sup> discussed the effects that the oxidation step has on the reactions that lead to fuel insolubles. While the exact mechanisms are debatable, it is generally agreed that oxygen is involved in a bimolecular reaction with some classes of compounds in a fuel. In the D2274 test, oxygen is bubbled into the fuel, rises to the surface through 305 to 315 mm of fuel, and enters into the gas phase above the fuel. During the passage of the bubbles of oxygen through the fuel, enough

oxygen must diffuse into the liquid and to the reaction site. The reaction products must be distributed into the body of the fuel by the agitation induced by the passage of the oxygen bubbles and by thermal convection currents. It is instructive to examine some of the physical factors involved in this process.

A bubble of oxygen is formed on the end of the oxygen delivery tube, reaches a size determined by the physical properties and geometry of the system, and then frees itself from the tube and ascends through the fuel. The rate of rise depends on the size of the bubble, the relative densities of the bubble and the fuel, and the fuel viscosity at test temperature. If the delivery tube is exactly vertical, the bubble tends to ascend along the delivery tube, and its rate of rise may be slowed by adhesion. The bubble will rise free of this effect if the delivery tube is sufficiently angled. The bubble carries a body of surrounding fuel with it as it rises; hence the bubbles act as a pump to move fuel to the surface. This action helps to circulate the fuel and disperse the products of the instability reaction throughout the fuel.

The size of the bubble becomes important if oxygen diffusion into the fuel is the rate-limiting step. The 3 L/hr volume of oxygen dispersed into small bubbles will have a greater interface area than when the bubbles are larger. Fick's law of diffusion states that the rate of diffusion is proportional to the concentration gradient and to the surface across which diffusion occurs. Consequently, other factors being equal, we would expect the rate of oxygen diffusion to be greater with smaller bubbles, and oxidation rates should be higher with more oxygen reaching the reaction sites in the fuel body. Also, the residence time of a small bubble will be greater than that of a large bubble, thus allowing more time for oxygen to diffuse from the bubble to the liquid phase.

Bubbles of unreacted oxygen escape into the gas phase above the liquid when they reach the surface of the fuel. This displaces an equivalent volume of gas through the condenser into the atmosphere. The gas that reaches the condenser is a combination of oxygen and vapors whose composition depends upon the vapor pressures and concentrations of the fuel components. By lowering the temperature of the off gas, the condenser reduces the vapor pressure and condenses out some fuel components; this prevents excessive losses of fuel during the 16-hr test.

Acidic components can be produced as a result of the oxidation reactions. We showed<sup>2</sup> that acidic materials can abet the instability reactions in a fuel. By reducing the amount of products that can escape, the condenser may permit a more rapid formation of insolubles in the fuel. If so, the temperature of the cooling liquid passing through the condenser should be a factor in the quantity of total insolubles produced.

The age of the oxidation tube (the number of prior uses) also may be a factor. The nature of the surface available for deposition of the adherent insolubles could play a critical role if (as some work indicates) the major difference between adherent and filterable insolubles is the location and not the chemical nature of the material. Assuming that the use of detergents and cleaning brushes gradually creates small scratches on the surface of the oxidation cell, then the more often a cell has been used, the more scratches there will be in its surface. Such scratches increase the total surface available for deposition of insolubles. Older cells with more scratches could favor the deposition of more adherent insolubles and change the ratio of adherent to filterable insolubles.

The temperature responsiveness of the heating bath is another variable that could affect D2274 results. When a batch of oxidation cells containing fuel to be aged is inserted into a temperature bath, the temperature of the bath fluid drops

from the 95°C control point. The magnitude of the temperature drop and the time required to return to the control point temperature depend upon the quantity of liquid in the heating bath and the rate of heat input from the electrical heaters. In general, the liquid in our heating baths returns to the control point in about 10 minutes if an 8-cell bath is used and 30 minutes if a 12-cell bath is used; see Fig. 2.

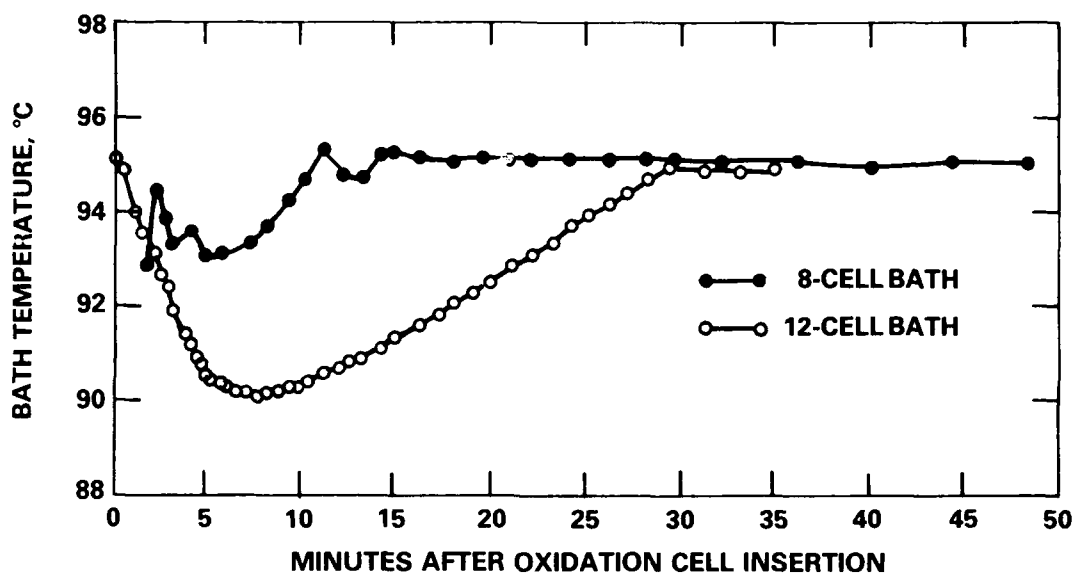


Fig. 2. Temperature recovery response curves showing the difference between using 8- or 12-cell temperature baths for the ASTM D2274 test procedure.

The fuel samples in the oxidation cells slowly warm in the heating bath; they reach within a degree of the desired 95°C in about 20 to 35 minutes in our baths; see Fig. 3. The differences in the rates at which the fuels reach the test temperature will affect the average reaction rates, hence the quantities of insolubles formed. As White noted,<sup>2</sup> reaction rates increase 1.7 to 3 times for each 10°C increase in

temperature. Consequently, a fuel sample that takes longer to reach operating temperature will produce less insolubles. The question is whether the first 30 minutes of the 16-hr aging period are critical (e.g., in forming the precursors to the insolubles).

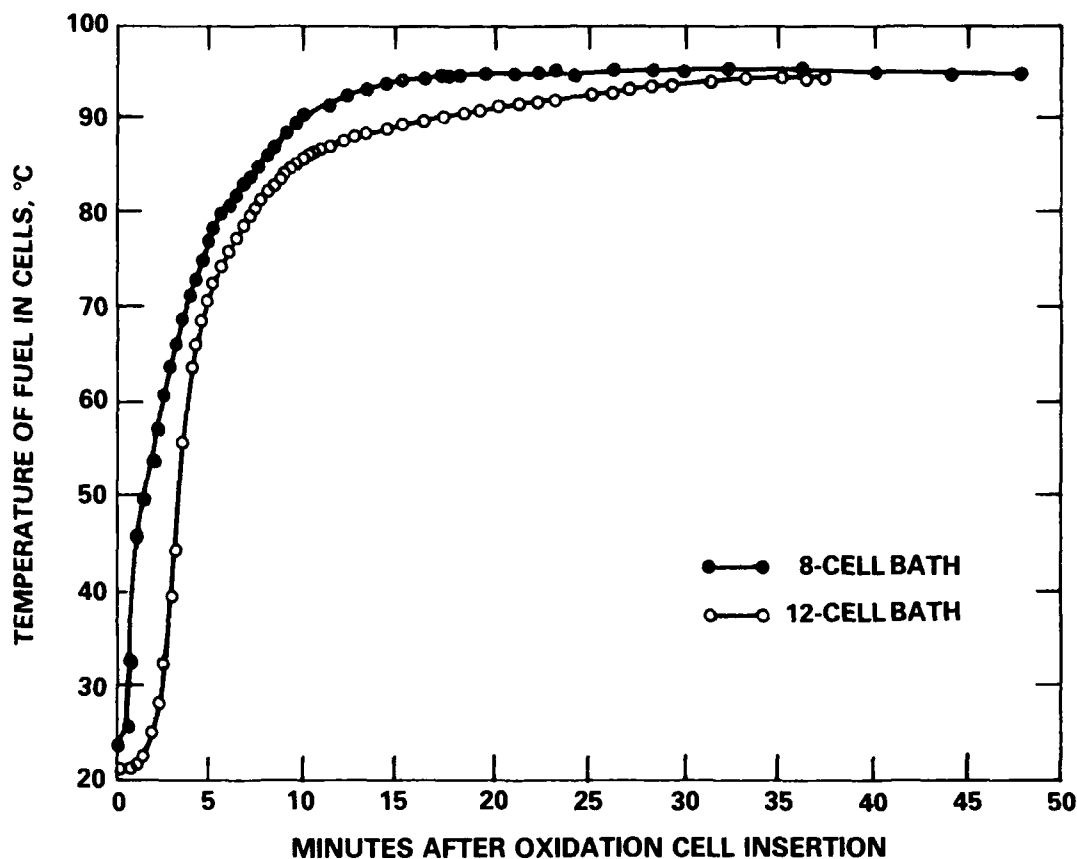


Fig. 3. Times required for the fuel in oxidation cells to reach operating temperature using 8- and 12-cell baths for the ASTM D2274 procedure.

#### VARIABLES IN THE POSTAGING STEPS

The filtration step, including conditioning the sample by cooling, may be one of the more critical steps in the D2274 test procedure. After the aged fuel is removed from the heating bath and cooled, its final temperature determines how much of the "insolubles" drops out of solution. The rate at which the fuel reaches its final temperature will determine the nature and particle size distribution of the "insolubles."

The porosity and configuration of the filter medium during the filtration step will determine how much of the fine solids escapes capture and ends up in the filtrate. In addition, the intensity of the vacuum applied to the vacuum filtration step will determine the quantity of amorphous insolubles pulled through the filter, the density of the packing of the filtered insolubles on the filter medium, and the temperature reached by the filtrate through evaporative cooling. The density with which the filterable insolubles are packed on the filter medium will affect the solvent washing step and determine whether all unreacted fuel components are washed out of the filterable insolubles.

A Gooch crucible with glass fiber filter paper forms the filter in the D2274-74 procedure. Neither the filter paper nor the vacuum to be used is specified, although a footnote indicates a grade of filter paper that was "found satisfactory for this purpose." A 47-mm-diameter cellulose ester membrane filter of specified porosity is used in the revised D2274-88 procedure, and a suction of approximately 8 kPa (12 psi) is indicated.

After all the aged fuel has been filtered, the filter insolubles on the filter are rinsed with hydrocarbon solvent (isooctane) to remove occluded fuel. The oxidation cell and the oxygen delivery tube assembly are rinsed also with isooctane and these rinsings are passed through the filter. Then, the Gooch assembly or the membrane filter (depending on the procedure used) is dried in an oven. The time required to drive off all the isooctane and reach constant weight depends on how much of the solvent is left in the filterable insolubles which, in turn, is dependent on the vacuum level and how long the vacuum source is allowed to draw air through the filter. D2274-74 specified a 1-hr drying time at 99°C; D2274-88 specifies 30 minutes at 80°C.

As indicated earlier, a trisolvent consisting of equal volumes of toluene, acetone, and methanol is used to remove adherent insolubles from the oxidation cell and the oxygen delivery tube assembly. There is no indication of the volume of trisolvent to use in the D2274-74 procedure. D2274-88 specifies that the operator should use "three equal rinses totaling  $75 \pm 5$  mL of trisolvent and, if there is still evidence of a stain, "rinse with an additional 25-mL volume of trisolvent." The adequacy of rinsing in the older procedure must be questioned. Further, it may not be advisable to use hot trisolvent to assist recovery of adherent insolubles because solubility generally increases with temperature.

## DESCRIPTION OF EQUIPMENT AND MATERIALS

### OVERVIEW

Most tests were conducted in apparatus designed for ASTM D2274. Bottle tests used in several experiments were conducted in apparatus similar to that specified in ASTM D4625-86 Test Method for Distillate Fuel Stability at  $43^{\circ}\text{C}$  ( $110^{\circ}\text{F}$ ),<sup>4</sup> but other temperatures were used. Solvents used in both the D2274 and D4625 test methods were reagent grade, except the hydrocarbon solvent which was the knock engine grade iso-octane specified in D2274-74. (D2274-88 specifies isooctane of 99.75% purity or better and containing no more than 0.10% n-heptane.) We used only one fuel in some of the experiments and two or more fuels in others.

### DESCRIPTION OF EQUIPMENT

An 8- or 12-cell temperature bath, shown in Fig. 4, was used in experiments conducted by the D2274 procedure. The 8-cell unit is a Lawler Manufacturing, Inc., 25-liter bath heated by a 100-watt heater that draws 9 amperes from a 115-volt, 60-Hz power supply. Thus, the bath contains 3.12 liters of heat transfer fluid per oxidation cell and has 125 watts per cell available.

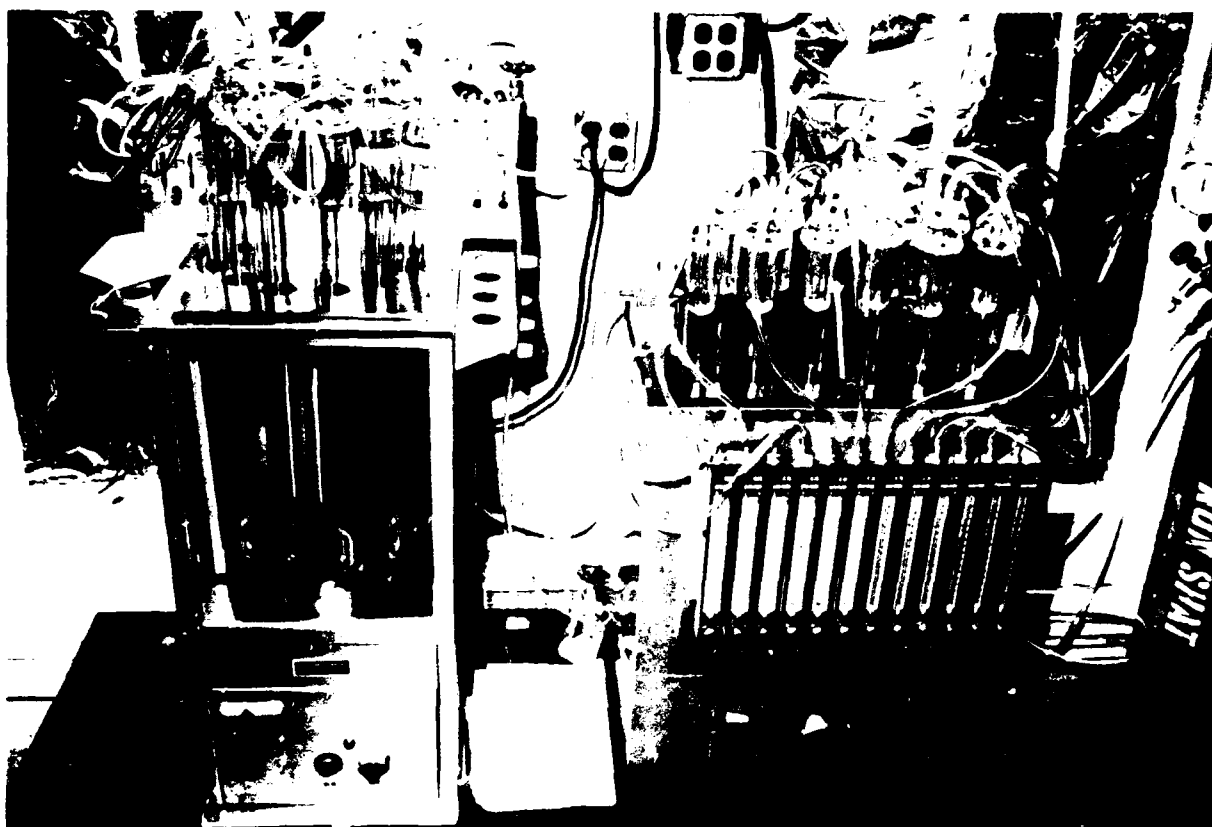


Fig. 4. Configuration of the 8-cell unit to the left and the 12-cell unit to the right.

The 12-cell unit is a product of the Koehler Instrument Company, Inc.<sup>5</sup> It has a 72-liter bath equivalent to 6 liters per oxidation cell. It is heated by two 1500-watt heaters that can be turned on or off by toggle switches, and by a 750-watt thermostatically controlled heater. There are 312.5 watts per oxidation cell with all three heaters activated. There are 62.5 watts available per oxidation cell if only the thermostatically controlled heater is on line. The Koehler unit is designed for a 230-volt, 50-/60-Hz, 16-ampere power supply.

## DESCRIPTION OF FUELS USED

Most experiments used one or more of the four fuels whose properties are shown in Table 1. Three of the fuels were the same as those used in earlier work.<sup>1,2</sup> All four were diesel-range fuels but were from different sources. Fuel N was a conventional MIL-F-16884 naval distillate fuel (NDF). Fuel A was 70/30 (by volume) blend of an aged NDF with an aged LCO.<sup>6</sup> Fuels B and E were Army VV-F-800 diesel fuel oils obtained from Army depots in Arkansas and Michigan, respectively.<sup>6</sup>

Table 1. Selected properties of four test fuels.

	Fuel N	Fuel A*	Fuel B*	Fuel E*
Gravity, °API, 15.6°C	39.0	31.1	35.0	34.8
Viscosity, cSt, 40°C	3.4**	NA	2.3	2.6
Color (ASTM)	NA	L3.5	2.5	2.5
Flash Point, °C	80	>60	77	80
Pour Point, °C	NA	NA	-31	-32
Cloud Point, °C	NA	NA	-21	-18
Distillation, °C				
50% Point	286	276	256	253
90% Point	340	339	302	303
End Point	366	360	330	338
Copper Strip at 100°C	No. 1b	NA	No. 1	No. 1
Carbon Residue (10% bottom), %	0.09	NA	0.05	0.13
Sulfur, % (wt)	0.52	NA	0.40	0.39
Ash, % (wt)	NA	NA	0.003	0.002
Acid Number, mg KOH/g	0.02	NA	0.02	0.05
Accelerated Stability, mg/100 mL	3.9	2.4	3.1	2.4
*Data from NRL.				
**Measured as 3.5 cSt at 38°C.				
NA - Not available.				

A contractor reported that Fuel N consisted of 75% saturates, 23% aromatics, and 2% olefins. NRL personnel used HPLC techniques to determine that Fuel A consisted of 67% saturates, 21% monocyclic aromatics, and 12% dicyclic and polycyclic aromatics;

Fuel B consisted of 71% saturates, 19% monocyclic aromatics, and 9% dicyclic and polycyclic aromatics; and Fuel E consisted of 73% saturates, 20% monocyclic aromatics, and 7% dicyclic aromatics.<sup>7</sup>

## TEST PROCEDURES

### OVERVIEW

We varied one factor at a time to evaluate the importance of the physical factors that may affect the results of the ASTM D2274 test. In most experiments, we varied the selected factor to a much greater extent than would be encountered in normal practice. This was done to produce an observable change in insolubles formation that would determine definitively if the factor was critical. Results were evaluated with the help of statistical inference using pooled sample deviations.<sup>8-10</sup> Details of the experiments follow.

### PHYSICAL VARIABLES IN THE AGING STEP

#### Bubbler Geometry

The standard oxygen deliver tube system was modified in several ways to evaluate the effect of system geometry; see Fig. 5. The standard D2274 system is to the extreme left in the figure, and various modifications are shown to the right. Fuels A, B, and N were used in various phases of these experiments.

As oxygen leaves the delivery tube, it forms a bubble that grows in size until a combination of interfacial tension, buoyancy, and shear forces effect its release. A bubble tends to follow the delivery tube to the surface of the fuel because the bubble release point is not offset. However, the bubbles may not follow a vertical path because circulatory currents are setup in the fuel by thermal gradients and the pumping action of the rising stream of oxygen bubbles. Coalescence and shearing of the bubbles may result.

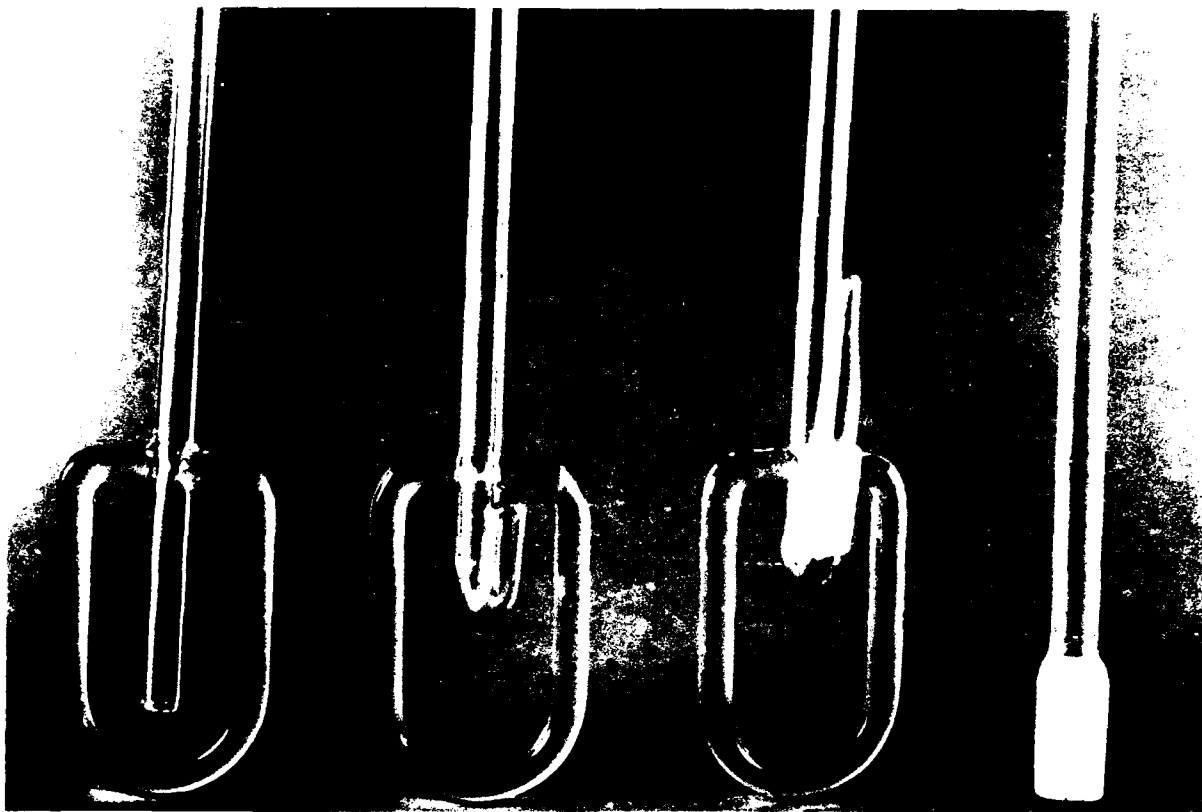


Fig. 5. Oxygen delivery systems used to evaluate geometry effects.

The first change in oxygen delivery that was examined is shown next to the standard delivery tube in Fig. 5. The standard delivery tube was bent to discharge upward and the opening was displaced from the axis of the delivery tube. The oxygen bubbles thus discharge eccentrically to the axis of the oxidation cell and create different mixing patterns than those created by the standard system.

In a further change shown to the right of the simple up-bend version, a tip of reduced diameter was appended to the tube. The standard tube has a 7-mm OD and a 4-mm ID. The reduced size tips were 3.3 to 3.4 mm for the medium tip and 1.7 to 1.8 mm for the fine tip. These were expected to produce smaller bubbles that would provide more total oxygen surface in contact with the fuel.

The actual number of bubbles produced by each of the tips at the standard 3 L/hr oxygen delivery rate was estimated by scaling up from the number of bubbles produced at 0.22 L/hr. The lower rate was used to develop discrete bubbles at a rate that could be counted. The bubbles coalesce and break up into various sizes at higher oxygen flow rates, making this technique only an approximation.

The final oxygen delivery device used in the tests is a fritted glass sparger, shown at the extreme right in Fig. 5, which delivers a multitude of very fine bubbles. The sparger was a 20-mm-long cylinder with a 12-mm OD and a porosity of 40 to 60  $\mu\text{m}$ .

#### Oxygen Release Depth

The tip of the standard oxygen delivery tube is 15 mm above the bottom of the oxidation cell. We ran tests with the delivery point one-third and two-thirds of the liquid height above the bottom to evaluate the effect on insolubles formation of differences in the oxygen delivery depth. The actual depths were about 90 and 190 mm, respectively, above the bottom of the cell. Such differences were expected to reduce the oxygen residence time in the cell and cause changes in the fuel circulation patterns. The depth effect also was evaluated for the other types of oxygen delivery devices.

#### Fuel Volume

Again, we conducted experiments that accentuated the change on the premise that operators might measure volumes of fuel that differ slightly from the 350 mL specified in D2274. We used volumes of 250 and 300 mL in addition to the control volume. Also, we used a 250-mL volume of fuel that was raised to the height that 350 mL would occupy by adding glass beads.

### Ratio of Bottle Surface to Fuel Volume

It has been suggested that the adherent and filterable insolubles measured in the stability tests of fuels are the same species, and that the ratio of the two is a function of the available container surface area and characteristics. If these hypotheses are correct, the ratio of adherent to filterable insolubles should be a function of the ratio of the container surface to the fuel volume. A contractor was assigned the task of checking these hypotheses in several bottle storage experiments at 65°C.<sup>11</sup>

Fuel B was doped with 270 mg of 2,5-dimethylpyrrole per liter of fuel, a substance known to result in insolubles formation. The resultant blend was stored in 125-, 250-, 500-, and 1000-mL borosilicate bottles. Fuel volumes in the bottles were 100, 200, 400, and 800 mL, respectively. We thermally stressed the fuel in one set of bottles of each size at 65°C for 21 days. We stressed the fuel in a second set for 32 days. Filterable and adherent insolubles were determined as specified in the standard 43°C bottle test, ASTM D4625; all tests were run in triplicate.

### Oxidation Cell Age

We conducted one experiment that compared results obtained when we used new cells with results from cells that had been used a number of times. This was to determine whether the deterioration of D2274 oxidation cell from the scratching or etching of the surface during the cleaning process would influence the amounts of filterable and adherent insolubles obtained in the test. In another experiment, we kept track of the number of times an oxidation cell had been used to evaluate whether there was a progressive change in the results. We obtained results with cells that had been used 0, 1, 2, 3, 4, 5, and more than 10 times.

### Condenser Temperature

The condenser temperature effect was evaluated first in an experiment in which refrigerated water was passed through one set of condensers, normal tap water (the control) was passed through another set, and water flow was stopped in a third set (thus allowing the water temperature to rise in an uncontrolled manner). The temperature of the water flowing through the condensers was controlled in another test at 43°, 73°, and 98°F (6°, 23°, and 98°C).

### Bath Factors

#### Cell Location in Bath

We tested our new D2274 temperature bath thoroughly before placing it in use several years ago. The 12-cell bath is a rectangular unit (Fig. 4) with the cells fit in a staggered arrangement (Fig. 6). One test evaluated the uniformity of results regardless of the position of an oxidation cell in the bath.

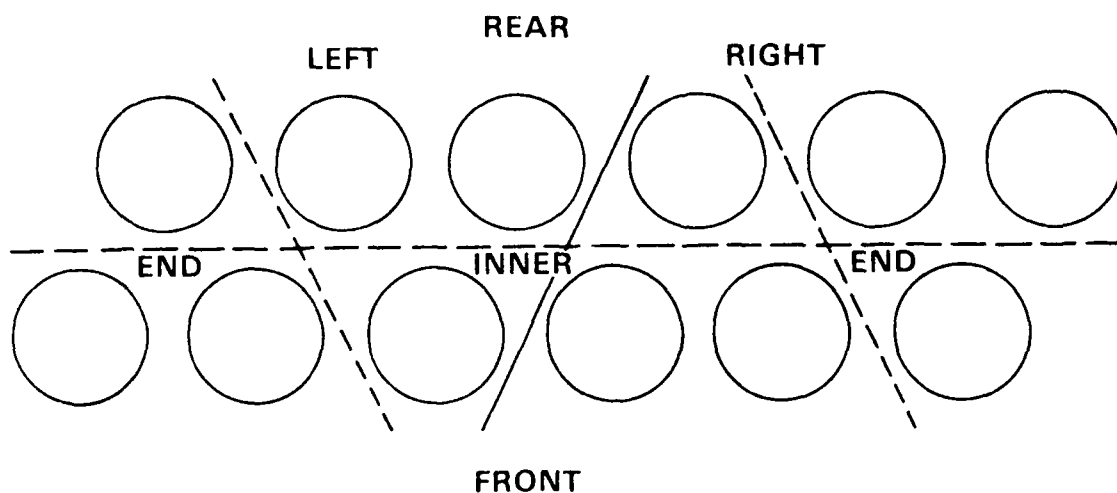


Fig. 6. Designation of cell locations in the 12-cell temperature bath.

A standard D2274 test was conducted with care taken to identify each cell by location. The results were combined in three ways to analyze the data:

1. The front row was compared with the back row.
2. The end cells were compared with the inner cells.
3. The right-hand cells were compared with the those on the left.

The Student-t null hypothesis technique was used to assist with the analysis.

#### Comparison of Two Baths

As noted earlier, our two D2274 baths did not respond at the same rate to the impact of cold oxidation cells that were placed in the baths. Hence, the fuel in the oxidation cells approached the test temperature at different rates. We investigated the affect this difference had on the quantities of insolubles formed during the test.

The 8- and 12-cell units were run simultaneously. Four oxidation cells containing Fuel N and four containing Fuel B were placed in the 8-cell bath. Six cells containing Fuel N and six containing Fuel B were placed in the 12-cell bath. We monitored the bath and fuel temperatures in one cell in each bath during the 16-hr stress period. Then, the cells were removed from the paths and processed as specified in ASTM D2274-74 to determine filterable and adherent insolubles. The results were analyzed with the help of the Student-t test.

#### POSTAGING VARIABLES

##### Postaging Steps

Fuel is cooled to room temperature after aging at 95°C for 16 hr, then filtered to remove insolubles that have formed. The filtered solids are rinsed with isooctane to remove adherent fuel, and the Gooch crucibles containing the filtered solids and the filter paper are dried in an oven. The oxidation cells and the oxygen delivery tubes also are rinsed with isooctane to remove fuel, and then with a trisolvant that is evaporated to obtain the adherent insolubles.

## Filter Medium

### Filter Porosity

ASTM D2274-74 specified the use of glass fiber filter paper in the postaging filtration step. We compared three grades of filter paper to ascertain the effect of filter porosity on the level of measured filterable insolubles. Nominal porosities of the Whatman International filter papers were 0.7  $\mu\text{m}$  (Grade GF/F), 1.6 (Grade GF/A, the standard), and 2.7 (Grade GF/D). The fuel was filtered twice through GF/A paper in a subsequent test. Standard D2274 conditions were used with Fuel N for all four tests.

### Cellulose Ester versus Glass Fiber

The newer ASTM D2274-88 specifies a 47-mm-diameter cellulose ester membrane filter with a porosity of 0.8  $\mu\text{m}$  to replace the glass fiber filter paper as the filtration medium. Therefore, another series of experiments was conducted to compare the two types of filters; i.e., the Millipore<sup>TM</sup> 47-mm membrane and the Whatman GF/A glass fiber paper. Four replicate filterable insolubles obtained with the Millipore system were compared with six replicates obtained using the Gooch crucible, glass fiber filter paper system; Fuel B was used.

### Drying Time

ASTM D2274-74 specified that the Gooch crucibles containing filterable insolubles be dried for 1 hr in a 99°C oven. The filterable insolubles did not always seem dry after the hour in the oven; therefore, we conducted several experiments to determine how long it takes to reach constant weight. In the first experiment, eight replicate filterable insolubles from Fuel A were dried for the specified hour, weighed, returned

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<sup>TM</sup>Millipore is a trade name of Millipore, Corp., Bedford, MA 01730.

to the oven for an additional 16 hr, and reweighed. Another set of eight replicates was dried for 1.5 hr, weighed, returned to the oven for 3 hr, and reweighed. A final set of eight replicates was dried for 3 hr, weighed, returned to the oven for 70 hr, and reweighed.

In a later experiment, a set of 12 replicate filterable insolubles obtained from Fuel B were placed in a 100°C oven for an additional hour (a cumulative drying time of 1.5 hr), cooled, and reweighed. They were returned to the oven several more times to obtain cumulative drying times of 4.5, 12.5, 36.5, and 129 hr.

ASTM D2274-88 indicates that the cellulose ester filter medium and filterable insolubles should be dried at 80°C for only 30 minutes. We tested the adequacy of these drying conditions with 12 replicates formed with Fuel B and 12 replicates formed with a recently acquired 27.5° API west coast fuel containing 30% light cycle oil. Two bottles containing Fuel B were removed from the 80°C oven after residence times of 0.25, 0.5, 1.0, 2.0, 3.5, and 21 hr. Two bottles containing 27.5° API fuel were removed after residence times of 0.25, 0.5, 1.0, 2.0, 3.0, and 19 hr. Each sample was cooled and weighed after removal from the oven.

#### Trisolvent Usage

ASTM D2274-74 did not specify the quantity or the temperature of the trisolvent used to recover adherent insolubles from the oxidation cells and oxygen delivery tubes. ASTM D2274-88 specifies the use of three 25-mL rinses followed by a fourth 25-mL rinse if there is visual evidence of stain or color remaining on the glassware.

We conducted several experiments to evaluate the effects of solvent quantity and temperature on the completeness of adherent insolubles recovery. In the first experiment, six samples of Fuel N were stressed by bottle storage at 66°C (150°F) for 4 weeks. A 25-mL volume of trisolvent was used at room temperature to recover

adherent insolubles. A second 25-mL volume then was used to determine whether any appreciable quantity of adherent insolubles had been left on the walls of the bottles.

In the two other experiments, samples of Fuel N were stressed by 150°C bottle storage for 4 weeks. Boiling trisolvant was used to recover adherent insolubles from some of the glassware, and trisolvant at room temperature was used to recover adherent insolubles from the remaining glassware. A single 25-mL rinse was used in one experiment, and two 25-mL rinses were used in the other.

## DISCUSSION OF RESULTS

### AGING STEP VARIABLES

#### Bubbler Geometry

##### Nonconcentric Oxygen Delivery

Table 2 shows the levels of total insolubles obtained in three different fuels with the standard D2274 oxygen delivery system and an up-turned nonconcentric oxygen delivery system. Only total insolubles (and the sample standard deviations of duplicate determinations) are shown because past experience has shown that more consistent results are obtained than with filterable or adherent insolubles.

Table 2. Effect of nonconcentric oxygen discharge (total insolubles, mg/100 mL).

Fuel	Standard		Nonconcentric	
	Mean	Std Dev	Mean	Std Dev
A	2.6	0.3	3.1	0.2
B	3.7	0	4.4	0.1
N	1.8	0	1.8	0.1

Nonconcentric delivery seems to increase the formation of total insolubles in Fuels A and B, but not in Fuel N. The result is statistically highly significant (>99% confidence level) with Fuel B, but it is probably not significant (<95% confidence level) with Fuel A. The effect of the nonconcentric oxygen delivery system

is ambiguous; it appears significant with Fuel B, borderline with Fuel A, and far from significant with Fuel N. The departure from concentric discharge of oxygen was accentuated; therefore, we may conclude that minor deviations from the concentric discharge of oxygen will not produce major differences in the amounts of ASTM D2274 total insolubles.

#### Tip Size Effects

The estimated number of bubbles produced by passing 3 L/hr of oxygen through the several sizes of tips is shown in Table 3, together with the estimated area where bubbles are in contact with the fuel. As a rough approximation, the bubble area may be related to the top size by the equation:

$$A_b = 21,400 - 2,600(d_t),$$

where  $A_b$  is the area in  $\text{cm}^2/\text{L}$ , and  $d_t$  is the tip diameter in millimeters. This is an approximation because the scale-up from 0.22 to 3 L/hr does not take into consideration the effects of agglomeration of bubbles.

Table 3. Effects of tip size on bubble formation.

Configuration	No. of Bubbles/Minute	Contact Area ( $\text{cm}^2/\text{L}$ )
Standard D2274	546	10,534
Pointing Up		
Regular	594	11,033
Medium	931	12,815
Small	1,947	16,566

Table 4 shows the total insolubles obtained in three fuels when using the three different size tips. Tip size had no major effect; this was confirmed by low confidence levels when the Student-t null hypothesis was applied.

Table 4. Effect of tip size on insolubles formation  
(total insoluble, mg/100 mL).

Type of Tip	Distance Off Bottom (mm)	Fuel A		Fuel B		Fuel N	
		Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
Regular	55	3.1	0.1	4.4	0.1	1.8	0.1
Medium	95	2.9	0	4.8	0.5	1.9	0.1
Small	97	2.9	0	4.3	0.2	1.9	0.1

#### Sparger Effect

Table 5 shows insolubles formed in three fuels with the standard D2274 oxygen delivery configuration and with oxygen delivery through a fritted glass sparger. The quantity of total insolubles produced with the sparger seems greater than the quantity obtained with the standard oxygen delivery system, regardless of the fuel involved. This is supported by the Student-t null hypothesis technique applied to Fuels A and B, with confidence levels of >95%. The high standard deviation (0.4) obtained with Fuel N reduced the confidence level to less than 90%.

Table 5. Effect of sparger on insolubles formation (insolubles, mg/100 mL).

Type of Insoluble*	Fuel A		Fuel B		Fuel N	
	Standard	Sparger	Standard	Sparger	Standard	Sparger
Filterable	2.5	2.6	3.3	2.9	1.0	1.0
Adherent	0.7	1.1	0.4	1.2	0.7	1.2
Total	3.2	3.6	3.7	4.1	1.7	2.2

\*Insolubles are averages of duplicates.

Further examination of Table 5 shows that the increase in total insolubles obtained with the sparger delivery system can be ascribed to an increase in the formation of inherent insolubles. Filterable insolubles remained essentially constant with Fuels A and N. Null hypothesis testing supports the conclusion that adherent insolubles are increased by sparging. Confidence levels range from 90% to 95% with Fuels A and B to >99.5% with Fuel N.

## Oxygen Release Depth

### Standard Oxygen Delivery Tube

Table 6 shows the levels of total insolubles obtained when oxygen is delivered at 15 (standard), 90, and 190 mm off the bottom of the oxidation cell. The height off the bottom had little effect on the total insolubles formed in the test. Standard deviations ranged from 0 to 0.2 mg/100 mL. Confidence levels of <90% for Fuels A and B and 90% to 95% for Fuel N in the Student-t test indicate little probability that the 90-mm values differ from the standard values. Similar confidence levels were obtained when the results obtained at the 190-mm location were compared with those at the standard location.

Table 6. Effect of height D2274 oxygen delivery above bottom of oxidation cell (total insolubles, mg/100 mL).

Height (mm)	Fuel A	Fuel B	Fuel N
15 (Standard)	3.2*	3.6*	1.7*
90	3.4*	3.8*	2.0*
190	3.3**	3.8**	1.4*

\*Averages of two data points.  
\*\*Averages of three data points.

In a further effort to ascertain whether height of oxygen delivery above the bottom of the oxidation cell affects the results, we used regression analysis to fit a straight line to the data from Fuel A and B for filterable, adherent, and total insolubles. While the correlation coefficients were poor (0.24 to 0.77) in most cases, the resultant equations had very low slopes (0.0005 for Fuel A and 0.0010 for Fuel B). These slopes implied that an oxygen delivery site 200 mm above the bottom of the oxidation cell would result in an increase in total insolubles of only 0.1 to 0.2 mg/100 mL; i.e., the effect would be of no consequence considering the precision of the method.

### Up-Turned Normal Tubes

When the up-turned tubes were located at various heights above the bottom, the results supported the general insensitivity of the total insolubles formation to the location of the delivery of oxygen. A straight line fitted to the data from Fuel A had a slope of 0.0006 mg/100 mL per millimeter change in height; i.e., a change of only 0.12 mg/100 mL for a height of 200 mm above the bottom. Null hypothesis testing of the data from Fuel B showed a confidence level of <95% that the total insolubles formed with the up-turned tube 122 mm off the bottom was less than that formed when the tube was nearer to the bottom (about 54 mm off the bottom). The confidence level was <70% when the tube opening was 186 mm off the bottom, compared with the total insolubles when the tube was at its lowest point (54 mm off the bottom). These confidence levels indicated that the distance off the bottom probably had no effect on the results.

### Sparger Height

Table 7 shows the total insolubles formed in Fuels A and B when oxygen was introduced through a porous sparger at three different heights above the bottom of the oxidation cell. The data shows little change in the total insolubles.

Table 7. Effect of sparger height above the bottom of the oxidation cell.

Height (mm)	Insolubles (mg/100 mL)					
	Fuel A			Fuel B		
	Filterable	Adherent	Total	Filterable	Adherent	Total
Bottom	2.58	1.06	3.64	2.93	1.23	4.18
90	2.66	1.16	3.81	2.90	1.29	4.20
190	2.94	0.71	3.65	3.24	1.04	4.28

Note: Data are averages of two sets of data for bottom and 90-mm values, but only a single data point was available for 190-mm values. Available standard deviations ranged from 0.17 to 0.30 mg/100 mL for the total insolubles.

Null hypothesis testing of the 90-mm data relative to the bottom data yielded <60% confidence levels that there is any statistically significant difference between the two sets of results. There is some evidence that filterable insolubles increase and adherent insolubles decrease, which leaves the total unchanged.

#### Overview of the Effect of the Oxygen Discharge Site

We noted in all three cases that neither the height of the standard oxygen distribution configuration, of the up-turned version, nor of the sparger has a significant effect on the total insolubles formed. We can postulate that the fuel will be essentially saturated with oxygen as long as the flow of oxygen induces effective circulation of the fuel. Consequently, the reaction rate will not be oxygen-limited; rather, it will be controlled by diffusion and other rate-limiting factors.

#### Fuel Volume

Table 8 shows the amounts of insolubles obtained with Fuel N when the quantity of fuel used in the ASTM D2274 procedure was varied and glass beads were used to maintain a fuel level despite lower fuel volume.

Table 8. Insolubles formation in Fuel N with different fuel volumes.

Fuel Volume (mL)	Insolubles (mg/100 mL)			Ratio of Filterable to Adherent Insolubles
	Filterable	Adherent	Total	
350*	1.6	0.9	2.4	1.8
300**	1.5	0.6	2.1	3.0
250*	1.4	0.8	2.2	1.7
250* (GB)	1.4	1.7	3.1	0.8

\*Averages of duplicates.  
 \*\*Averages of triplicates.  
 (GB) - Glass beads were present.  
 Note: Insolubles standard deviations ranged from 0 to 0.4 mg/100 mL. The ratio standard deviations ranged from 0.1 to 0.2; the 300-mL ratio was 1.3.

The filterable, adherent, and total insolubles were unchanged as the fuel volume as decreased from the standard 350 mL to 300 and then to 250. Null hypothesis testing supports this view. The confidence level that there is a change between the 350- and 250-mL results was 80% for total insolubles, far from significant.

Table 8 shows that similar ratios exist for the 350- and 250-mL fuel volumes. The 300-mL case yielded an anomalous 3.0, which may be related to a poor 1.3 standard deviation for the ratio. The ultimate cause may be a slightly inconsistent 0.6 mg/100 mL adherent insolubles value, which had a standard deviation of 0.4 mg/100 mL.

An appreciably higher level of adherent insolubles resulted when glass beads were used, as compared to the 250- or 350-mL volumes alone; glass beads also produced a lower filterable/adherent insolubles ratio (0.8). Null hypothesis testing yielded a 90% to 95% confidence level that there is a difference between the 250-mL volume with glass beads and the standard 350-mL case, and a 99% to 99.5% confidence that there is a difference between the 250-mL cases with and without glass beads.

We conclude from the fuel volume experiments that minor errors in measuring the prescribed 350-mL volume in the D2274 procedure will have minor effects. Also, the additional surface presented by the glass beads increased the formation of adherent insolubles.

#### Ratio of Bottle Surface to Fuel Volume

The concept that the level of adherent insolubles may be a function of surface area resulted from the study with glass beads, and led to an experiment in which the size of the vessel was changed to provide different ratios of wetted surface to fuel volume. Bottle tests (similar to ASTM D4625 but conducted at 65°C) were run in triplicate using bottles ranging from 125 to 1000 mL in size and corresponding fuel volumes ranging from 100 to 800 mL.<sup>8</sup>

Figure 7 shows the levels of insolubles obtained after 21 and 32 days of 65°C storage. The total insolubles remained constant in each of the two cases, while adherent insolubles increased and filterable insolubles decreased as the surface area to fuel volume ratio increased. These observations are supported by a null hypothesis test. Comparison of the extreme gives a confidence level of less than 80% that there was a change in total insolubles but a 95 to 99.95% confidence that there were changes in the filterable and adherent insolubles levels.

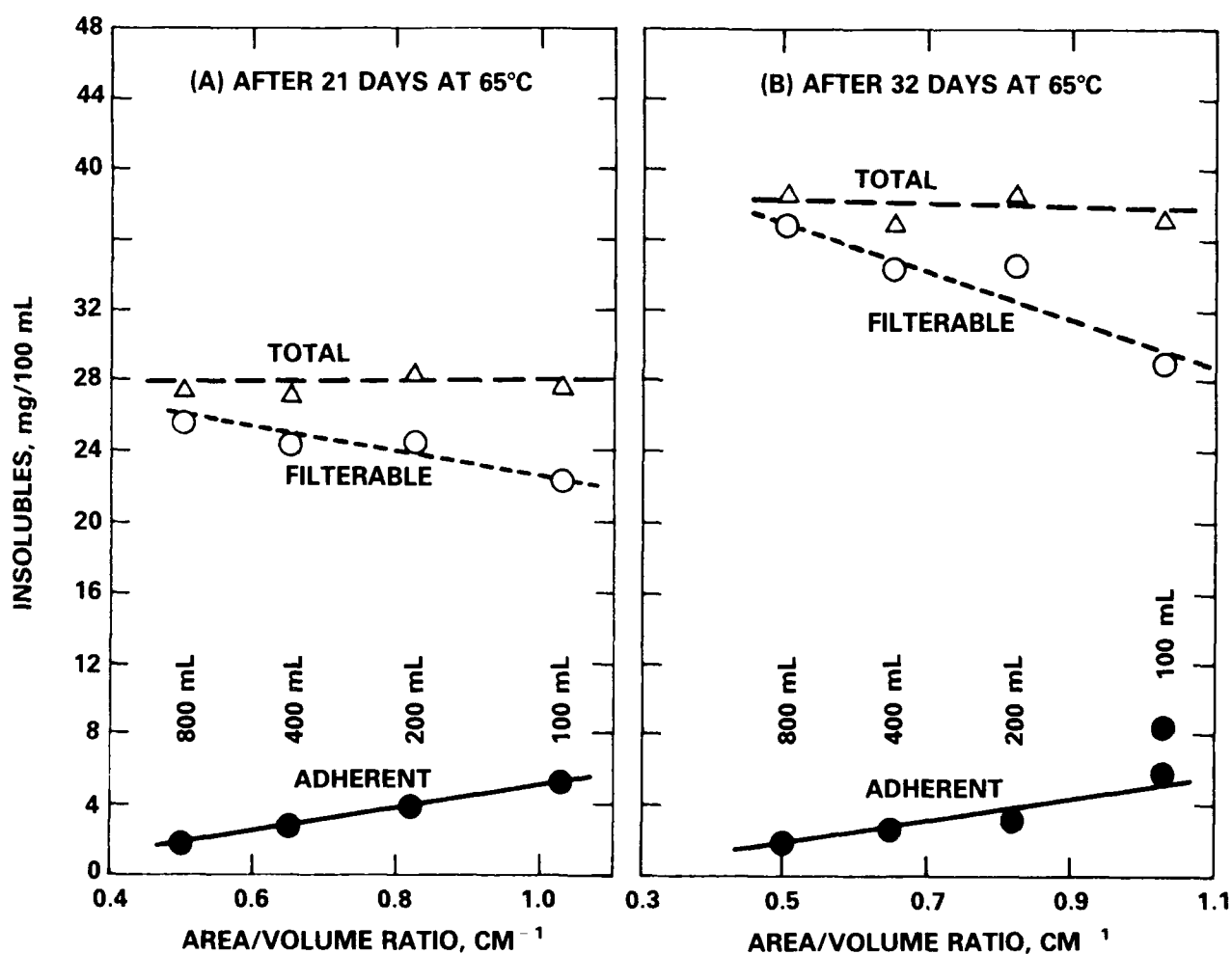


Fig. 7. Variations in insolubles formation as a function of the ratio of wetted surface to fuel volume during 21 and 32 days of bottle storage at 65°C.

One of the adherent insolubles data points in the 32-day case may be an outlier. There is little basis on which to exclude the suspected data point; therefore, we have shown both the average of the triplicate (including the suspect point) and the average with the data point excluded. The two-point average falls closer to the straight line at a ratio of 1.03.

We concluded from these results that the surface present in a test vessel helps determine the ratio of filterable to adherent insolubles; the test conditions (e.g., temperature and time of stressing) determine the amount of insolubles formed. This may explain why different test operators may get similar total insolubles but deviate widely in the amounts of filterable and adherent insolubles obtained. The need for each to use the same basic test vessel is apparent.

#### Oxidation Cell Age

In an earlier study of cell age effects using Fuel N (see Table 9), we found that new cells yielded the same levels of total insolubles as cells that had been used an appreciable but unknown number of times previously. However, we found the ratio of filterable to adherent insolubles decreased from new cells to older cells. These conclusions were supported by null hypothesis tests.

Table 9. Comparison of insolubles formation in new oxidation cells versus older cells when testing Fuel N by the ASTM D2274 method.

Insolubles*	New Cells	Older Cells
Filterable	1.6	1.4
Adherent	0.1	0.3
Total	1.7	1.7
Filterable/Adherent Ratio	4.7	15.0
*Std dev was -0.1 mg/100 mL. Note: All data are averages of triplicate determinations.		

There was a confidence level of <60% that there was a difference in the total insolubles and a 95% to 97.5% confidence that a change would occur in the ratio of filterable to adherent insolubles.

We suspected that the increase in adherent insoluble may have resulted from repeated cleanings of the oxidation cell using reagents and brushes that could etch or scratch the surface. Figure 8 shows the results of an experiment in which we started with new oxidation cells and noted the number of times they were used; we obtained 67 sets of data.

<u>Number of Uses</u>	<u>Sets of Data</u>
1	12
2	11
3	12
4	12
5	8
6	4
>20	8

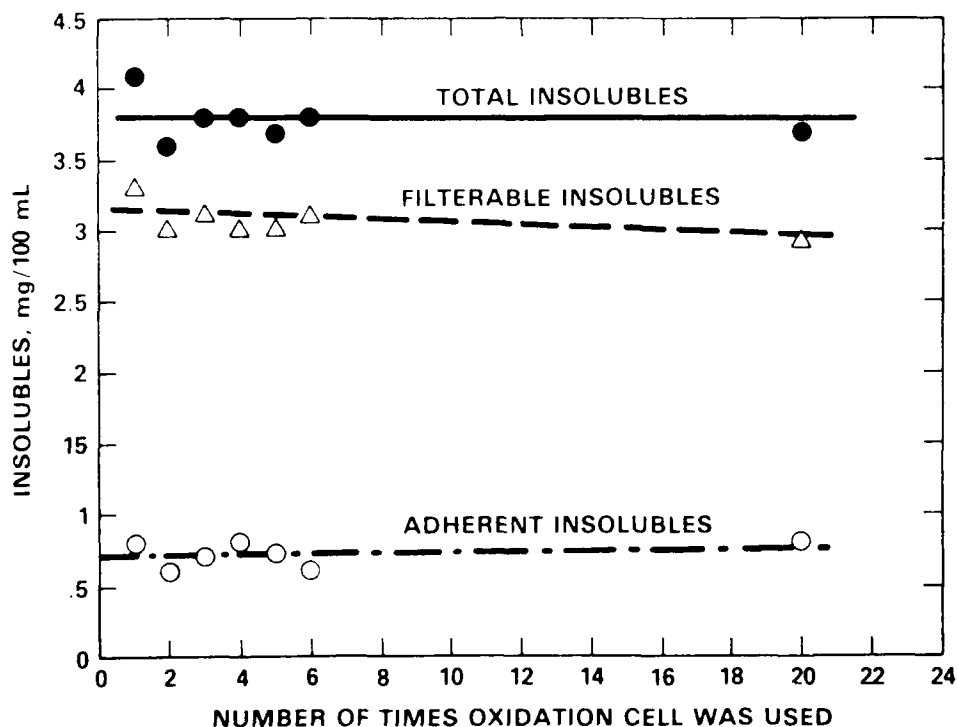


Fig. 8. Insolubles formation as a function of cell use.

The following simple averages of standard deviations were obtained for all data sets:

<u>Insolubles</u>	<u>mg/100 mL</u>
Filterable	0.08
Adherent	0.13
Total	0.13

It should be noted that the range of standard deviations was small, from 0.05 to 0.19 mg/100 mL.

When we attempted to fit straight lines to the curves by linear regression methods, we obtained:

$$\begin{array}{ll} F = 3.14 - 0.012(N) & r_F = -0.46 \\ A = 0.70 + 0.002(N) & r_A = +0.10 \\ T = 3.84 - 0.009(N) & r_T = -0.27 \end{array}$$

where F, A, and T are the filterable, adherent, and total insolubles, respectively; N is the number of times the oxidation cell has been used; and  $r_F$ ,  $r_A$ , and  $r_T$  are the correlation coefficients for the corresponding equations. The slopes are consistent with earlier data in that they indicate filterable insolubles would decrease and adherent insolubles would increase as the cells age. However, the correlation coefficients indicate a very poor fit of the data. Further, even if the slopes are significant, the effects are small, giving a maximum shift of 0.2 mg/100 mL between the filterable and adherent insolubles after the cell has been used 20 times. We can conclude that the effects are minimal, unless an oxidation cell becomes badly etched; therefore, we should continue to report only the total insolubles when indicating the stability of a fuel.

#### Condenser Temperature

Table 10 shows the total insolubles and the filterable/adherent insolubles ratio obtained when the condenser temperature was varied in experiments with Fuels N, A, and B.

Table 10. Results obtained with three fuels in experiments with varied condenser temperature.

Fuel	Condenser Temperature (°F (°C))	Total Insolubles* (mg/100 mL)	Filterable/Adherent Insolubles Ratio**
N	40 <sup>#</sup> (4.4)	2.3	2.5
	73 <sup>#</sup> (22.8)	2.3	2.8
	98 <sup>#</sup> (36.7)	2.4	2.9
A	50 <sup>##</sup> (10.0)	2.8	3.2
	64 <sup>##</sup> (17.8)	3.0	2.4
	109 <sup>##</sup> (42.8)	2.8	3.3
B	44 <sup>##</sup> (6.7)	3.7	3.3
	74 <sup>+</sup> (23.3)	3.7	2.8
	78 <sup>++</sup> (25.6)	3.7	3.6

\*Standard deviation of total insolubles ranged from 0.04 to 0.35 mg/100 mL.  
 \*\*Standard deviation of ratio ranged from 0.2 to 0.8.  
 #Average of duplicate.  
 ##Average of four determinations.  
 +Average of five determinations.  
 ++Water was shut off and temperature allowed to rise from 74° to 80°F (23.3° to 26.7°C).

The data shows that condenser temperature has little, if any, effect on the quantity of total insolubles or the filterable/adherent insolubles ratio. This was supported by a null hypothesis test. The confidence level for a difference between the lowest and highest temperature with each fuel was less than 70% in all cases.

We conclude from the data that the normal range of cooling water temperatures has little effect on the results and need not be specified in the method.

#### Bath Factors

##### Cell Location

Results obtained while qualifying the 12-cell ASTM D2274 heating bath are summarized in Table 11. The terminology was defined in Figure 6. The data reveal no major differences ascribable to location in the bath.

Table 11. Effect of cell location in the 12-cell bath on total insolubles formation in Fuel B.

Location	Range	Average	Std Dev
Front Bank	3.75 - 4.09	3.91	0.15
Rear Bank	3.48 - 4.06	3.77	0.21
Right Side	3.48 - 4.09	3.85	0.23
Left Side	3.58 - 4.06	3.83	0.16
End Group	3.48 - 3.88	3.79	0.15
Inner Group	3.58 - 4.09	3.89	0.22

Note: All values are expressed in mg/100 mL.

Rounded averages for six cells in the various combinations ranged from 3.8 to 3.9 mg/100 mL, and null hypothesis tests showed that none of the differences was significant at the 95% confidence level. We conclude that the uniformity of the bath temperature and of the oxygen flow reaching each cell in the 12-cell unit was sufficient to preclude major differences. Any well-designed and regulated ASTM D2274 bath should do equally well.

#### Comparison of Two Baths

Results obtained when operating the 8- and 12-cell baths simultaneously on the same fuels are shown in Table 12. The two baths yield significantly different amounts of insolubles. Null hypothesis tests confirmed this conclusion. The confidence levels that the insolubles (filterable, adherent, and total) formed in the 8-cell bath were higher than those formed in the 12-cell bath exceeded 99.5% for Fuel B in all cases. The confidence levels exceeded 95% in all cases for Fuel E. Null hypothesis tests of the ratio of filterable to adherent insolubles could not exclude the possibility that the ratios were the same. A confidence level of <70% was obtained with Fuel B and 90% with Fuel E.

Table 12. Comparison of results obtained in 8- and 12-cell baths.

Fuel	Insolubles* (mg/100 mL)			Filterable/Adherent Insolubles Ratio**
	Filterable	Adherent	Total	
<u>8-Cell Bath</u>				
B	4.7	1.3	6.0	3.63
E	0.36	0.28	0.64	1.29
<u>12-Cell Bath</u>				
B	4.0	1.1	5.1	3.57
E	0.25	0.17	0.42	1.51
*Standard deviations ranged from 0.05 to 0.16 mg/100 mL for Fuel B and 0.04 to 0.21 mg/100 mL for Fuel E.				
**Standard deviation ranged from 0.20 to 0.35.				

We consider the difference between the insolubles levels obtained in the two baths a major finding. It implies the need for a better definition of the apparatus in ASTM D2274. The drop in the bath temperature and the rapidity with which the temperature returns to the control point should be the same for all baths if similar results are to be expected. It may be necessary to specify the volume of bath fluid per oxidation cell, the heater wattage per cell, and possibly the response curve. ASTM Committee D-2 (Sections E-5 and 9-B) has been asked to start the response curves for their units and forward the results to this Center for compilation and analysis.

#### POSTAGING VARIABLES

##### Filter Medium

##### Filter Porosity

Table 13 shows the average of duplicate results obtained when Fuel N was stressed by the standard ASTM D2274 procedure (95°C for 16 hr) but filtered through various porosity glass fiber filter papers. Grade GF/D was the coarsest porosity (2.7 µm nominal) and GF/F the finest (0.7 µm). Grade GF/A is the standard grade filter with a porosity between the other two (1.6 µm nominal).

Table 13. Insolubles levels obtained with different grades of glass fiber filter paper.

Filter Grade	Insolubles (mg/100 mL)			Filterable/Adherent Insolubles Ratio
	Filterable	Adherent	Total	
GF/D	1.1	0.4	1.5	2.83
GF/A*	1.3	0.7	1.9	2.00
GF/F	1.3	0.4	1.7	3.25
GF/A**	1.3	0.5	1.8	2.79

\*GF/A is the standard filter grade.  
 \*\*The stressed fuel was filtered twice through GF/A.  
 Note: Standard deviations ranged from 0.02 to 0.18 mg/100 mL for insolubles and from 0.01 to 0.74 for the ratios.

Examination of the filterable insolubles averages in Table 13 reveals that double filtration through GF/A grade filter paper appears to remove more solids than single filtration through GF/A or GF/D. The statistical confidence level that double filtration with GF/A paper removes more solids than the coarse GF/D paper was 97.5% to 99%. Filtration through the fine porosity GF/F paper produced no greater removal of solids than single or double filtration through GF/A paper.

Examination of adherent insolubles revealed that the GF/A value was out of line with the other values. A high standard deviation for this value (0.16 mg/100 mL) indicated that this was an anomaly. Using hypothesis test values, we find confidence levels below 95% that a significant difference exists between the GF/A values and those from the GF/D or GF/F papers. Therefore, we conclude that there is no significant difference in the values of adherent insolubles obtained, because the ability of a filter to remove solids should not affect the subsequent step of recovering adherent insolubles.

The effect of the aberrant adherent insolubles level carries over so that the GF/A total insolubles value also is inconsistent with the surrounding values. Accepting the value for a null hypothesis analysis, we find a confidence level less

than 90% that there is any difference between total insolubles obtained with GF/A and GF/F filter papers. However, there is a 95% to 97.5% confidence level that GF/A total insolubles are higher than those obtained with the coarse GF/D paper. We conclude that GF/A grade paper is a satisfactory filter medium and that finer porosity paper is not needed; a coarser porosity such as GF/D would be unsuitable.

#### Cellulose Ester Versus Glass Fiber

Table 14 presents the results obtained in a comparison of Millipore 47-mm cellulose ester filter membrane with GF/A grade glass fiber filter paper in a Gooch crucible. The data show no indication that one filter medium gives a value different from the other filter medium. Null hypothesis statistics indicate a <80% confidence level that different filterable insolubles are obtained. The confidence level is less than 70% that there is any statistically significant difference between the total insolubles obtained. We conclude that the two ways to remove solids from the stressed fuel give essentially the same results.

Table 14. Results obtained using a membrane filter and glass fiber paper to filter fuel after D2274 stressing.

	Insolubles (mg/100 mL)			Filterable/Adherent Insolubles Ratio
	Filterable	Adherent	Total	
<u>Glass Fiber Filters (Five Replicates)</u>				
Range of Values	2.99 - 3.80	0.73 - 1.14	3.94 - 4.89	2.6 - 4.4
Average Values	3.28	0.96	4.24	3.5
Standard Deviation	0.31	0.19	0.39	0.7
<u>Cellulose Ester Membrane (Four Replicates)</u>				
Range of Values	2.67 - 3.51	0.89 - 1.33	3.58 - 4.49	2.4 - 3.9
Average Values	3.09	1.05	4.14	3.0
Standard Deviation	0.35	0.20	0.41	0.7

## Drying Time

Table 15 shows the additional losses in weight of filterable insolubles when sets of eight replicates were dried for 1, 1.5, or 3 hr, then returned to the 99°C oven for additional periods of time. The results indicate that the 1 hr of drying specified in D2274-74 is probably inadequate when using glass fiber filters, and that up to 3 hr drying may be needed to reach constant weight.

Table 15. Additional weight losses in drying filterable insolubles for periods beyond 1 hr at 99°C.

Original Drying Time (hr)	Additional Drying Time (hr)	Further Weight Loss (mg/100 mL)
1	16	0.50
1.5	3	0.25
3	70	0.08

Figure 9 shows the results of drying filterable insolubles for up to 5 hr. The experiment continued to 129 hr of drying, but constant weight was obtained in 2.5 to 5 hr.

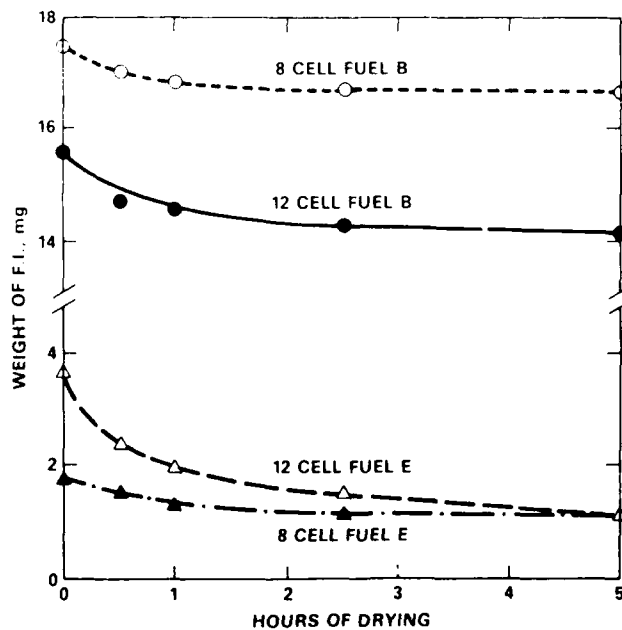


Fig. 9. Weight of filterable insolubles versus hours of drying.

Figure 10 shows that drying a cellulose ester membrane filter for 30 minutes at 80°C specified in the revised accelerated stability test (D2274-88) is adequate. No further weight loss is obtained beyond the first 15 minutes.

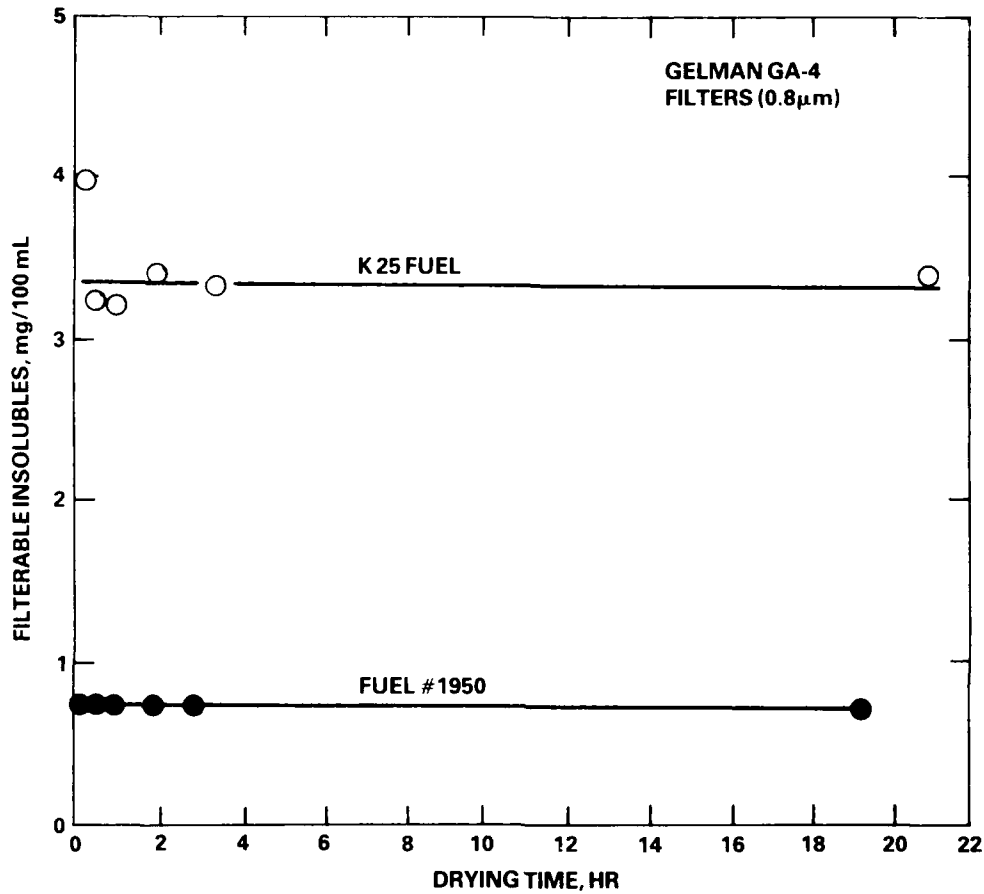


Fig. 10. Effect of drying time on filterable insolubles weight using cellulose ester membrane filters.

### Trisolvent Usage

#### Repeat Trisolvent Rinses

An average of 0.53 mg/100 mL when a single 25-mL trisolvent rinse was used to recover adherent insolubles from six bottles in which Fuel N had been aged for 4 weeks at 66°C (150°F). The adherent insolubles were lower (0.50 mg/100 mL) when a second 25-mL trisolvent rinse was added to the first, but they were still within the

precision expected. We concluded that the second rinse was not required in many instances but that it should be used to ensure recovery of all adherent insolubles. ASTM D2274-88 specifies three 25-mL rinses, a practice we consider conservative.

#### Hot Trisolvent Rinses

One experiment evaluated the effect of using hot trisolvent and single 25-mL rinse, rather than room temperature solvent. The adherent insolubles had been formed in bottle storage. Triplicate determinations were made. The room temperature trisolvent recovered an average of 0.32 mg/100 ml with a standard deviation of 0.09 mg/100 mL. The hot trisolvent recovered an average 0.54 mg/100 mL with a standard deviation of 0.08 mg/100 mL. The difference is statistically significant when the null hypothesis is used since the resultant confidence level is 97.5% to 99%.

A later experiment tested two rinses each of 25 mL of trisolvent using Fuel N in 66°C (150°F) bottle storage. Tests were conducted in triplicate. Room temperature trisolvent rinses recovered an average 1.40 mg/100 mL of adherent insolubles with a standard deviation of 0.26 mg/100 mL; hot trisolvent rinses (61°C) recovered an almost identical average of 1.43 mg/100 mL with a standard deviation of 0.06 mg/100 mL. Null hypothesis evaluation of the data yielded a confidence level below 60% that there was any difference in the amounts of adherent insolubles recovered by the trisolvent at the two temperatures.

We conclude from the two experiments that the use of hot trisolvent may be useful if a single rinse is to be used (or if a large quantity of adherent insolubles is involved); normal room temperature trisolvent is adequate if multiple rinses are to be used, as specified in D2274-88.

## SUMMARY OF FINDINGS AND CONCLUSIONS

Within the normal limits of variation expected in the conduct of the ASTM D2274 accelerated stability procedure, the following variables have little or no effect on the measured amount of total insolubles (mg/100 mL).

- Bubble geometry (except use of sparger),
- Depth of oxygen release,
- Volume of fuel sample in cell,
- Wetted area/fuel volume ratio,
- Cell age (unless badly etched),
- Condenser water temperature,
- Location of oxidation cell in temperature bath,
- Glass fiber filter porosity not coarser than GF/A, and
- Trisolvent temperature if using multiple rinses.

Three variable factors were found to affect the measured quantities of total insolubles (mg/100 mL).

1. The use of a fritted glass sparger in place of the specified oxygen delivery system results in the formation of additional adherent insolubles and therefore more total insolubles.

2. Drying times greater than the specified 1 hr at 99°C of D2274-74 are required when drying filterable insolubles on glass fiber filter paper or higher levels of filterable insolubles; hence, higher levels of total insolubles will be measured. Drying times of 2.5 to 5 hr were necessary to reach constant weight.

3. Heating baths can yield different levels of insolubles due to different temperature recovery times from the temperature drop caused by the introduction of cold oxidation cells. This observation helps explain why different laboratories report different results, resulting in poor reproducibility for the D2274 procedure.

The following observations also were made during the experiments.

1. Placing glass beads in the oxidation cell during the D2274 test resulted in the formation of more adherent and total insolubles.

2. As the surface of wetted vessel area per volume of fuel increases, the filterable insolubles decrease and the adherent insolubles increase; the total insolubles remain constant. This means the vessel shape and size must remain constant in different laboratories or experiments to avoid erroneous conclusions. This is not a problem in ASTM D2274 because the oxidation cell is specified; however, it can be a problem in bottle tests where different size bottles may be used.

3. Cell age does not seem to affect the total insolubles level measured and does not have a major effect on the ratio of filterable to adherent insolubles, unless the cell is badly etched from use.

4. The Millipore cellulose ester filter and the glass fiber GF/A filter give the same results for filterable insolubles if properly dried. The 30-minute drying time at 80°C specified in D2274-88 for the cellulose ester membrane filter seems adequate.

#### RECOMMENDATIONS

Standardize the ASTM D2274 temperature bath, so that the temperatures of all baths drop to essentially the same level on the introduction of cold oxidation cells containing fuel samples, and the speed of returning to the 95°C control point is the same.

1. Conduct a survey of ASTM D-2, Sections E-5 and 9-B, to determine the range of:

- Bath liquid volume per oxidation cell,
- Bath wattage available per oxidation cell,
- Control system for heaters,

- Temperature of bath on introducing cells, and
- Time required to reach 95°C.

Collect and analyze temperature curves obtained during typical D2274 runs.

3. Recommend and ballot changes in the D2274-88 procedure to specify baths and bath usage more completely.

Study the consistency of results obtained by the use of fritted spargers of various sizes and porosities. The additional adherent insolubles produced by such spargers may result in more consistent results among laboratories.

Study compositional differences among filterable and adherent insolubles, and attempt to explain differences among filterable to adherent ratios from different laboratories. More consistent results may permit the attachment of some significance to the ratio.

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