

RAPID TEST METHOD FOR THE DETERMINATION OF THE BENZENE-
AND QUINOLINE-INSOLUBLE CONTENT OF PITCHES

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Introduction

Tests to determine the amount of benzene- and quinoline-insoluble matter in pitch are widely used by producers and consumers of pitch. For example, several thousand solvent-insolubles tests are performed annually at U. S. Steel's pitch-producing facilities. The present test method for determining the benzene-insoluble content of pitch is based upon a test that was developed by the Barrett Company (presently a division of Allied Chemical Corporation).

Briefly, the Barrett procedure involves digestion of the pitch sample in toluene, filtration, and then extraction of the residue in refluxing benzene. Because of the time-consuming extraction phase, the Barrett test requires in excess of 24 hours to complete. The undesirability of lengthy analytical procedures, especially in plant control work, prompted the Applied Research Laboratory of U. S. Steel to develop a rapid benzene-insolubles test that could be completed in about 6 hours.

This paper describes the salient features of the rapid method for determining the benzene-insoluble content of pitch. A rapid method for determining quinoline insolubles is also described and discussed briefly.

Experimental Work

The Barrett method for determining benzene insolubles is an empirical method that has been used throughout the industry over a number of years and has been accepted as a more or less standard procedure. To date, no ASTM (American Society for Testing Materials) test method for benzene insolubles has been devised. In developing a rapid method, the following objectives were fixed: (1) The time required to complete the test should be 8 hours or less. (2) The values obtained by the new method should be equivalent to those obtained by the Barrett method. (3) The general principles of digestion and extraction should be retained.

The rapid benzene-insoluble test closely duplicates the Barrett method in all phases except that the size-consist of the particles in the sample is controlled and the reflux extraction apparatus and technique are changed. A number of modifications have been made in the procedure and in the design of the apparatus. These changes provide the same degree of extraction as the Barrett method but in much less time. The apparatus used in each method is shown in Figure 1. In the new method, the special extraction flask and the filter paper thimble of the Barrett test are replaced with the more modern and versatile Soxhlet extraction apparatus and Soxhlet paper extraction thimble.

Important added features of the Soxhlet extraction apparatus are shown in Figure 2. The wire spacer, which rests on the bottom of the extraction cup of the Soxhlet apparatus, positions the thimble so that the middle of the thimble is at the top of the siphon tube. This provides an adequate liquid level in the thimble and at the same time prevents loss of sample through overflow. A reflux guide, built onto the bottom of the condenser, directs all of the refluxing stream into the thimble. Without the guide, considerable solvent by-passes the thimble.

The coal-tar pitches selected for use in this study represent a wide range (15 to 35 wt %) of benzene-insoluble contents. Table I shows some of the more common properties of these pitches. Three of the pitches were obtained from tars recovered during the high-temperature carbonization of bituminous coal. The fourth pitch was produced from tar from the low-temperature carbonization of sub-bituminous coal. The table shows the benzene-insoluble content of the pitches as determined by the Barrett method.

In the new rapid method, standard sampling procedures (ASTM D 140-55 and ASTM D 346-35) are followed to insure that the portion used for analysis is representative of the pitch sample. In addition, when the pitch is sufficiently hard it is ground to pass through a U. S. No. 60 sieve and the test sample is collected from material retained on a U. S. No. 100 sieve. This is done to obtain a sample with a particle size (0.0058-in. to 0.0082-in. diameter) that will insure good solvent contact. The particles should be sufficiently small so that the solvent can be rapidly absorbed, but not so small that agglomeration or packing of fines can prevent or retard solvent contact. The sample size is adjusted to yield approximately 0.25 gram of insoluble material (usually 1 or 2 grams). The sample is weighed into a beaker and digested in 60 milliliters (ml) of toluene for 30-minutes on a steam bath. The contents of the beaker are then transferred to a 30- by 77 mm (single weight) Soxhlet extraction thimble that has been previously tared in a weighing bottle. The thimble is placed in a crucible holder over a beaker and the insoluble matter is transferred to the thimble by the use of a brush and a small amount of toluene. Figure 3 shows this operation. When the liquid portion of the suspension has passed through the thimble, the thimble is washed with benzene and then placed into a 44-mm Soxhlet apparatus for extraction. Heat is applied gradually to the flask to avoid the possibility of liquid erupting into the extraction tube. The gradual heatup period requires approximately 15 minutes and the close attention of the operator. Once the desired throughput is achieved, the test will proceed practically unattended. The extraction is conducted for a total of 4 hours with a siphoning cycle of approximately three minutes. This approximates a solvent reflux rate of about 1800 ml per hour. At the end of this period the thimble is removed, air-dried for 15 minutes, oven-dried for 30 minutes at 105 C, cooled in a desiccator, and weighed. Six hours are required to complete the determination of the amount of sample insoluble in benzene.

Results and Discussion

Several steps were involved in arriving at the proper operating conditions for the Soxhlet extractor. They were (1) determination of the permeability of the Soxhlet thimble relative to the filter-paper thimble, (2) establishment of the maximum throughput capacity for benzene in the Soxhlet apparatus, and (3) establishment of the throughput of benzene in the Barrett apparatus when operating at the recommended boilup rate.

That the Soxhlet thimble is no more permeable to the retained insoluble matter than is the filter-paper thimble was established by an experiment in which the Soxhlet thimble was used in the extraction apparatus of the Barrett method. This experiment showed that the use of the Soxhlet thimble gave results identical to those obtained in a test in which the filter-paper thimble was used.

The Soxhlet thimble was found to be capable of handling all the benzene returned to the siphon cup of the Soxhlet extraction apparatus at maximum boilup, which was 1800 ml per hour.

The average throughput of benzene in the Barrett test (about 80 drops per minute) is about 6600 ml in 24 hours. At maximum boilup, the Soxhlet apparatus required slightly less than 4 hours to reflux the same quantity of benzene.

Another matter that was considered concerned the temperatures to which the samples were subjected in the rapid test. Since the exterior of the thimble in the Soxhlet apparatus is partially immersed in the benzene condensate during a portion of the extraction cycle, it was conceivable that the condensate could lower the temperature of the contents of the thimble. In the Barrett apparatus, the thimble is constantly bathed by solvent vapors and refluxing solvent. To ascertain whether there was a temperature difference, an experiment was performed in which thermocouples were suspended in the liquid and vapor portions of the solvent in an operating Soxhlet extractor. After the first few siphon cycles, the temperature differential was within one degree Centigrade. A thermocouple was also suspended in the vapor portion of the Barrett apparatus and it was established that the vapor temperatures were the same in both apparatus.

The rapid benzene-insolubles test was performed by each of three operators, who conducted three duplicate tests on each pitch sample, to establish the repeatability of the test. The results of the tests are shown in Table II and plotted in Figure 4. The horizontal line across the center of the chart in Figure 4 represents a scale for benzene-insolubles values as determined by the Barrett test method. The points on the scale are the average of three duplicate determinations for benzene-insoluble contents of the four samples when tested by the Barrett method. The vertical scale represents the deviation, expressed in percentage of sample, from the values obtained by the Barrett method (the horizontal center line). The lines digressing from the horizontal center line represent the limits of reproducibility as established by the Barrett method. This is expressed in percentage of sample as $0.1 + 0.05 \times$ percent insoluble matter in benzene. The points above and below the center line represent the values obtained by the rapid benzene-insolubles method. The different symbols represent different operators and each point represents a mean value as determined from the values of duplicate tests; as stated before, each operator performed three duplicate tests or six tests per pitch sample, to obtain three mean values for comparison with the standard value (center line).

As may be seen on the graph, most of the values obtained by the rapid procedure fall within the limits of reproducibility set for the values by the Barrett method.

Mean and standard deviation values for each of the pitches analyzed by the rapid method are shown in Table III.

Because of the exceptionally good reproducibility and the savings in time, we feel the rapid test method for benzene insolubles is a good replacement for the Barrett test method.

Quinoline Insolubles

The less time-consuming a quality control test or specification test is, the more desirable it is. Even though the commonly used method for determining the portion of sample insoluble in quinoline requires only about 3 hours to complete, the possibility of shortening the time requirement was investigated. As in the investigation of the rapid benzene-insolubles test, the objectives included the limitation that the empirical values as obtained by the presently used procedure would be duplicated, and that the general principles of digestion and extraction should be retained.

A test meeting these requirements was developed which could be completed in less than 1 hour. The new rapid procedure differs little from the old procedure in principle. Time requirements were decreased by changing the techniques of extraction and drying.

Experimental Work

The pitch samples tested were the same as those used in the benzene-insolubles study. Also, the same techniques of sample preparation were followed.

In the rapid quinoline-insolubles test, a weighed sample of sufficient size to yield 0.1 gram of insoluble material is digested with hot (170 C) quinoline for two minutes. The digested sample is then filtered with the aid of suction, as shown in Figure 5, through a Selas crucible (fine porosity) containing a quantity of diatomaceous filter aid. When substantially all of the material has been transferred from the beaker to the crucible, the beaker is rinsed with 20 ml of hot (170 C) quinoline; this material is also transferred to the crucible. Any particles that adhere to the beaker are washed into the crucible with benzene. The filter cake in the crucible is then washed with 80 ml of benzene and then with 80 ml of acetone. After the acetone wash, the filter cake is dried while still under suction by means of a 250-watt infrared lamp mounted about 12 inches above the crucible. This operation should be conducted in a well ventilated hood, to remove the small amount of acetone vapors that are evolved. When dry (about 15 minutes), the crucible is cooled in a desiccator and weighed.

Results and Discussion

To develop a rapid quinoline-insolubles test method that would retain the basic principles of the old method, it was necessary to reduce the time requirement by altering the techniques of operation. One area studied was the conditions of digestion. It was determined that increasing the temperature of the quinoline from 80 C to 170 C and shortening the time of digestion from 20 to 2 minutes did not alter the end result. Adding an acetone wash to the procedure shortened the drying process. The acetone removes benzene, which is more difficult to vaporize, from the quinoline-insoluble matter. Subsequent removal of the acetone was quickly accomplished by the application of heat from a heat lamp. Further time savings were derived by using previously dried crucibles and filter-aid material. The sum of these time savers resulted in a rapid method that required less than 1 hour to complete as opposed to the 3 hours for the old method.

Table IV and Figure 6 show the results of rapid quinoline-insolubles tests as determined by three operators. The horizontal line across the center of the chart represents a scale for quinoline-insolubles values as determined by the old method of test. The points on the scale are the average of three sets of duplicate determinations of quinoline-insoluble contents of the four samples tested by the old method. The vertical scale represents the deviation, expressed in percentage of sample, from the values by the old method (the horizontal center line). The lines digressing from the center line represent the limits of reproducibility as established by the old method. This is expressed in percentage of sample as $0.10 + 0.02 \times$ percent insoluble matter in quinoline. The points above and below the center line represent the values obtained by the rapid quinoline-insolubles method. The different symbols represent different operators and each point represents a mean value as determined from the values of duplicate tests. Each operator performed three duplicate tests, or six tests per pitch sample, to obtain three mean values for comparison with the standard value or center line.

As was true with the benzene-insolubles values, nearly all the quinoline-insolubles values obtained by the rapid method fall within the limits of reproducibility set for the values obtainable by the old method for quinoline insolubles.

Mean and standard deviation values for each of the samples analyzed by the rapid method are shown in Table V.

Summary

Methods have been developed for the rapid determination of benzene- and quinoline-insolubles in pitches. The rapid benzene-insolubles test requires 6 hours to complete as compared to the 24 hours necessary for the generally used Barrett method. The rapid quinoline-insolubles test requires 1 hour to complete as opposed to 3 hours for the old method. Results obtained with the rapid test methods correlate well with those of the standard methods. It is hoped that the time advantages gained warrant the consideration of these rapid tests as acceptable methods for analysis of benzene- and quinoline-insoluble matter.

Table I
Properties of Pitches

	Pitch			
	A	B	C	D
Benzene Insolubles, wt %	14.73	22.57	33.94	35.42
Quinoline Insolubles, wt %	2.25	9.98	12.23	28.99
Softening Point, C	78.3	105.5	117.5	64.9
Coke Value, wt %	42.5	56.0	58.9	35.8

Table II
Results of Benzene-Insolubles Determinations

Rapid Method		Pitch, wt %							
		A		B		C		D	
Operator	Run No.								
I	1	14.17		21.72		32.60		36.09	
	2	14.26	14.22*	21.80	21.76	32.39	32.50	35.60	35.85
	3	14.50		21.61		34.62		36.01	
	4	13.85	14.18	22.46	22.04	34.39	34.56	36.10	36.06
	5	14.82		21.41		33.70		34.90	
	6	15.22	15.02	22.40	21.92	33.50	33.60	34.82	34.86
II	1	13.86		22.50		33.55		37.29	
	2	14.13	14.00	23.44	22.97	33.33	33.54	36.63	36.96
	3	13.89		21.61		33.53		36.84	
	4	13.37	13.63	21.41	21.51	33.59	33.55	36.56	36.70
	5	14.52		22.57		32.92		36.33	
	6	14.69	14.50	23.22	22.90	33.17	33.04	36.53	36.43
III	1	14.40		22.06		32.20		36.36	
	2	14.37	14.39	22.02	22.04	33.83	33.02	36.91	36.64
	3	15.40		23.38		33.77		36.19	
	4	15.31	15.35	23.64	23.51	34.24	34.00	35.83	36.01
	5	15.08		22.56		35.05		35.74	
	6	15.97	15.53	21.85	22.20	34.94	35.00	35.14	35.44
<u>Barrett Method</u>		14.73		22.57		33.94		35.42	

* Mean values

Table III

Statistical Data for the Rapid Benzene-Insolubles Test

	Pitch			
	A	B	C	D
Number of Runs	18	18	18	18
Mean	14.53	22.31	35.57	36.10
Standard Deviation	0.663	0.718	0.912	0.682

Table IV

Results of Quinoline-Insolubles DeterminationsRapid Method

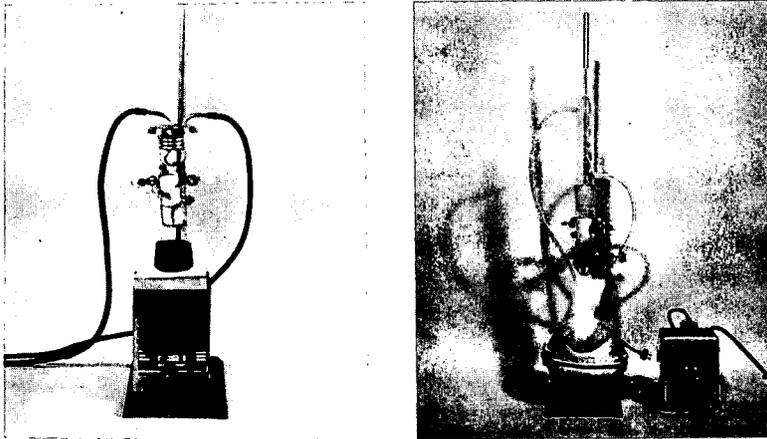
Operator	Run No.	Pitch, wt %							
		A		B		C		D	
I	1	2.20		10.21		12.16		29.46	
	2	2.22	2.21*	10.26	10.24	12.17	12.17	29.98	29.22
	3	2.31		10.23		12.20		28.07	
	4	2.33	2.32	10.23	10.23	11.99	12.10	28.41	28.24
	5	2.17		10.15		12.11		28.50	
	6	2.15	2.16	10.16	10.16	12.23	12.17	28.54	28.52
II	1	2.33		10.26		12.17		28.99	
	2	2.30	2.32	9.74	10.00	12.18	12.18	28.86	28.94
	3	2.28		10.20		12.93		28.95	
	4	2.30	2.29	10.23	10.22	12.79	12.86	28.90	28.93
	5	2.28		10.24		11.93		28.92	
	6	2.27	2.28	10.17	10.20	12.94	12.44	28.85	28.89
III	1	2.33		9.84		12.31		28.47	
	2	2.45	2.39	10.05	9.95	13.27	12.79	28.76	28.62
	3	2.22		10.13		12.13		28.64	
	4	2.35	2.29	10.11	10.12	12.69	12.41	28.79	28.72
	5	2.45		10.29		12.27		28.38	
	6	2.32	2.40	10.32	10.30	12.23	12.25	28.33	28.36
<u>Barrett Method</u>		2.25		9.98		12.23		28.99	

* Mean values

Table V

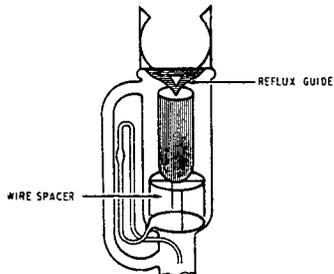
Statistical Data for the Rapid Quinoline-Insolubles Test

	Pitch			
	A	B	C	D
Number of Runs	18	18	18	18
Mean	2.29	10.16	12.38	28.71
Standard Deviation	0.081	0.150	0.377	0.325



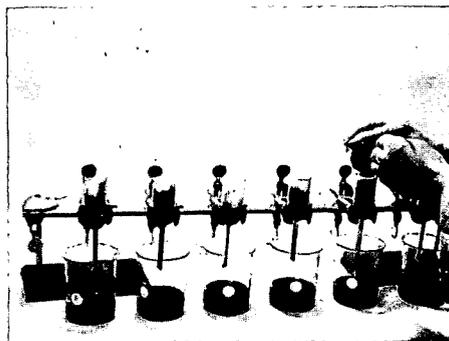
Extraction Apparatus for Benzene-Insolubles Tests

Figure 1



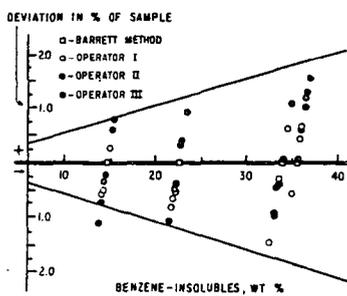
Modifications of Soxhlet Extractor
for Rapid Benzene-Insolubles Test

Figure 2



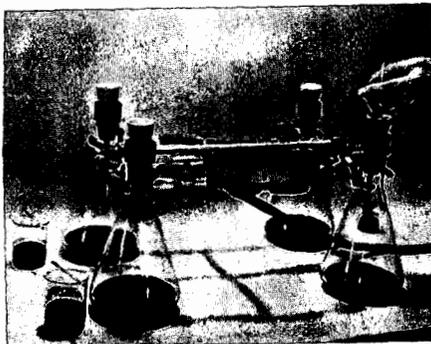
Transferring Insoluble Matter to Thimbles in
Rapid Benzene-Insolubles Test

Figure 3



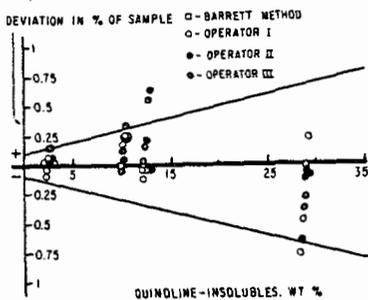
Statistical Data for Benzene-Insolubles Test

Figure 4



Quinoline-Insolubles Filtering Apparatus

Figure 5



Statistical Data for Quinoline-Insolubles Test

Figure 6