

THE DETERMINATION OF THE QUINOLINE-INSOLUBLE (QI) CONTENT OF TAR AND PITCH

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Abstract—A new method for the determination of quinoline insolubles (QI) in tars and pitches, using elevated pressure instead of vacuum for filtration was developed. The apparatus is described and the outline of the procedure is given. The procedure was simplified by omitting the addition of filter aid and washing the filter cake with toluene.

Key Words—Quinoline insolubles, tar, pitch, determination.

1. INTRODUCTION

The principle of the determination of quinoline insolubles (QI) in pitch and tar[1] involves digesting the sample in hot quinoline to decrease its viscosity and filtering the solution. The insoluble material is washed, dried and weighed.

Because the filtration is performed according to ASTM procedure by vacuum filtration, the achievable vacuum is deteriorated due to the vapor pressure of hot quinoline, and, therefore, the filtration rate is very slow. A filtration aid—Celite—is used according to the ASTM procedure to increase the filtration rate.

Analysis of the isolated QI is often required for better characterization of pitches, such as in determination of carbon and hydrogen, particle size distribution, evaluation of QI by scanning electron microscopy, etc. The presence of the filtration aid (Celite) would interfere with the above evaluations of quinoline insoluble properties. Therefore, the filtration aid cannot be used; the filtration usually takes excessive time and is, in some special cases (e.g. heat-treated pitches), impossible.

Therefore, we designed and developed a procedure circumventing the above difficulties. The vacuum filtration is replaced by filtration under elevated pressure. This allows the operator to increase by several times the driving force across the filtration plate during the separation by filtration. Therefore, filtration proceeds rapidly, and filter aid is not necessary. In addition, we omitted washing the isolated QI with toluene and washed with acetone only.

The improvement in filtration rate by applying elevated pressure during the filtration step also allowed an increase in the amount of sample used and an improvement in the accuracy of the determination.

2. EXPERIMENTAL

2.1 Apparatus (Fig. 1)

The pressure filtration vessel (see Fig. 1) is a stainless steel-jacketed block, heated by steam or cooled with water,

sealed by a lid, flat gasket and a quick-release clamp. The interior of the block is designed to accept a 3A2 Berlin porcelain filtration crucible. The crucible is sealed within the block by the use of three O-rings, a crucible sealing collar and an adjustable plunger. The seal is accomplished when the sealing lid is placed on top of the block and clamped. The adjustable plunger applies a force to the crucible sealing collar, which, in turn, pushes downward on the edge of the crucible and simultaneously compresses O-ring gaskets to seal the surface of the crucible against the wall of the block. The filtration of material is accomplished by nitrogen (pressure 10–30 psig) introduced through the lid of the pressure filter. The filtrate exists from the drain tube at the bottom of the block. The filtrate is collected in a Buchner flask attached to the drain tube of the filter by a rubber stopper. A hose is attached to the Buchner flask side tubing and submerged below the surface of water in a 100-ml beaker. A high rate of bubbling by the exiting nitrogen indicates the end of filtration.

2.2 Procedure

The desired amount of sample (usually 2.5 g) is stirred for about 15 minutes in quinoline (2 ml of quinoline used per gram of sample) in a 50-ml beaker at a temperature of about 75°C. The entire sample is quantitatively transferred into the 3A2 Berlin crucible inserted into the pressure filter heated with steam. The pressure filter is closed, and the liquid is pushed through the filter by applying gas pressure on the order of 10–30 psig. The end of the filtration cycle is indicated by an accelerated rate of gas bubbling through the water seal attached to the filter exit. Usually three washings of the filter cake with 5–10 ml of hot quinoline are used.

Then steam in the jacket is replaced by water, and the separated QI is washed three times with about 30 ml of acetone.

The crucible with the filter cake is removed from the pressure filter, dried in an oven (105°C) for about one-half to one hour and weighed after it has cooled down in a desiccator for about half an hour.

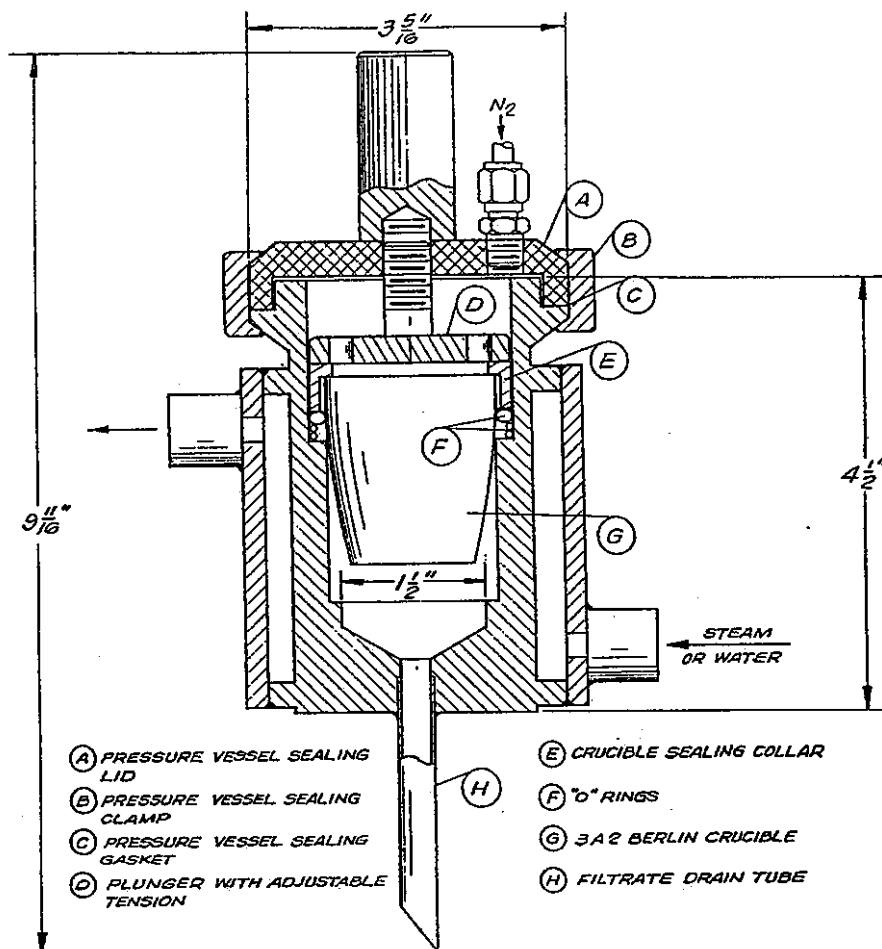


Fig. 1. Pressure filter for QI separation.

The concentration of QI is calculated by using the following equation:

$$QI(\%) = \frac{W_3 - W_2}{W_1} \times 100,$$

where W_1 —weight of the sample,
 W_2 —weight of the empty crucible,
 W_3 —weight of crucible with QI.

3. RESULTS

The accuracies of the determinations were checked by repeatedly analyzing one sample of pitch with and without the addition of Celite and also with the recycle filtrate. The results were compared with the results obtained with Celite and vacuum (Table 1).

Table 2 presents a comparison of results obtained with several pitches analyzed by using Celite and vacuum and by the above outlined procedure.

Table 1. QI Determination by different procedures in one sample of pitch

1	2	3	4	5
Vacuum Filtration with Celite	Pressure Filtration with Celite	Pressure Filtration without Celite	Pressure Filtration without Celite Rinsed with Acetone Only	Pressure Filtration Same as Column #4 But Filtrate Recycled
QI(%)	QI(%)	QI(%)	QI(%)	QI(%)
8.18	8.29	8.40	8.37	8.48
8.26	8.27	8.40	8.37	8.70
	8.30	8.41	8.33	
	8.28	8.43	8.33	
	8.32	8.34	8.33	
	8.30	8.39	8.32	
Avg. 8.22	8.29	8.40	8.34	8.59

All results given in this table are within the limits of errors allowed by ASTM procedure D 2318.

Table 2. Comparison of results by the revised and ASTM procedures obtained with different pitches

Vacuum Filtration with Celite	*Pressure Filtration without Celite
QI %	QI %
8.12	8.18
9.74	9.91
8.14	8.06
8.71	8.68
8.32	8.28
10.40	10.23
9.01	8.99
13.37	13.28
10.15	10.12
8.52	8.52
8.22	8.29
9.20	**9.30
11.13	**10.63

*The sample size was doubled for better accuracy.

**Samples are the average of (4) four determinations—all others are the average (2) two determinations.

All results obtained by the new procedure are within the repeatability limits permissible by ASTM D 2318.

4. DISCUSSION

Ever since ASTM D 2318 was adopted as the standard method for determination of QI, criticism has been voiced against it because the method is cumbersome, and various laboratories have frequently shown poor agreement.

The amount of quinoline (5 ml) used for digesting the sample is critical. Small amounts give values significantly lower than large amounts (ASTM recommends 25 ml).

If it is considered that the purpose of QI determination is the quantitative determination of insolubles in tar or pitch, then it must be concluded that the most desirable method is that which gives the lowest results. Quinoline is a somewhat poorer solvent for high molecular weight constituents in tar or pitch than the latter are themselves. The use of large amounts of quinoline obviously precipitates material not originally insoluble, and a false picture is therefore obtained.

The filtration time in the ASTM procedure is largely governed by the amount and position of filter aid. The ASTM choice of 0.5 g in crucible and 0.5 g in beaker is a particularly unhappy one. In its form as written, the ASTM method does not work at all with high softening point pitches (S.Pt. over 120°C), because filtration stops entirely.

The revised procedure outlined here eliminates both problems and renders the determination the much desired accuracy.

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REFERENCES

1. ASTM D 2318.