

Technical White Paper

# **Analytical Method to Measure Water in Asphalt**

## **Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 02**

March 2015

Prepared for  
Federal Highway Administration  
Contract No. DTFH61-07-D-00005

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I N S T I T U T E

# ANALYTICAL METHOD TO MEASURE WATER IN ASPHALT

## INTRODUCTION

Excess water functions to soften asphalt binders by breaking up asphaltene associations. The addition of water to binders through the use of warm and cold mix technologies such as foaming and asphalt emulsions increases the need for accurately measuring water in asphalt. Several analytical techniques have been developed for quantifying water in bituminous material including the use of infrared spectroscopy (IR), gas chromatography (GC), nuclear magnetic resonance (NMR), and others which vary in accuracy, cost, sensitivity, specificity, and ease of operation.

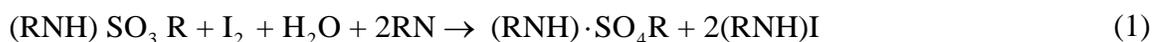
Development of these methods has met with limited success at WRI in the past. Many of the measurements produced unreliable results that rarely agree amongst one another. Early IR work by Petersen showed less than 0.1% water in binder which is lower than the detection limit of his technique (Petersen 1967). Work published by van de Voort et al. (2007) introduced an IR method for measuring the water content of lubrication oils via a liquid liquid extraction with acetonitrile. After a number of exploratory tests at WRI to evaluate this method, it appears that the technique may not be applicable to asphalt because of interference of alcohols and phenols in the asphalt. Application of a  $^{31}\text{P}$  NMR technique to asphalt at WRI showed around 1% water in binders, but upon further testing, the results had poor repeatability (Miknis 2008). It is believed that benchtop sample preparation caused contamination of the samples and glassware by atmospheric moisture.

Some work at WRI was performed on development of a headspace gas chromatograph (HSGC) technique. The method involves reacting water with calcium carbide to produce acetylene that is quantified with a flame ionization detector (Loeper and Grob 1988). Although HSGC was successful on a variety of organic solvents containing between 60-400 ppm water, application to asphalt was not fully developed due to several issues including reaction time to equilibrium.

Subsequent to evaluation of GC, FTIR, and NMR techniques, the Karl Fisher (KF) method, which is the “gold” standard for measuring the water content in lubricating oils, was given consideration. KF titration was not believed appropriate to measure the water in asphalt because of interference reactions with mercaptans, sulfides, and ketones. With innovations in KF reaction solutions such as Hydranal®, new hope was given to the idea that the KF titration could be applied to bituminous material. In preliminary studies, samples of asphalt were sent to a commercial lab for KF analysis. Inconsistent results suggested that atmospheric water may have contaminated the samples. New lab techniques including storing samples, solvents, and glassware in a dry atmosphere and performing all wet chemistry in a dry environment were employed in an effort to improve reproducibility.

## EXPERIMENTAL

A Mettler coulometric C20 Karl Fischer (KF) titrator and Hydranal-Coulomat reagents (Sigma-Aldrich pt# 34840-50ML-R and 34868-500ML-R) were used for all titrations. Coulomat reagents are designed to minimize interfering reactions that prevent accurate titration of samples containing thiol and ketone functional groups. Additionally, the fast reaction rate and quick titration prevent the relatively slow interference reactions from causing appreciable error. Coulometric KF titrators use an electric current to generate iodine (I<sub>2</sub>) from iodide (2I<sup>-</sup>) in solution which reacts rapidly with water as described by equation 1. A sudden voltage drop indicates free iodine in solution and the titration end point. Utilizing Faraday's law, the current required to reach the end point is proportional to the iodine generated. This method and procedure is suitable for solutions with low moisture content (10 to 50000 ppm).



All sample preparation was performed in a glove box with dry nitrogen atmosphere. A plastic glove bag (Sigma-Aldrich pt# Z530212 or similar) may be used if a glove box is not available. Addition of drierite or activated silica further dried the air inside the glove box. All glassware was heated at 140°C for at least 1 hour, and while the glassware was still hot, it was placed inside the glove box with constant nitrogen purging and allowed to cool. One gram asphalt and four grams anhydrous toluene (stored over activated molecular sieves) was added to a 10 mL glass vial and capped with a sureseal Teflon crimp lid. After the asphalt dissolved, at least three grams of this solution was injected into the KF reaction vessel with a dry disposable syringe (Restek Norm-Ject pt# 22769 or similar) and hypodermic needle and allowed to react. The quantity of sample injected was measured using an analytical balance. During this process, only very dry air contacted the toluene, asphalt solution, and cooled glassware minimizing the chances of contamination by atmospheric moisture.

### KF Method Applied to Asphalt Emulsion Recovery

Debate over the applicability and effectiveness of various emulsion recovery procedures is evidenced by industry's struggle to develop a standard method (Takamura and Lubbers 2000; Reinke et al. 2012). In this study, three methods were employed to recover asphalt emulsion residue in the laboratory including a novel approach developed at WRI. The first, AASHTO PP72-11 method B, involves spreading a 0.015" thick emulsion layer with a fixed thickness spreader bar onto a rubber mat and drying in a forced draft oven at 60°C for 6.0 hours. The second method uses the equivalent mass of emulsion to achieve a 300 μm (0.0118") thick recovered emulsion residue on a Universal Simple Aging Test (USAT) aluminum plate and drying in a vacuum oven at 60°C for 2.0 hours (Reinke et al. 2012). The third method also uses equivalent mass of emulsion to achieve a 300 μm thick recovered emulsion residue on a USAT plate and a forced draft oven at 60°C for 6.0 hours (Farrar et al. 2012). The 300 μm residue thickness was chosen so that laboratory aging of the sample could occur without transfer to a separate container for standard (R28) PAV aging. In a separate study it was demonstrated that aging a 300 μm asphalt film on a USAT plate under standard PAV conditions for 8 hours resulted in equivalent oxidation to R28 which requires a 3.2 mm thick film and conditioning for 20 hours (Farrar et al. 2012).

Emulsions were stored at room temperature in sealed containers for 2-6 months prior to testing. On the day an emulsion recovery was performed, the respective emulsion was heated for 1 hour in a 60°C oven, gently stirred with a glass rod until consistency was achieved, and while still warm the emulsion was spread onto either the USAT plate or rubber mat. Upon allotted emulsion recovery time in the oven, samples were placed in a glove box with dry nitrogen purge and allowed to cool to room temperature. Sample preparation and KF analysis was then performed as described in the above experimental section. Emulsions used in this study, listed with descriptions in Table 1, were named according to ASTM D2397 with the addition of LM or P denoting latex modified or polymer modified.

Table 1. Descriptions of emulsions used in this study.

Name	Description	Origin
LMCRS-2	latex modified cationic rapid set - high viscosity	Utah DOT
CSS-1H SLC	cationic slow set - low viscosity	Utah DOT
CRS-2 Cache	cationic rapid set - high viscosity	Utah DOT
Micro	unknown description	Utah DOT
LMCRS-2 Tank 11	latex modified cationic rapid set - high viscosity	Utah DOT
CRS-2P WRI	cationic rapid set - high viscosity polymer modified	WRI confidential
CSS-1H WRI	cationic slow set - low viscosity	WRI confidential
CRS-2 WRI	cationic rapid set - high viscosity	WRI confidential

Attempting to understand the proper amount of remaining moisture in the residue after recovery, several samples of 300 µm thick recovered emulsion residue and neat binders were treated in a 100% humidity atmosphere at 60°C for 2 weeks in a forced draft oven. The samples were then analyzed by KF titration to determine the equilibrium water content of each sample.

Previous to the application of the KF method to asphalt, effectiveness of emulsion recovery was evaluated by drying a sample to constant mass and quantifying residual water in the residue by calculating mass loss. This method of water quantification in emulsion residue was evaluated by comparing KF results to mass lost after drying at 135°C.

## RESULTS AND DISCUSSION

Results from KF titration of SHRP core binders are listed in Figure 1 and are given in ppm water or µg water/g solution. The binders were from sealed cans that had been heated, sampled, and capped with argon several times over the past 15 years. It was still unclear if the measured KF values were due to interfering reactions between the Couloamat oil and functional groups on asphalt molecules or to water in the binder. Addressing this issue, an azeotrope of toluene and water was formed by dissolving several grams of binder in 50 mL of toluene and evaporating the toluene, and consequently the water, on a rotary evaporator with a dry nitrogen purge and vacuum. The KF results for these azeotropic dried samples showed, on average, nearly 70 ppm

water remaining. While it is likely that some portion of the measured water in asphalt is due to interference reactions, the reduction of water in the azeotroped samples indicate that at least a portion of the very small KF response in the neat binders is due to moisture. It is estimated that 75-175 ppm water exists in an untreated binder because this is the difference between the neat binder and the azeotrope dried binders. AAD-1 and AAC-1 PAV aged at 100°C for 100 hours was titrated with the theory that an increase in ketones may cause a change in the titration end point. Aged AAD-1 azeotroped shows nearly double the amount of water than unaged AAD-1 indicating that interference reactions are likely occurring during KF titration. From the samples tested to date, a maximum of 170 ppm water false positive is due to interference and this number is more likely much lower in unaged binder.

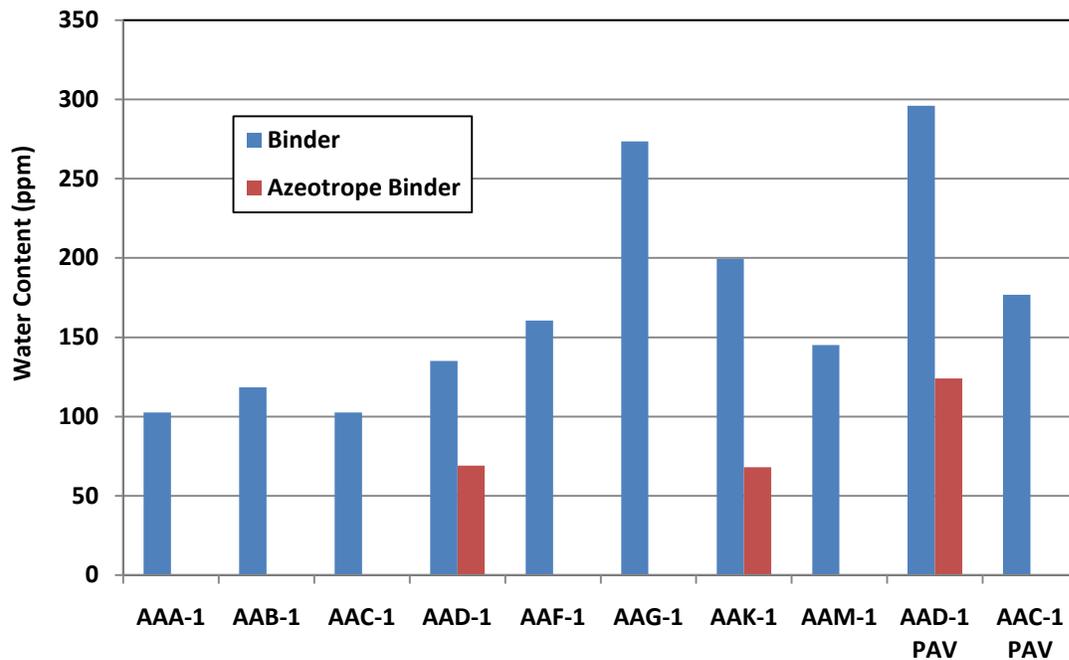


Figure 1. SHRP binders water content by KF titration. The water in three of the binders was azeotroped away to determine the amount of KF response due to interference.

### KF Titration Applied to Asphalt Emulsion Recovery

Figure 2 shows the amount of the water in each emulsion residue with the respective recovery method. No clear trends in water content are apparent with a specific emulsion or recovery method. It is probable that differences in water content between residues and recovery method are primarily due to variations in sample preparation on the rubber mat or USAT plate. Data collected by Reinke et al. (2012) suggesting that <1% water (wt/wt) is the threshold level where the viscosity of a recovered emulsion matches or exceeds that of the base binder used to create the emulsion indicates all three methods are satisfactory for emulsion recovery. Reinke's method for determining water content in residues involves heating at 135°C until constant mass is obtained and calculating water content by weight lost during drying. KF titration values on recovered residues prior to drying at 135°C are always lower than water content by measured

weight loss. For one CSS-1H residue, the discrepancy was as much as 9,000 ppm. Recovered residues before and after drying at 135°C were analyzed by mass spectrometry with the hypothesis that some volatile additive was evaporated while at elevated temperature. After mass spectrometry analysis, it was determined that a significant amount of 2,2,oxybis ethanol was evaporated from the CSS-1H residue with the 9,000 ppm water content discrepancy. Some of this compound was also present in other residues with water content discrepancies <3,000 ppm but was completely evaporated by exposure to 135°C temperatures. These data are a possible explanation for the conflicting results from the two methods of water quantification in residues and support the assertion that the KF method is more accurate for a wider variety of asphalt emulsions. Time did not permit a more exhaustive study looking for volatiles in all 8 emulsion residues. The reason 2,2,oxybis ethanol was added to these emulsions is unknown, but this compound may be an antifreeze agent or cutback.

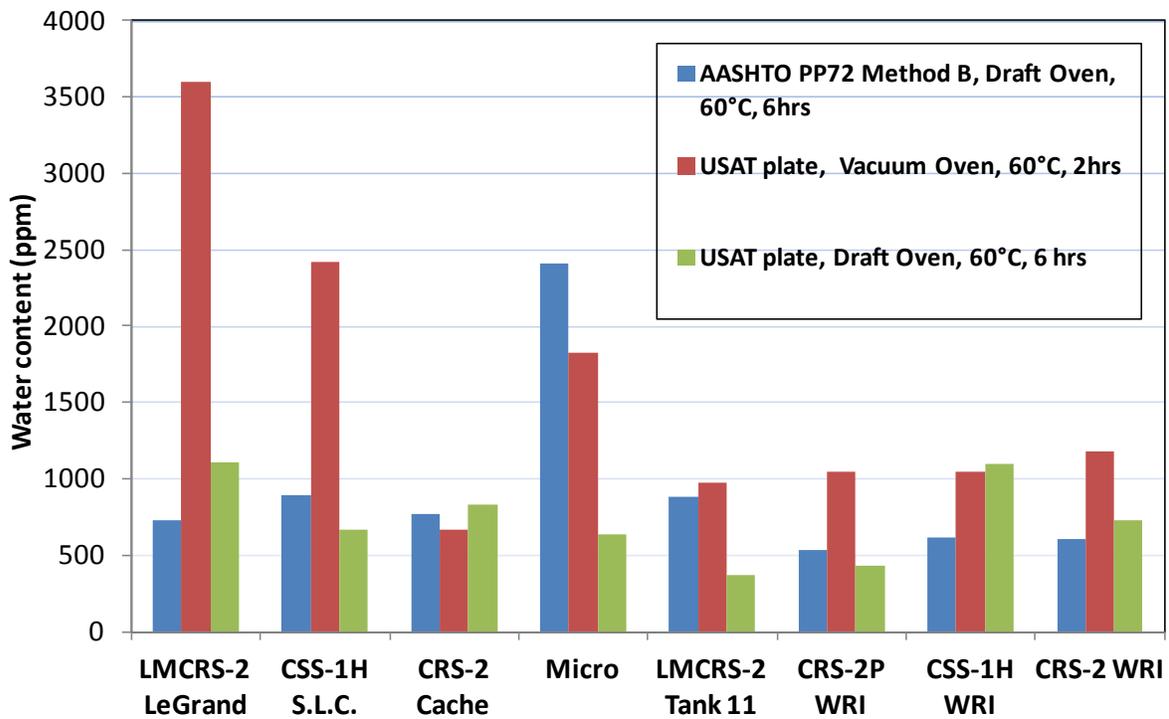


Figure 2. Water content of 8 emulsion residues after 3 recovery methods.

In an effort to further understand the appropriate water content after laboratory recovery of emulsion residue, several USAT plates were prepared with 300 μm thick recovered emulsion residue or neat binders and treated in 100% humidity atmosphere at 60°C for 2 weeks. The samples were then analyzed by KF titration to determine the equilibrium water content and results are presented in Figure 3. Assuming that sufficient time was given to the samples in the humidity chamber, the equilibrium water content of recovered emulsion residues and neat binders is very similar to water content of recovered residues.

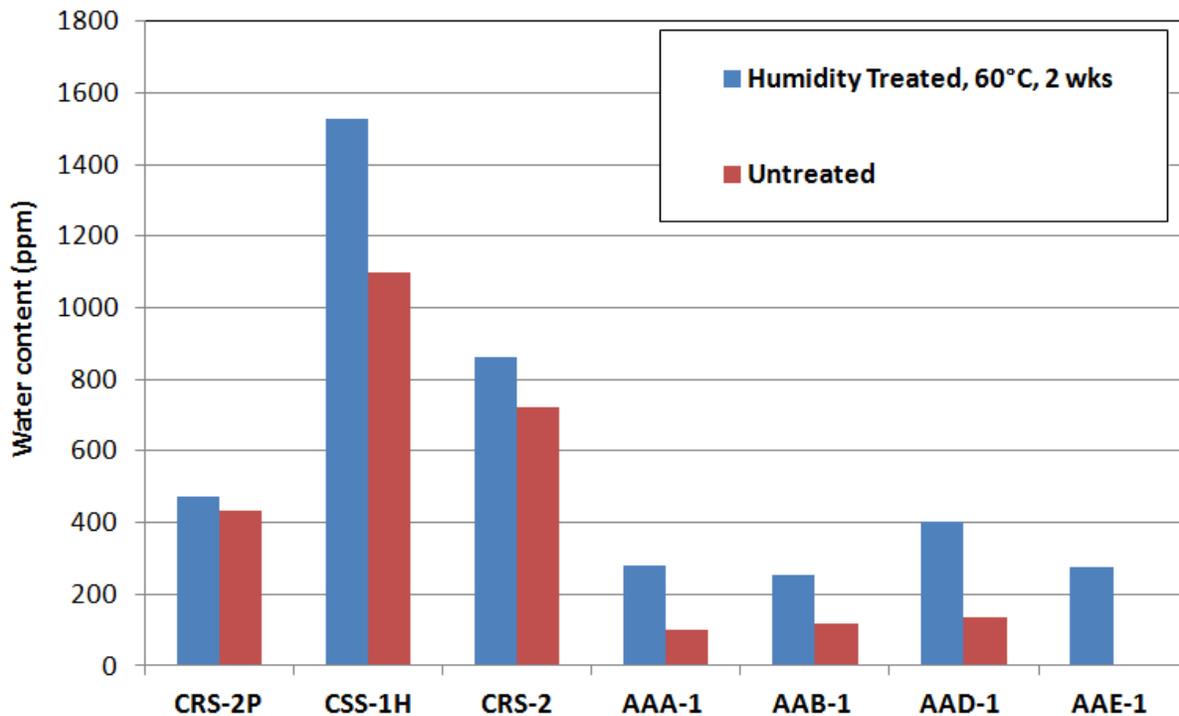


Figure 3. Untreated asphalt and recovered asphalt emulsion residue water content after treatment for 2 weeks in a 60°C oven with 100% humidity.

## CONCLUSIONS

A method for quantifying water in asphalt and asphalt emulsions has been developed that is accurate, quick, and highly sensitive. The method's detection limit is ~ 100 ppm. All SHRP binders varied from 100-275 ppm water. The method's utility was demonstrated in the evaluation of three emulsion recovery procedures and indicated that each procedure removed sufficient water for rheologic measurement of the residues. Binder films and emulsion residue films (300 μm thick) that were treated in a 60°C 100% humidity environment showed a maximum of 1500 ppm water and generally contained ~200 ppm more water than non humidity treated films. The method of quantifying water in emulsion residues by heating at 135°C until constant mass is obtained and calculating water content by mass loss was evaluated using KF titration. It was determined that some residues may contain volatile material that is evaporated at 135°C yielding artificially elevated and inaccurate water content by the mass loss method.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the Federal Highway Administration, U.S. Department of Transportation, for financial support of this project under contract no. DTFH61-07D-00005.

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