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Detection of Antistrip Additives
(Phase II)

Richard Ulrich, Brett Krepps

Final Report

1996

Detection of Antistrip Additives (Phase II)

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16. Abstract
The purpose of this project is to further develop quantitative tests for determining the concentration of antistrip additives in asphalt and to attempt to make these proposed tests applicable to intact pavement samples. After performing an extensive literature review of possible methods for this purpose, we chose two: organic phase titration for the determination of amine-based additives and atomic absorption spectroscopy for the determination of powdered lime additives. In the organic phase titration, the concentration of basic groups in the asphalt-additive mixture, or basicity, is determined and is assumed to be proportional to the concentration of additive in the sample. Also, an organic phase titration implies that the titration is carried out in a non-aqueous environment, therefore eliminating an aqueous extraction step, which could be a source of error and complication. This measured absorption is proportional to the concentration of the substance to be determined; calcium in this case, since this method will be used for lime-based additives and lime is by definition calcium hydroxide.

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METRIC CONVERSION FACTORS

Approximate Conversions to Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
in	inches	*2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km
AREA				
in²	square inches	6.5	square centimeters	cm²
ft²	square feet	0.09	square meters	m²
yd²	square yards	0.8	square meters	m²
mi²	square miles	2.6	square kilometers	km²
	acres	0.4	hectares	ha
MASS (weight)				
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons (2000 lb)	0.9	tonnes	t
VOLUME				
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft³	cubic feet	0.03	cubic meters	m³
yd³	cubic yards	0.76	cubic meters	m³
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C

*1 in = 2.54 (exactly). For other exact conversions and more detailed tables, see NBS Misc. Publ. 286, Units of Weights and Measures, Price $2.25, SD Catalog No. C13.10:286.


Approximate Conversions from Metric Measures

Symbol	When You Know	Multiply by	To Find	Symbol
LENGTH				
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi
AREA				
cm²	square centimeters	0.16	square inches	in²
m²	square meters	1.2	square yards	yd²
km²	square kilometers	0.4	square miles	mi²
ha	hectares (10,000 m²)	2.5	acres	
MASS (weight)				
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	
VOLUME				
ml	milliliters	0.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m³	cubic meters	36	cubic feet	ft³
m³	cubic meters	1.3	cubic yards	yd³
TEMPERATURE (exact)				
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F
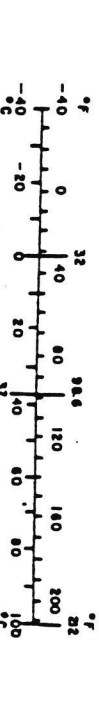
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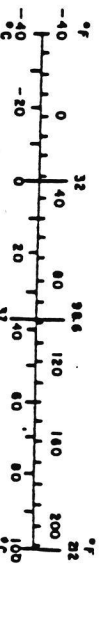
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Detection of Antistrip Additives - Phase II

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PREFACE

This report was prepared was prepared in cooperation with the U.S. Department of Transportation, Federal Highway Administration. The contents of this report reflect the views of the authors who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Arkansas State Highway and Transportation Department or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation. The results of this study are accurate to the best of the knowledge of the authors at the time of publication.

The authors wish to thank the Arkansas State Highway and Transportation Department for the opportunity to perform this work.

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ABSTRACT

The adhesion of asphalt and aggregate is an important factor in determining the durability of bituminous pavements. In order to promote this adhesion, liquid amine-based and powdered lime-based additives are routinely added to asphalts in amounts of 0.5 to 2.0 % by weight. The purpose of this project is to further develop quantitative tests for determining the concentration of antistrip additives in asphalt and to attempt to make these proposed tests applicable to intact pavement samples. After performing an extensive literature review of possible methods for this purpose, we chose two: organic phase titration for the determination of amine-based additives and atomic absorption spectroscopy for the determination of powdered lime additives. In the organic phase titration, the concentration of basic groups in the asphalt-additive mixture, or basicity, is determined and is assumed to be proportional to the concentration of additive in the sample. Also, an organic phase titration implies that the titration is carried out in a non-aqueous environment, therefore eliminating an aqueous extraction step, which could be a source of error and complication. Atomic absorption spectroscopy is a method useful in elemental analysis which measures the absorption of a sample at a specific wavelength through a flame that contains the substance of unknown concentration. This measured absorption is proportional to the concentration of the substance to be determined; calcium in this case, since this method will be used for lime-based additives and lime is by definition calcium hydroxide.

1. INTRODUCTION

1.1 Statement of Problem

For years scientists and engineers have struggled with the problem of how to measure concentrations of antistrip additives in asphalts and pavements. These additives, which play a vital role in the adhesion of the asphalt (glue) to the aggregate (rocks) in bituminous pavements and thus in the durability of the world's roads and highways, are difficult to detect in complex matrices such as asphalt. We intend to develop routine and inexpensive methods that will accomplish this task: the detection of antistrip additives in asphalt-additive mixtures and possibly in samples of existing pavement.

Although our project will only concern the measurement of additive concentration, this accomplishment could lead to other areas of research. If reliable methods can be developed, it could lead to a quantification of the relationship between stripped pavements and the additive concentration in those pavements. This might be accomplished by searching for stripped pavements in the field and taking samples of that pavement for additive concentration analysis. Hopefully, this relationship will allow for the determination of an ideal concentration of additive or possibly even give some insight as to how additive concentration changes with time. A better understanding of the chemistry of each one of these components, asphalt and additive, is helpful in understanding the problems faced and the solutions proposed.

1.2 Asphalt Chemistry

The chemical structure of asphalt is quite complex and varies from one sample to another. Chemists often refer to asphalt as a hydrocarbon, which simply means that it is composed primarily of atoms of carbon and hydrogen. In fact, asphalts used for paving contain between 90 and 95 weight percent hydrogen and carbon atoms [1]. The remaining 5 to 10 percent of the atoms in the asphalt consist of two other types: heteroatoms and metals.

The heteroatoms are nitrogen, oxygen, and sulfur. They are called heteroatoms because they can replace carbon atoms in the asphalt molecular structure. But, since their chemistry is very different from that of carbon, and since they are responsible for most of the hydrogen bonding that occurs in asphalt, they contribute to many of asphalt's unique chemical and physical properties by forming associations between molecules. Therefore, the kind and amount of heteroatoms present in a given asphalt, which are a function of both the crude oil(s) from which the asphalt was produced and the state of aging of the asphalt, are very important factors in the durability of pavements. This is also true because the heteroatoms, especially sulfur, play an important role in the aging of asphalt because they are more chemically reactive than either carbon or hydrogen and can oxidize, or incorporate oxygen, more easily than the hydrocarbons. This oxidation process plays a major part in the natural aging of pavements.

The last group of atoms that asphalt contains, along with the hydrocarbons and heteroatoms, are the metals such as vanadium, nickel, and iron (V, Ni, Fe) that are present in very small quantities in the asphalt, usually less than 1

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percent [1]. They, too, may play an important role in the aging process, and the also serve as a "fingerprint" for the asphalt because the amount of metals present in the asphalt is usually indicative of the crude source from which the asphalt was refined. Also, since one phase of this project focuses on the measurement of calcium in asphalt and mix samples, it is important to know the amount of calcium already present in a given asphalt. This point will be more fully discussed and explained later in this paper.

The hydrocarbons, heteroatoms, and metals are all combined in the asphalt in a wide range of different molecules. All of these molecules can be grouped into three broad categories: aliphatics, cyclics, and aromatics. There are literally millions of different aliphatics, cyclics, and aromatics in a given asphalt, and their sizes vary as well as their numbers, ranging from those containing about 20 carbon atoms up to nearly 100. The term aliphatic, which literally means "oily", can best be described as a linear or chain-like molecule in which the carbon atoms are linked end to end. A cyclic molecule is one in which the carbon atoms link together to form a ring, giving up hydrogen atoms in the process. This ring formation has a very large effect on the chemical properties of the molecule. This is due to both the change in shape of the molecule, as well as the interaction of the individual atoms in the molecule with each other. Aromatics, so named for their strong odor, are also ring shaped molecules but are distinguished from cyclics by their "ring" of aromaticity, or shared electrons. The unique property that aromatics bring to asphalt structure is their flat shape. Cyclics and aliphatics are three dimensional and form shapes that keep the molecules apart. On the other hand, aromatics are flat and can be closely stacked on top of one another,

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which can also account for certain physical properties of the asphalt, such as viscosity.

All of the hydrocarbons, heteroatoms, and metals are combined into the millions of different molecules that make up asphalt. Each asphalt has a unique assortment of these molecules, and the molecules change as the asphalt ages. The heteroatoms are incorporated into the aliphatic, cyclic, and aromatic hydrocarbon molecules; they affect the chemical behavior of the individual molecules, as well as the associations which the molecules form.

As a result of the intensive chemical investigations of the Strategic Highway Research Program (SHRP) researchers, which was a group dedicated to research concerning the improvement of asphalt and pavement performance, we have now achieved a much better picture of asphalt's chemical makeup [1]. In simple terms we can now characterize asphalt as follows:

1. Asphalt consists of two (and only two) *functional* families of molecules:

    Polar

    Non-polar

2. Polar molecules differ according to:

    Strength and number of polar group(s)

    Molecular weight

    Degree of aromaticity

3. Non-polar molecules differ according to:

    Molecular weight

    Degree of aromaticity

4. The "compatibility" of the polar and non-polar fractions, or the degree to which they can dissolve in each other, is controlled by the relative aromaticity (a measure of the amount of aromatic versus aliphatic and cyclic molecules) of the two fractions.

1. Polar vs. Non-polar molecules. All of the molecules in asphalt behave in one of two ways. If they are polar at service temperatures they participate in the formation of a network, through such relatively weak molecular interactions as pi-pi and hydrogen bonding, that gives asphalt its elastic properties. The non-polar molecules form the body or matrix of the material in which the network is formed and contribute to the viscous properties of the asphalt.

2. Polar molecules. As stated above, polar molecules form the network of associated molecules and comprise a wide variety of molecular types and sizes. The most important attribute of the polar molecules is the relative strength and number of polar sites per molecule because this directly affects the network formation. The degree of aromaticity of the polar molecules, which can be determined by a nuclear magnetic resonance (NMR) analysis, is also an important parameter. The molecular weight of the polar molecules is not as important a parameter as the other two and plays a minor role in the performance of the asphalt cement [1].

3. Non-polar molecules. An important feature of the non-polar molecules is their molecular weight, because this directly affects the low-temperature cracking properties of the asphalt. A preponderance of high molecular weight

non-polar molecules will lead to asphalts that stiffen and perform poorly at low service temperatures due to brittleness.

The degree of aromaticity of the non-polar molecules is also important. If the non-polars are waxy (a type of aliphatic molecule) in nature, they may precipitate or crystallize at low temperatures, contributing to poor performance. Cyclic or aromatic non-polars may resist the effects of low temperature better.

4. Compatibility. The non-polar molecules are also important to asphalt's performance because they are the substance in which the polar molecules must interact. If the molecules are similar in chemistry they will mix easily and be compatible. On the other hand, if they are quite different they will be incompatible, and the molecules may not want to stay in solution.

As a result of extensive research by the SHRP group and others and the use of powerful new analytical tools such as ion exchange chromatography and size exclusion chromatography, a new model of the relationship between asphalt chemistry and pavement performance has rapidly evolved.

There are several different types of interactions that take place between the different molecules in asphalt. The polar molecules interact with each other through polar-polar or hydrogen-bonding interactions, thus forming associations that create a network within the non polar "solvent" molecules. Other interactions take place through pi-pi bonding of aromatic rings and Van der Waals interactions of long-chain hydrocarbons. All of these interactions are weak relative to covalent bonds and they are constantly being

broken and reformed as the asphalt is subjected to heat and/or stress. This concept of weak interactions between molecules explains why asphalt behaves as a Newtonian fluid (its viscosity change is proportional to the amount the temperature is changed) at elevated temperatures, and why asphalt exhibits a behavior that is so dependent on temperature and loading. Due to the weak nature of the polar-polar and pi-pi bonding forces, bonds are constantly being broken and reformed, each time in a unique way that never yields the exact same material again.

Through the use of the ion exchange chromatography analytical technique, a new fraction which is believed to be asphalt's "key" building block has been isolated. This material has unique physical properties that explain the tendency of polar molecules in asphalt to aggregate and form associations. These materials are termed the amphoterics, which by definition is one that can exhibit either acidic or basic character. When applied to asphalt, the term means that an asphalt molecule has both an acid and a base group (one or more of each) on the same molecule, but not at the same site. Data has unequivocally demonstrated the large contribution of this class of molecules to the viscoelastic properties of the asphalt [1].

In terms of performance of an asphalt, a good asphalt will have a proper balance of polar and non polar molecules. Also, the molecular weight of the non polar materials is important, especially in low-temperature environments. Asphalts that have too much polar material will be subject to thermal cracking, brittleness, and fatigue cracking in thin pavements. Asphalts that have too much non polar material or that have non polar too

low in molecular weight will suffer from rutting, moisture sensitivity, and fatigue cracking in thick pavements.

Asphalts age through both chemical and physical processes. Heteroatoms, or sites near heteroatoms, react with and incorporate oxygen into the asphalt and become more polar. This adds to the amount of polar molecules that can interact and strengthen the network in the asphalt. Additionally, volatilization of low molecular weight molecules takes place, further stiffening the asphalt by removal of the solvent phase. However, the process of volatilization appears to be fairly short-term in duration, taking place during the mixing and laydown phases of asphalt-concrete production. Oxidative aging is a longer process, extending over the life of the roadway, and is controlled by the service temperature of the pavement. Aggregate has little or no effect on the oxidative aging of asphalt, although it does affect the molecular structure, and thus, its stiffness.

1.3 Antistrip Additives

Pavement, for the purposes of this study, can be thought of as consisting of two separate components: asphalt and aggregate. The asphalt can be thought of as the glue which holds together the tiny rocks, or aggregate, in this common and familiar mixture. The intimate association between asphalt and aggregate is vital to a road's durability: if the glue doesn't stick closely to the rocks, load-related stresses along with the natural action of the elements will eventually overwhelm the pavement and can literally wash away, or strip, the road. Antistrip additives are substances which do what their name implies. They prevent this stripping process when added to asphalt-aggregate

mixtures. Although the mechanism of their effect is still a subject for debate [2], we do know that they work. If we can learn to accurately quantify their concentration in pavement, we'll gain practical yet impirical knowledge invaluable to the cause of building better roads.

Amine-based additives are one of the two main types of additives used in the United States. Amines are a family of organic compounds which all contain a certain functional group: a nitrogen atom with either one (primary), two (secondary), or three (tertiary) carbon atoms chemically bonded to it. They are the main type of liquid antistrip additive and are usually added to asphalts at concentrations of 0.5 to 2.0 % of the asphalt's weight. They are soluble in asphalt and migrate to the aggregate surface, where they are adsorbed, thus resulting in a hydrophobic (water-repellent) aggregate surface which permits stronger adhesion of asphalt. The extent to which the aggregate surface becomes hydrophobic is proportional to the concentration of additive added, the efficiency of the migration, the strength of the adsorbing bond, as well as the aggregate type.

The proper concentration of amine-based additive in asphalt is crucial to the performance of the pavement. Even in proper concentrations, additives can have a softening effect on the asphalt cement both before and after aging. Maupin [3] found that asphalts containing antistrip additives were more likely to soften than those without. Anderson and Dukatz [4] concluded that excessive doses may also soften asphalt. It has also been speculated that some liquid additives may reduce the viscosity of asphalts below acceptable values, and that, if the concentration of the additive is in excess of that needed to satisfy all of the adsorption sites for the aggregate, hydrocarbon to

hydrocarbon interfacial orientation can occur, creating a mechanically weak, water susceptible, shear plane [5]. It is because of this that there is a need to determine the concentration of antistrip additive that will be effective for particular asphalt-aggregate mixtures. Amine-based antistrip additives are often preferred to lime-based additives due to their cost advantage and their ease of implementation during construction, but not necessarily for their effectiveness [2].

Lime-based or calcium-based additives are another common type of antistrip agent used. They are dry (or powdered) additives and work, according to one theory, by decreasing the surface tension between asphalt cement and water, which in turn results in improved adhesion between asphalt and aggregate. Another theory suggests that hydrated lime reacts with acidic compounds in the asphalt to form water insoluble compounds that are readily adsorbed onto the surface of the aggregate. A third suggests that the aggregate is made water resistant by calcium ions replacing certain cations on its surface [6].

Lime-based and other dry additives also prevent stripping by acting as mineral fillers. Not only do mineral fillers act as mineral aggregate, but they also fill up space between larger aggregate particles thus reducing the air void volume and making it more difficult for water to penetrate and spread in the pavement. Lime additives also stiffen the asphalt cement, thereby increasing the viscosity of the pavement.

It is still unclear as to which type of additive is more effective in the prevention of stripping. A safe assumption is that different additives work best in different asphalt-aggregate mixtures and different environmental

conditions. Hicks [7] has shown that the best results occur upon pre-treatment of the aggregate surface with lime, but other studies state that there is greater improvement in coating retention for amine-based additives. While both types have proven to be effective in certain instances, neither has shown effectiveness in all asphalt-aggregate mixtures.

1.4 Measurement of Amine-Based Antistrip Additives

1.4.1 Accepted Methods

When speaking of "accepted" methods for the measurement of amine-based antistrip additives, we essentially mean any method which is applicable to the detection of amine compounds or possibly other nitrogen-containing compounds, but preferably those which work when the species are dissolved in a complex matrix. Chromatography, which is a group of laboratory separation techniques based on selective adsorption by which components of complex mixtures (vapors, liquids, solutions) can be identified through a series of peaks on a spectrum called a chromatograph, is one technique widely used in recent years in the detection of amines. High-performance liquid chromatography (HPLC) is the term applied to new and more effective instrumental techniques developed in recent years which have greatly increased the scope of this analytical method.

Although HPLC is an effective method in the detection and quantification of amines, several problems exist in the context of our research. First, the exact composition of the additives we are attempting to detect is not known. Without this information, we cannot know where they will adsorb on the

spectrum. This makes it impossible to correctly determine their concentration. A solution to this problem would be to derivatize, or change into one common form, all of the amines in the sample. This would make the location of the peak identifying the amines on the spectrum known. But, since there are many different reagents used for amine derivatization and many different amine species present in each individual additive, the best match of reagent to additive would be tedious. Also, many derivatizing reagents are not applicable to all types of amines. This method is also relatively expensive, time consuming, and generally more complicated than others such as titration, which will be discussed later in detail.

Other types of tests have been used in the detection of amines. One group of qualitative tests is indicator tests [8, 9] which only reveal whether or not amines exist in the sample or not and tell nothing about their concentration if they do exist. This type of test is totally inappropriate for our purposes because it is qualitative only.

1.4.2 Method Developed in Phase I

During Phase I of this project [2], Dr. Richard Ulrich and Peggy Carroll investigated several methods for the detection of amine-based antistrip additives. After reviewing the literature and some experimentation, they came up with a simple, reliable, and cost efficient method which was termed the "Single Vessel Titration" test, or SVTT. They found that each of the AHTD approved amine-based additives could be detected in asphalt-additive mixtures to within a few percent error down to levels of additive-in-asphalt of less than 1% by weight. A sample of blank asphalt (no additive) and a

sample of the additive in question are required for the test, and it is necessary to construct calibration curves for each additive/asphalt combination. The test can be performed by virtually anyone after just a few hours of training; the procedure does not require an understanding of the chemical principles involved and the test interpretation is easily understood. The cost for lab equipment for the test is a couple of hundred dollars and the materials cost per test is under $10. Although this test is qualified for additive/asphalt mixtures, it has not yet been made applicable to samples where aggregate is present.

The SVTT requires several repetitions of the same analytical procedure: a titration for basicity. The basicity of asphalt, additive, or asphalt/additive blend is exactly what it says: how basic (or alkaline) the sample is. A basic chemical has a pH higher than the neutral point, pH=7. Amine antistrip additives are alkaline compounds detectable by the amount of basicity that they add to a given asphalt. The procedure is to measure the basicity of the blank asphalt (containing no additive), measure the basicity of the additive alone, and then measure the basicity of the asphalt/additive blend in question. From the known basicities of the asphalt and the additive alone, the weight fraction of additive in the blend can be determined.

The procedure for the basicity titration is as follows:

1. Dissolve 1 gram of sample in 50 ml of trichloroethylene (TCE) and then 50 ml of water in a 250 ml beaker. Agitate for 1 minute on the stir plate at a high enough speed to mix the two phases together.

2. Turn down the agitation until two phases form (water on top, TCE and asphalt bottom). Leave this low level of agitation on throughout the rest of the titration.

3. Place a pH electrode in the water (top) phase.

4. Titrate with 0.01 N HCl until pH of the water phase drops to 7.00. Take out pH electrode and stir vigorously, measure the pH again, and titrate, if necessary, until the pH remains at 7.00.
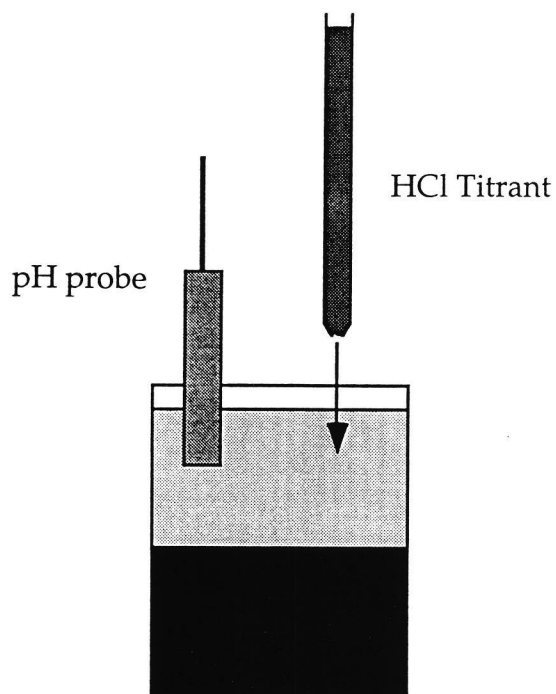

Figure 1. Performing the titration in the SVTT

5. Calculate the basicity from this equation:

$$\text{Basicity of Sample} = \frac{(\text{ml of acid titrant})(0.01 \text{ N})}{(1000 \text{ ml/liter})(\text{grams of sample})}$$

Using the titration procedure described above, a calibration curve is prepared for the particular asphalt-additive blend being analyzed. This curve will take the form of a graph having sample basicity on the y-axis and weight percent additive on the x-axis. The calibration curve need only be prepared one time for each blend; it is then applicable to any combination of these two components no matter how many samples are analyzed in subsequent testing, as long as the same asphalt and additive are present in the samples.

To prepare the calibration curve, measure the basicity of five independent one gram samples of the blank asphalt (containing no asphalt) and of five independent one gram samples of the pure additive by the titration method described above. Average the basicities of both groups of five. As an example, here are the results using Pave Bond AP:

Blank asphalt was analyzed at 1.26×10^{-5} moles base/gm
Pave Bond AP was analyzed at 1.70×10^{-3} moles base/gm

Next, make a graph with basicity on the y-axis and weight percent additive on the x-axis. Place the average for the blank asphalt as a single point positioned at weight percent additive equals zero (on the y-axis). Add the basicity of the blank asphalt to 1% of the basicity of the additive alone and plot that point at 1% on the x-axis. Draw a line between these two points and the result is a calibration curve for that particular mixture.
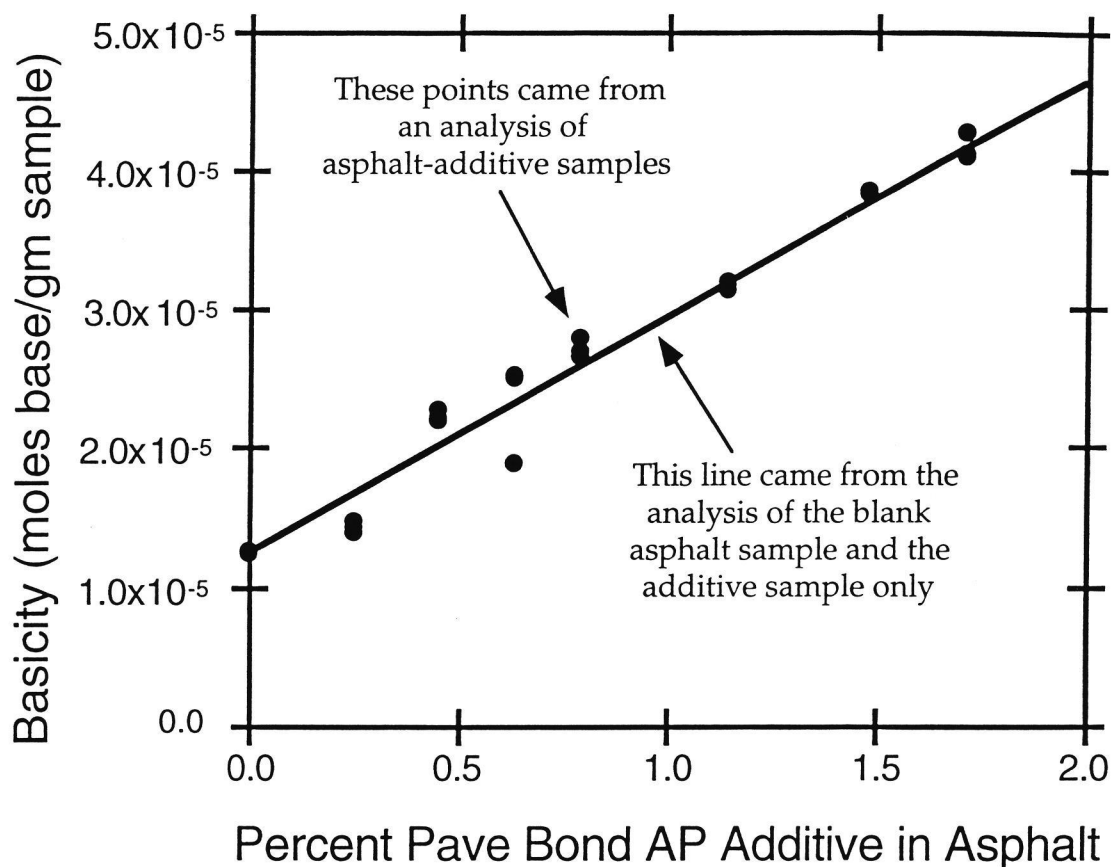
Figure 2. Calibration curve for Pave Bond AP

Now that the calibration curve is complete, the unknown samples can be analyzed by performing a basicity titration on the sample in question and then simply reading the percent additive from the plot.

1.5 Measurement of Calcium-Based Antistrip Additives

1.5.1 Accepted Methods

Just as for the detection of amine-based additives, accepted methods for the detection of calcium-based additives includes all methods which involve the detection of atomic calcium or calcium hydroxide, preferably in a complex

and dynamic matrix. Cardwell, Cattrall, Cross, and Mrzljak investigated a titration method involving a discontinuous-flow analysis (DFA) which detects total calcium in drinking water, wine, and milk [10]. This method, which uses a coated-wire, calcium-selective electrode to detect the calcium in solution, could be applicable because milk, like asphalt, has a complex matrix. Discontinuous-flow analysis is a very fast and reproducible procedure ideally suited to routine analysis and is easily automated. However, this particular procedure involves the use of a long list of chemicals and equipment, and also gives somewhat inaccurate results. The total calcium content in several different types of milk measured by DFA was underestimated, being only about 80% of the value obtained by an atomic adsorption spectroscopy method performed by the same group of researchers. They believed that some of the constituents which are known to bind calcium were causing these incorrect results, because the complexed calcium titrates more slowly, giving rise to the different shape of the curve compared with pure calcium solutions and to the underestimation of the end-point. This could also be a problem if the same procedure were performed on asphalt-additive solutions. A back-titration method, however, was found to give satisfactory results, but added yet another series of steps to the procedure. The negative aspects of this procedure seem to outweigh the positives, therefore it is not recommended for our research.

2. STATEMENT OF PURPOSE

The purpose of our research is to develop quantitative procedures which will accurately determine the concentration of antistrip additive in asphalt and asphalt-aggregate samples. These tests should be easy to implement and perform while being inexpensive at the same time. Two procedures, one for each class of additive, will be tested: non-aqueous phase titration for the determination of amine-based antistrip additive and atomic adsorption spectroscopy for the measurement of calcium antistrip additives.

3. ORGANIC-PHASE TITRATION FOR AMINE-BASED ADDITIVES

3.1 Development of Titration Method

When performing an acid-base titration there are basically two choices of liquid phases in which to carry out the procedure, aqueous and organic. Most, if not all, titrations in which a pH end point is detected and reported are performed in the aqueous phase, while titrations which detect and report a solution potential end point, or millivolt end point, can be carried out in both the aqueous and organic phases. If the asphalt sample is dissolved in an organic solvent and the antistrip additives are titrated directly in this solution, we are performing an organic phase titration. This implies two things: one, that the additives were not first extracted into the aqueous phase for titration as they were in Phase I of this project; and two, that the solution's potential will be the quantity monitored in the titration. This is the concept we intend to use to determine amine-based antistrip additive concentration in our samples.

The inherent advantage, at least for the purposes of our research, that organic-phase titration has over aqueous-phase titration is it's lack of the extraction step. Bypassing the extraction step is an advantage because this is a possible source of error. This is the case because when a gas, liquid, or solid is added to two partially miscible or completely immiscible solvents, such as an organic liquid and an aqueous liquid, it will, depending upon the amount of solute present, either partially or completely dissolve and be distributed unequally between the two liquid phases [11]. This is pertinent to our research because when the additive is extracted into the aqueous phase for

titration, as in the SVTT, we must ask ourselves, "is the fraction extracted constant for all conditions?" Experimental data on the partitioning of a solute between liquid phases are usually reported in terms of a distribution coefficient, K, defined to be the ratio of the solute concentration in the two phases:

$$K = \frac{\text{Concentration of solvent in phase I}}{\text{Concentration of sovent in phase II}}$$

This constant represents the physical limit of solute that can be extracted from one phase into another at a specified temperature, pressure, and solvent concentration. The bottom line is that if the extraction step is eliminated, all of these considerations are disregarded because the additives are titrated directly in the organic phase. Furthermore, an extraction step just makes the procedure more complicated.

In order to optimize the performance of the procedure, several considerations must be addressed. One of these is what solvent to use for the organic-phase titration. There are many solvents which are acceptable for titration of amines, but not necessarily suitable for our purposes. Solvents such as acetone, acetonitrile, and chloroform allow for the differentiating titration of mixtures of primary, secondary, and tertiary amines, like a typical antistrip additive contains. A differentiating titration is one in which two or more bases (or acids) is resolved with a distinguishable end point for each base. This is unnecessary for our purposes and is actually undesired because it would complicate calculations, which will be explained later. We are not concerned with finding respective concentrations of different types of amines

but instead are interested in measuring the total concentration of amine species in the mixture, regardless of their classification. Glacial acetic acid is a common solvent used for this very purpose. The properties of acetic acid solvent are sufficient to cause almost all amines (B) to react more or less completely with the solvent (HAc).

$$B + HAc \rightleftharpoons BH^+Ac^-$$
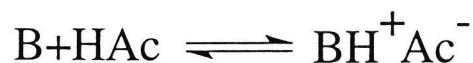
The ion pair is only partially dissociated because of the low dielectric constant of acetic acid.

$$BH^+Ac^- \rightleftharpoons BH^+ + Ac^-$$

The effect of these reactions is that all of the amine species are leveled to the same strength, thus acetic acid acts as a *leveling* solvent for aliphatic amines and simple aromatic amines. This means that all of the amines are changed into a form in which they all have the same alkaline strength. This is advantageous when calculations are performed determining the concentration of the amines in the sample because of the following reason. When a potentiometric titration is performed, the end point is determined by plotting the potential of the solution versus the volume of titrant added. As more and more titrant is added the potential slowly increases until the vicinity of the end point is reached. At this point a drastic increase in potential is observed followed by a leveling off of the potential as even more titrant is added. The following plot is illustrative of this phenomenon.
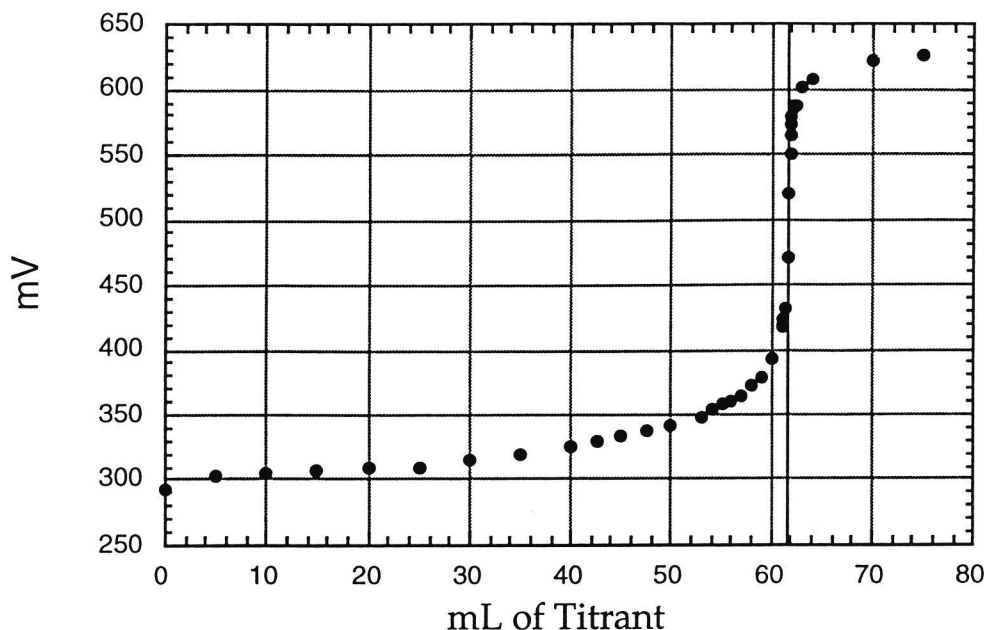
Amine Value Test

Figure 3. Example of plot prepared for end point determination in potentiometric titration

The end point of the titration corresponds to the midpoint of the inflection of this curve, which would be approximately 62 ml of titrant and 500 mV for this particular example. The value of the titrant added at the end point is then taken and used to calculate the concentration of amines in the sample. If a differentiating solvent is used, a plot like the one above would yield a curve with more than one inflection which interprets into more than one end point. This means that more than one calculation for concentration of amines would have to be made in order to determine the total concentration. The point is that if glacial acetic acid is used as the solvent in the non-aqueous titration of amines, only one inflection in the curve will appear and the total concentration of the amines can be determined from that inflection with one fairly simple calculation. This is also desirable if the use of an automated

titrator is employed, since only one end point can be programmed into the machine. It is important to remember that most amines can be titrated in acetic acid containing up to 2 or 3% water. If more water is present, the end point is not sharp and the results would be somewhat inaccurate. Finally, since glacial acetic acid is a polar solvent which will not dissolve asphalt, it will be necessary to add some non polar solvent to the glacial acetic acid to dissolve the asphalt. In Phase I of this project TCE was used, but we will use toluene because it is less hazardous than TCE.

Another consideration is choosing the most suitable titrant. The most widely applicable method for titration of organic bases involves using standard perchloric acid dissolved in either glacial acetic acid of 1,4-dioxane. In water and other solvents having significant basic properties, the leveling effect is such that other strong acids, such as hydrochloric or nitric, will serve as well as perchloric acid. However, perchloric acid is the preferred titrant for titrations carried out in acetic acid and other non-basic solvents because it gives a longer potentiometric break, or inflection in the ml vs. mV curve, than hydrochloric acid and a much longer break than nitric acid.

3.2 Application of Organic-Phase Titration Method on Additive Samples

3.2.1 Preparation of Additive Samples for Titration

The preparation of additive samples involved weighing out an amount of additive, usually about 0.2 grams, into a 250 mL beaker and then dissolving this sample in a mixture of 50 mL of glacial acetic acid and 60 mL of toluene.

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The solution was then stirred for approximately 5 minutes before the titration began.

3.2.2 Procedure for Organic-Phase Titration Method on Additive Samples

After the sample is thoroughly dissolved, its basicity was determined by the following procedure:

1. Titrate with 0.1 N perchloric acid, taking readings of the solution's potential (mV) every few mL of acid added until the vicinity of the endpoint is reached, then taking readings in smaller increments (about every 0.1 ml of added acid). If the mV readings drift, take an average of the highest and lowest readings observed.

2. Using the data obtained during the titration, make a plot of mL of perchloric acid added vs. the solution's potential (mV).

3. The endpoint of the titration is the midpoint of the inflection of the curve obtained in step 4. Note the mL of acid titrant added at this point.

4. Calculate the basicity of the sample using this equation

$$\text{Basicity of Sample} = \frac{(\text{ml of acid titrant})(0.1\ N)}{(1000\ \text{ml/liter})(\text{grams of sample})}$$

An example of a plot obtained from this procedure is pictured on the following page:

Permatac Plus (3/27/94)
Solvent: 60 mL Toluene/50 mL GAA
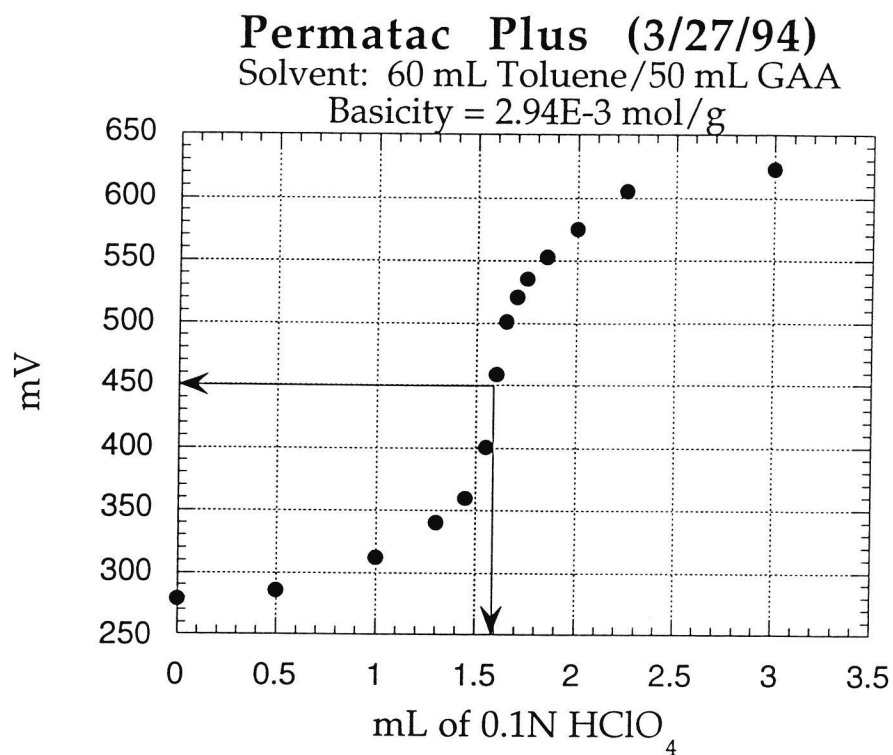### Basicity = 2.94E-3 mol/g

Figure 4. Organic-phase titration on Permatac Plus

The following table shows average basicities for three additives obtained by both the SVTT and the organic-phase titration.

Table 1. Comparison of basicities from SVTT and organic-phase titration

Antistrip Additive	SVTT Basicity (mol/g)	Organic-Phase Titration Basicity (mol/g)
Kling Beta LV(HM)	4.72E-3	4.21E-3
Permatac Plus	3.32E-3	2.70E-3
ACRA 2000	4.28E-3	5.73E-3

One can see from Table 1 that the SVTT and the organic-phase titration give comparable results.

3.3 Application of Organic-Phase Titration Method on Asphalt-Additive Samples

3.3.1 Preparation of Asphalt-Additive Samples for Titration

The asphalt-additive samples were prepared by two different methods in this project, both of which were used in Phase I [2]. In the first method, a certain amount of asphalt was weighed into a beaker followed by a certain amount of additive to obtain a desired concentration of additive in asphalt. Then the two were mixed together by dissolving them in 60 mL of toluene and 50 mL of glacial acetic acid. The second method was used mostly for the mixes and will be described later.

3.3.2 Procedure for Organic-Phase Titration Method on Asphalt-Additive Samples

The same procedure for basicity determination was used on the asphalt-additive samples. The following is a sample plot of the procedure performed on an asphalt-additive sample.

27
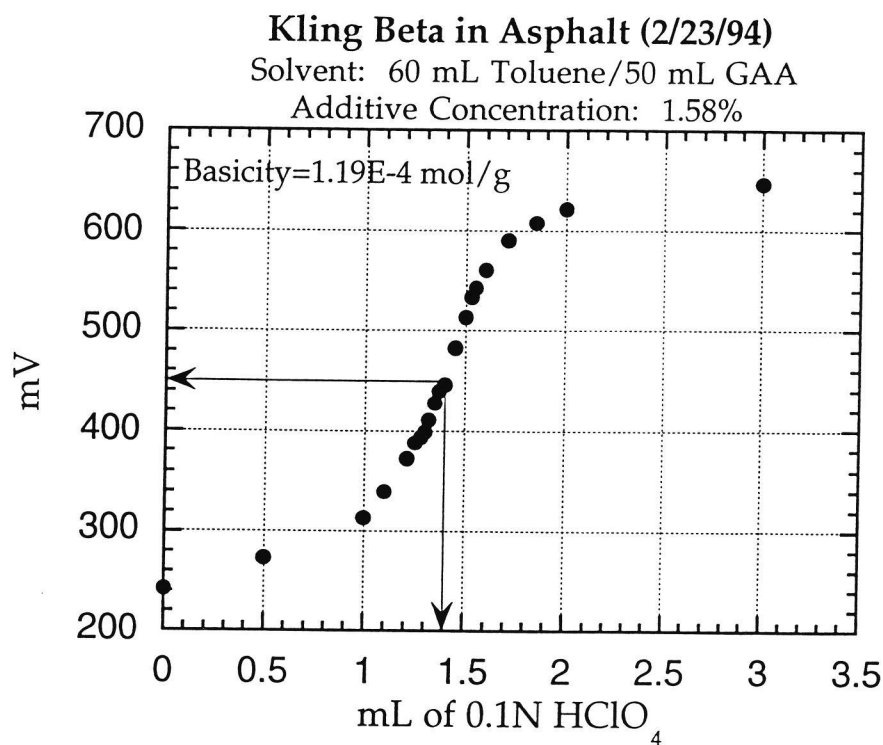
Figure 5. Organic-phase titration performed on an asphalt-additive mixture containing 1.58% Kling Beta LV(HM) in asphalt

3.3.3 Calibration Curves for Asphalt-Additive Samples

Calibration curves showing the percent additive in asphalt vs. basicity were prepared for three different additives in asphalt. If the organic-phase titration was to be successful, this relationship would be a linear one for all additives tested. The first curve is for Kling-Beta LV(HM) in asphalt:

Additive Concentration vs. Basicity Kling Beta LV(HM) in Asphalt

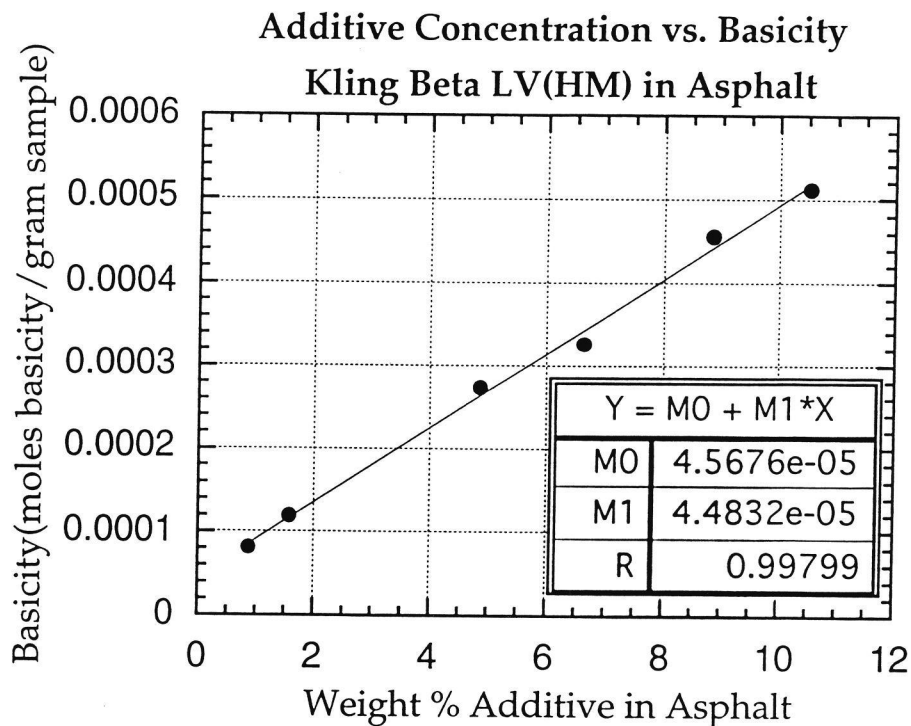| Y = M0 + M1*X	
M0	4.5676e-05
M1	4.4832e-05
R	0.99799

Figure 6. Calibration curve for Kling Beta LV(HM) in asphalt

Just as with the SVTT, the y-intercept of the best-fit line should equal the basicity of the pure asphalt and the slope should equal the basicity of the pure additive. The average basicity of the AC-30 asphalt used in this project was determined by the same method to be 5.47E-5 mol/g. Knowing this, and referring back to Table 1, we see that they match reasonably well (noting that since the x-axis is in units of percent, the slope must be multiplied by 100 for comparison with the basicity of the pure additive). The following are calibration curves for Permatac Plus and ACRA 2000, respectively.

Additive Concentration vs. Basicity
Permatac Plus in Asphalt

Y = M0 + M1*X	
M0	5.3904e-05
M1	2.9389e-05
R	0.99826
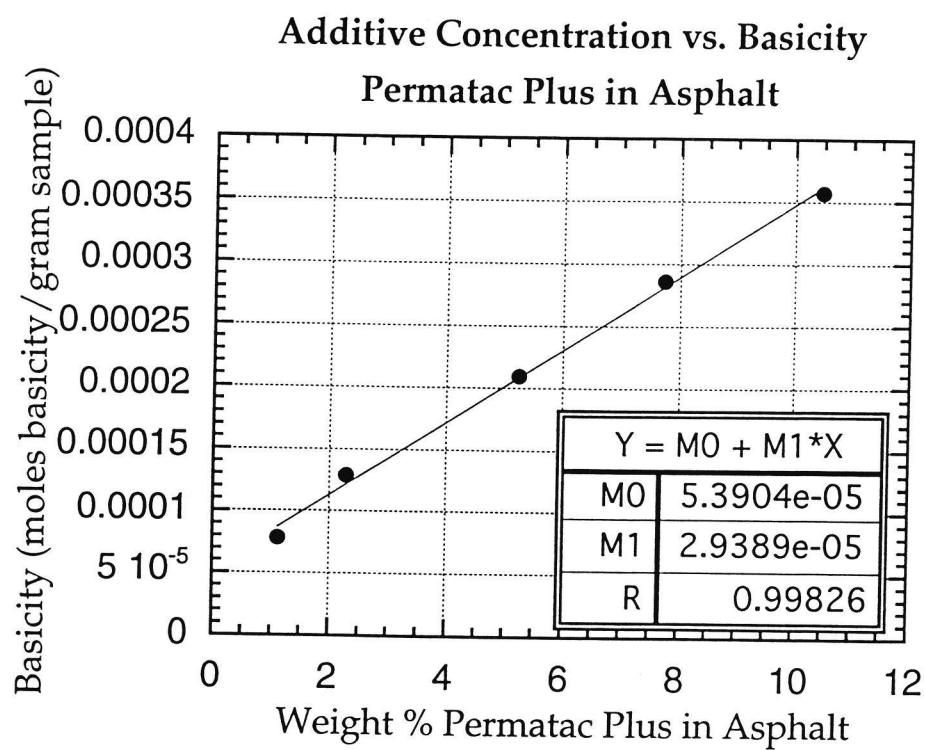
Figure 7. Calibration curve for Permatac Plus in asphalt

Additive Concentration vs. Basicity
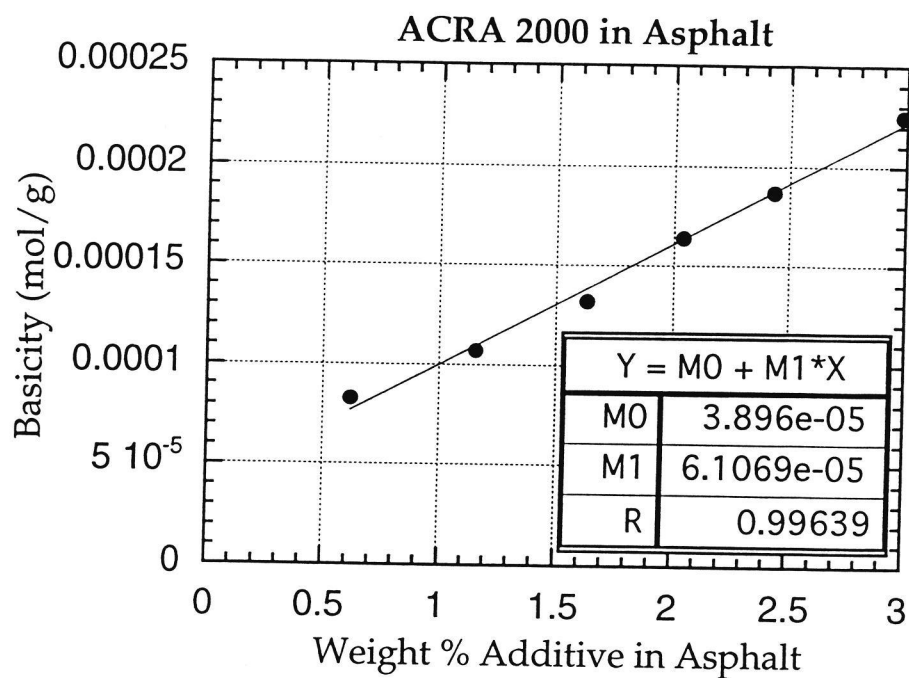
ACRA 2000 in Asphalt

Figure 8. Calibration curve for ACRA 2000 in asphalt

Again, these plots show that organic-phase titration produces a linear relationship between additive concentration and basicity, and that the values of asphalt and additive basicities predicted by the calibration curves compare well with the actual values.

3.4 Application of Organic-Phase Titration Method on Mixes

3.4.1 Preparation of Mix Samples for Titration

One goal of this project was to produce reasonably realistic mix samples for analysis. For this reason, mixes were prepared according to AHTD specifications. Two different types of mixes were prepared containing two different types of aggregates: limestone and siliceous. The total weight of each mix sample was 100 grams, 95 g of aggregate and 5 grams of asphalt (the additive weight was assumed to be negligible). The mixes were prepared by the following procedure:

1. Weigh out 20 g of asphalt (AC-30) and add additive at the desired weight percentage. Heat this mixture to 300°F and stir to assure thorough mixing.

2. Mix the different grades of limestone aggregate according to the specifications in the following table:

Table 2. Mix design for limestone aggregate

Sieve Size	Weight (grams)	Percentage of Mixture
1/2 "	4.7	5.0
3/8 "	9.5	10.0
No. 4	20.0	21.0
No. 10	19.0	20.0
No. 20	10.4	11.0
No. 40	6.7	7.0
No. 40 (less M. F.)	24.7	26.0

3. Mix the different grades of siliceous aggregate according to the specifications in the following table:

Table 3. Mix design for siliceous aggregate

Sieve Size	Weight (grams)	Percentage of Mixture
1/2 "	4.8	5.0
3/8 "	10.4	11.0
No. 4	19.0	20.0
No. 10	21.9	23.0
No. 20	11.4	12.0
No. 40	5.6	6.0
No. 40 (less M. F.)	21.9	23.0

4. Heat aggregate samples to 350°F for at least 24 hours.

5. Have AC-30 with antistrip additive in liquid state held at 300°F before mixing.

6. Add 5 g of hot asphalt-additive mixture to aggregate sample and stir to coat all of the aggregate thoroughly.

After the samples dried and hardened, they were ready for analysis.

3.4.2 Procedure for Organic-Phase Titration Method on Mixes

The procedure for the organic-phase titration performed on the mixes was slightly more complex for one reason: it was found that when the aggregate was still present in the solution to be titrated, the mV values obtained were random and very difficult to read. The exact reason for this is not known, but we hypothesized that the electric charge associated with each particle of aggregate may in some way be affecting the sensitive electrode used in these experiments. Whatever the reason, the question of how to get valid readings from the mix samples remained. An obvious answer was to remove the aggregate from the solution by vacuum filtration before titrating, and this was the route chosen.

In order for the basicity analysis used on additive, asphalt, and asphalt-additive mixtures to be applicable to mixes, it was necessary to determine whether or not the aggregate itself was adding any alkalinity to the solutions to be titrated. This is because in this analysis, the only "basicity contributing" species accounted for are the asphalt and additive.

The answer to this question came about after much trial and error. We finally decided that if we performed a titration on the pure solvent and showed that it had little or no basicity, then performed a titration on the filtrate from aggregate soaked in solvent and showed that it had little or no basicity, then we could conclude that the only species' in the mixes that contributed basicity were the asphalt and additive. But to truly answer this question, we found it necessary to dilute the perchloric acid to 0.01N instead of the 0.1N normally used, so that the resolution on the plots would be improved. A plot of the pure solvent titrated with 0.01N $HClO_4$ is shown below:

Pure Solvent w/ 0.01N Perchloric Acid (6/21/94)

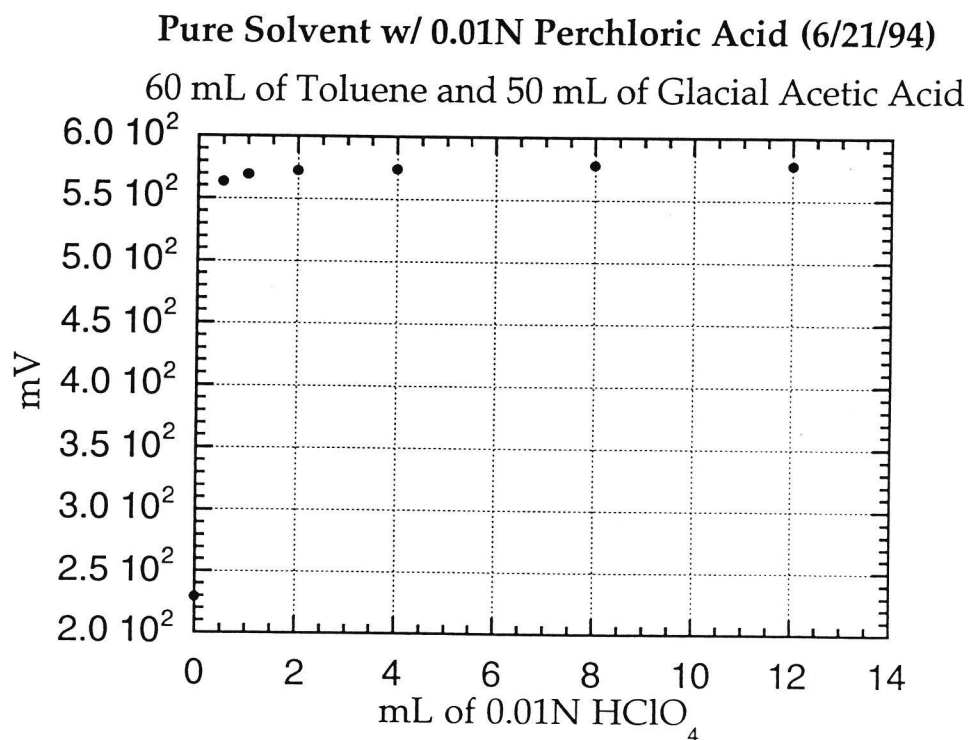60 mL of Toluene and 50 mL of Glacial Acetic Acid

Figure 9. Pure solvent titrated with 0.01N perchloric acid

If the solvent has little or no basic properties, the millivolt reading will increase dramatically after the first small amount of acid is added, then level off. The plot shows that this is exactly what happened. Next, limestone aggregate was soaked in the pure solvent, the aggregate was filtered off, and the filtrate was titrated with 0.01N HClO4. A plot of volume of acid vs. solution potential for this filtrate should, ideally, look identical to the same plot for the pure solvent. An example of two of the runs performed, plotted on the same graph, follows:

Aggregate Filtration (6/1/94)
Extraction Solvent: 60 mL of Toluene
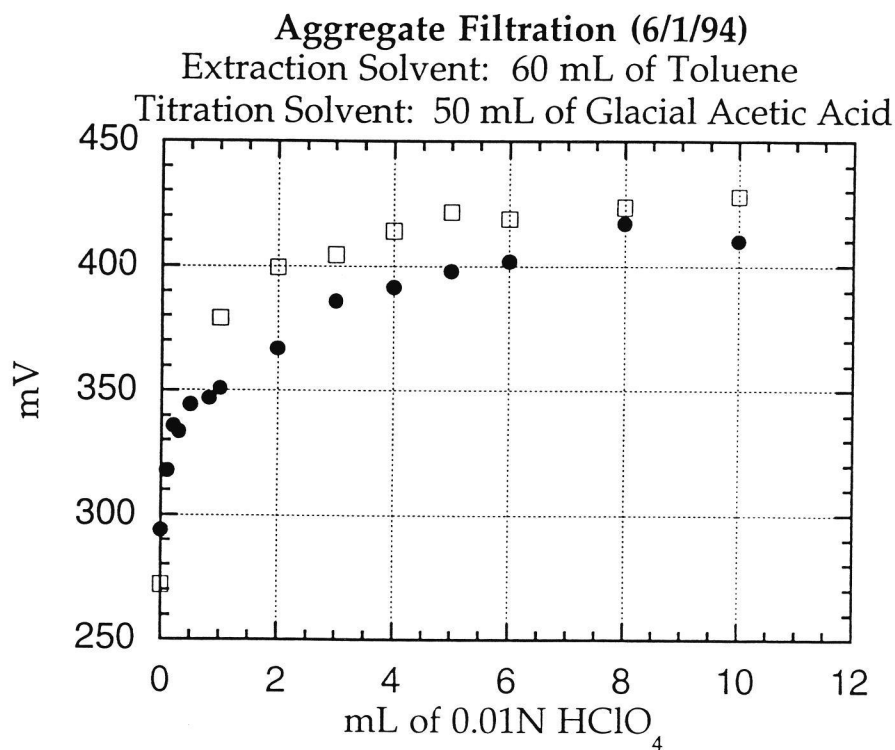Titration Solvent: 50 mL of Glacial Acetic Acid

Figure 10. Aggregate filtrate titrated with 0.01N perchloric acid

Both curves are as expected, with the large increase in potential after the first small amount of acid was added followed by the gradual leveling off. Therefore, with these experiments we showed that the aggregate contributes little or no basicity to our analysis. This is a main point of difference between

the SVTT and the organic-phase method. In the SVTT, it is believed that the water present dissolves basic species off of the limestone aggregate and that this is what caused the SVTT to perform poorly on mix samples.

A couple of new terms, extraction solvent and titration solvent, are introduced on Figure 10. These are terms used to help describe the procedure. The extraction solvent was the solvent used to dissolve the sample (in this case, the sample was not actually dissolved since it was aggregate alone). The titration solvent was the solvent added to the filtrate to dissolve any basic species. We performed other experiments to determine the best combination of extraction and titration solvent, and determined that toluene alone should be the extraction solvent. This is because if glacial acetic acid comes into contact with the mix sample, it dissolves basic species off of the surface of the aggregate, although only slightly.

The final procedure decided upon for the mix samples follows:

1. Weigh about 20 g of the mix into a 250 mL beaker and record the weight.

2. Add 60 mL of toluene to the beaker and stir on a hot plate for 10-15 minutes.

3. Remove the aggregate from the solution by vacuum filtration. Dry the aggregate in an oven at 300°F for 15 minutes and record the weight of *all* of the aggregate afterwards. Define the titration sample as the difference between the weight of the original sample and the weight of the dried aggregate. This is a difficult, but crucial, step in the procedure.

4. Transfer the filtrate to another 250 mL beaker. Add 50 mL of glacial acetic acid to the vacuum filtration flask and swirl to pick up any left over filtrate and then add this to the original filtrate.

5. Titrate the filtrate with 0.01N $HClO_4$ and plot the results as before.

6. Calculate basicity of the sample using the following equation:

$$\text{Basicity of Sample} = \frac{(\text{ml of acid titrant})(0.01N)}{(1000 \text{ ml/L})(\text{grams of titration sample})}$$

Figure 11, shown on the next page, gives an example of a plot obtained by using this procedure on a mix sample which contained limestone aggregate.

#5(7/25/94)

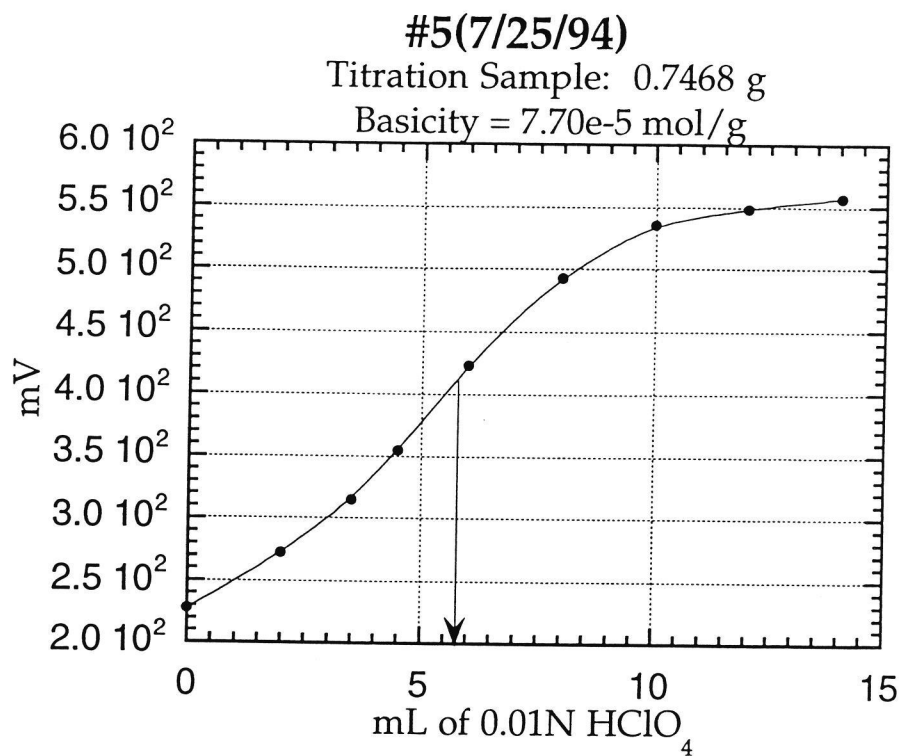Titration Sample: 0.7468 g

Basicity = 7.70e-5 mol/g

Figure 11. Organic-phase titration on mix with limestone aggregate

The flattening of the curve as displayed in Figure 11 was typical of the curves obtained from mix samples, especially when limestone aggregate was used. The flattening of the curves obtained from siliceous mixes usually was not as pronounced (see Figure 12 on next page), yet both types consistently displayed this feature to some degree, making the mid point of the inflection harder to identify. This is possibly (if not probably) due to the presence of fine particles of aggregate in the solution.

#10 (5/27/94)
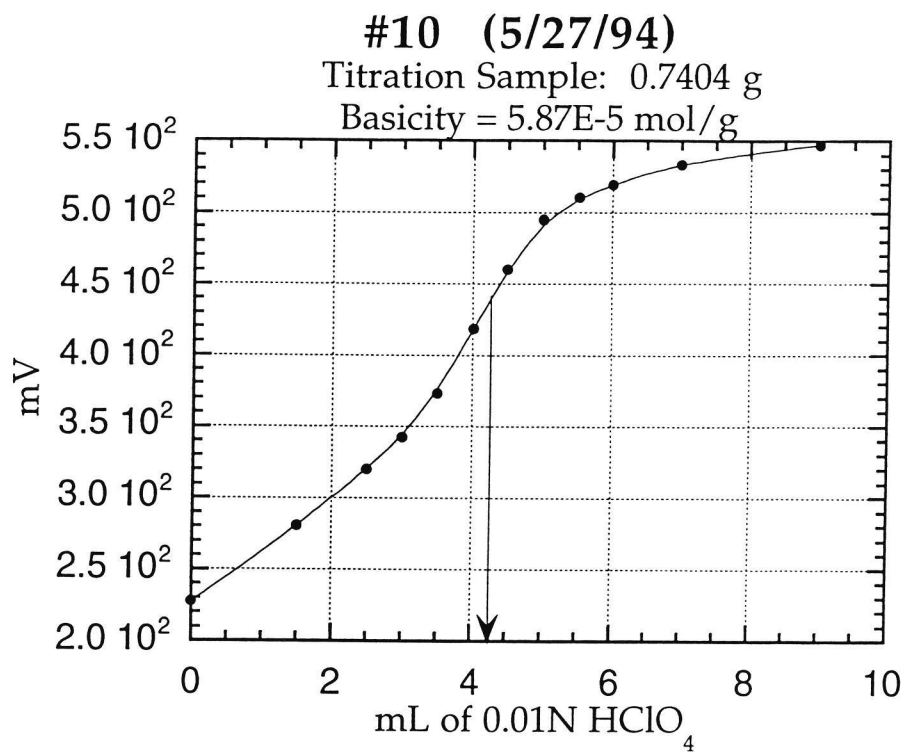Titration Sample: 0.7404 g
Basicity = 5.87E-5 mol/g

Figure 12. Organic-phase titration on mix with siliceous aggregate

In Figure 13, four mixes of increasing additive concentration (increasing from B to H) are plotted on the same graph, showing their expected relative positions.
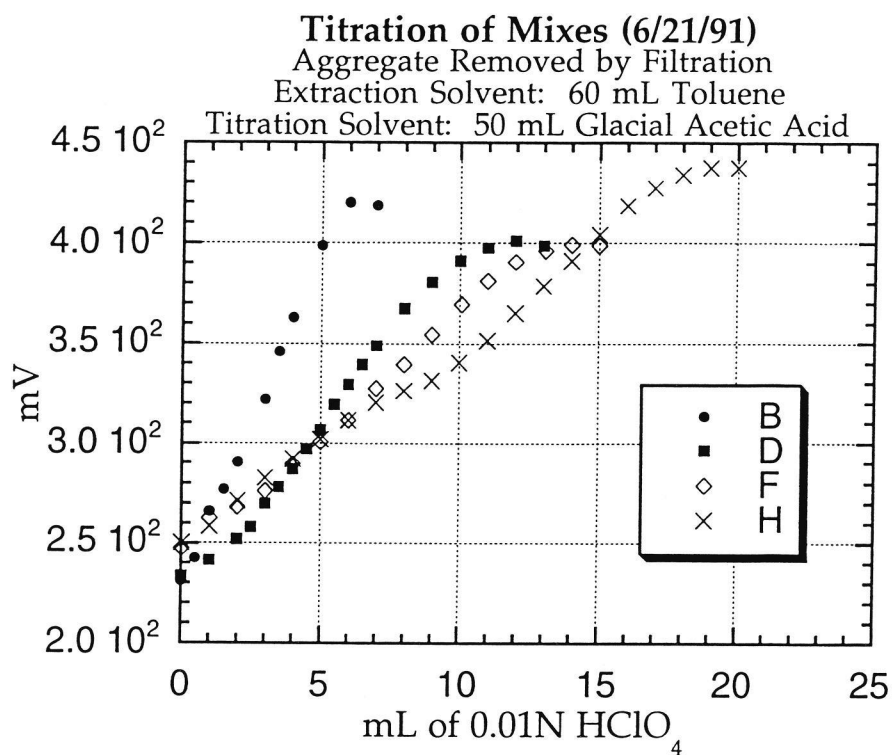
Titration of Mixes (6/21/91)
Aggregate Removed by Filtration
Extraction Solvent: 60 mL Toluene
Titration Solvent: 50 mL Glacial Acetic Acid

Figure 13. Organic-phase titrations on mixes with increasing additive

concentration

3.4.3 Calibration Curves for Mixes

The same type calibration curves were prepared for three different kinds of

mixes. The first were mixes containing limestone aggregate and Permatac

Plus, shown in Figure 14.

Concentration vs. Basicity for Graded Mixes with Limestone Aggregate and Permatac Plus

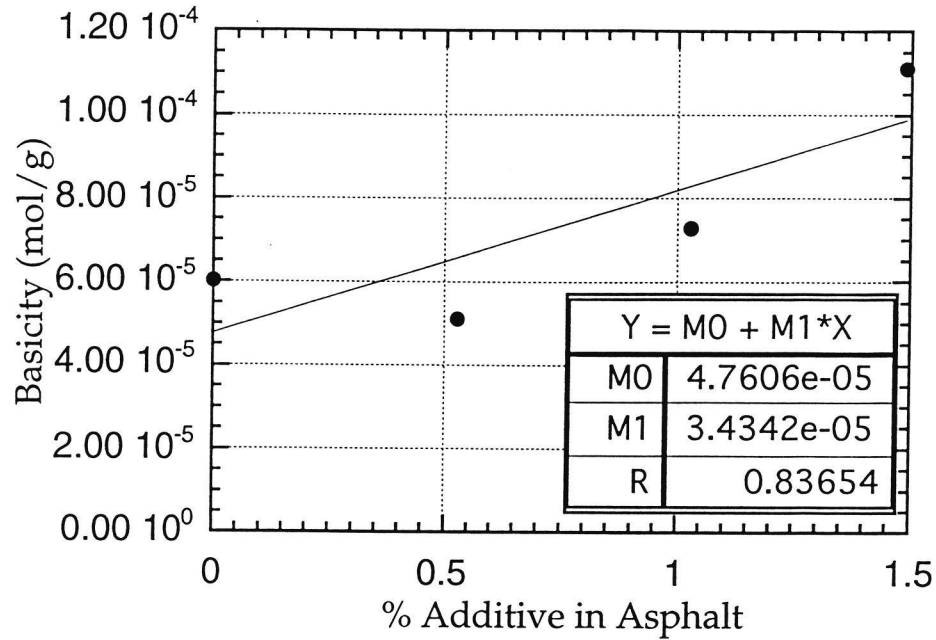| Y = M0 + M1*X	
M0	4.7606e-05
M1	3.4342e-05
R	0.83654

Figure 14. Concentration vs. basicity for limestone/AC-40/Permatac Plus mix

Again, the slope of the best-fit line multiplied by 100 should equal the average basicity of the pure additive and the y-intercept should equal the basicity of the pure asphalt. Siliceous aggregate with Permatac Plus and Kling Beta LV(HM), respectively, are shown next.
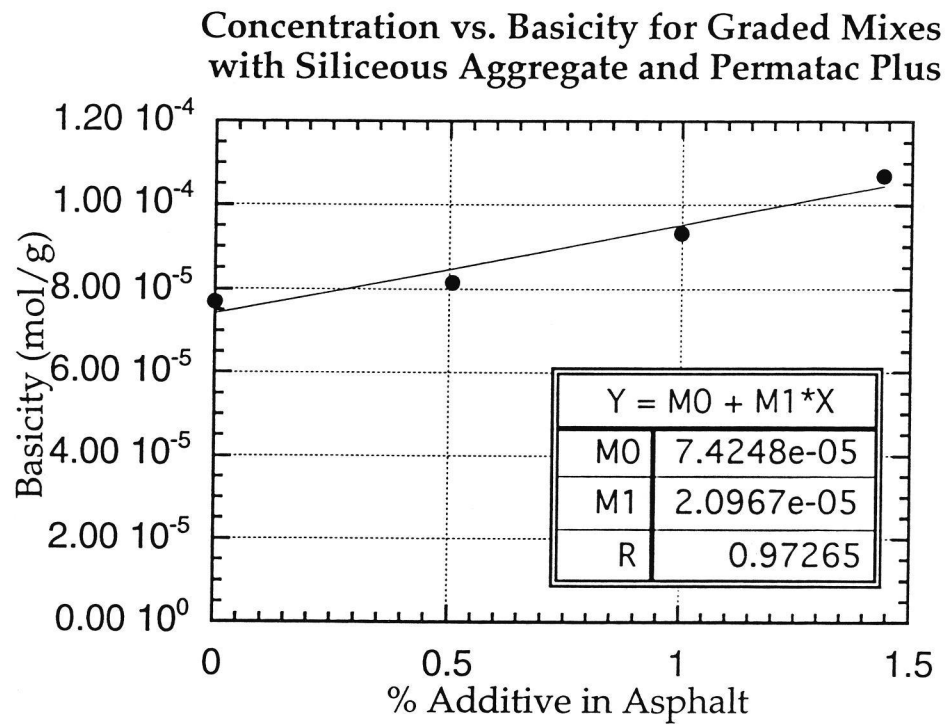
Figure 15. Concentration vs. basicity for siliceous/AC-40/Permatac Plus mix

Concentration vs. Basicity for Graded Mixes with Siliceous Aggregate and Kling Beta LV(HM)

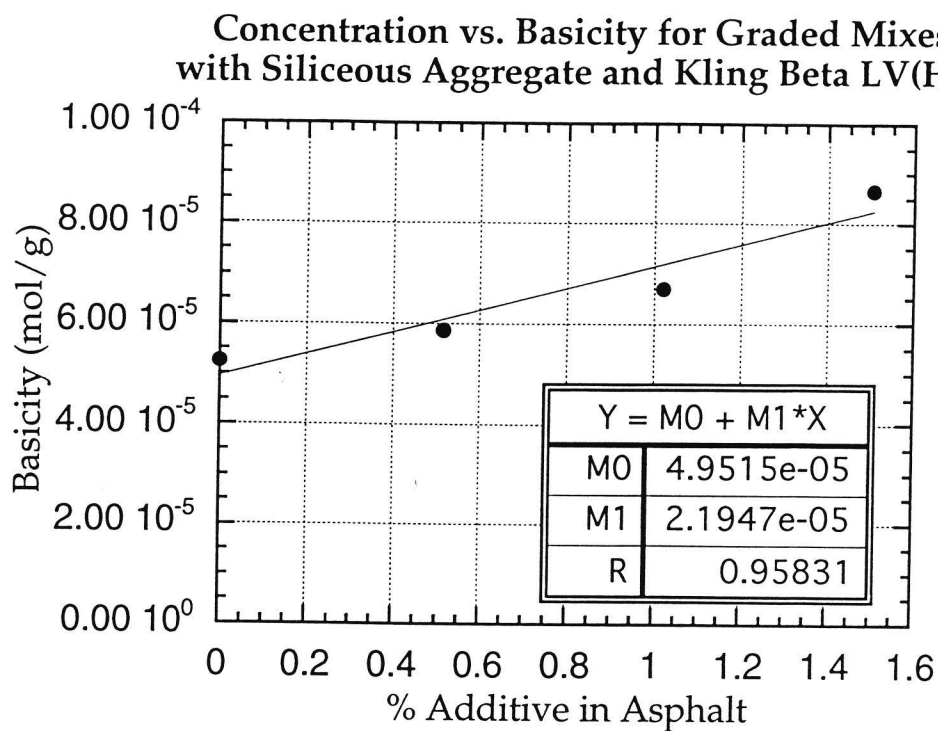| Y = M0 + M1*X	
M0	4.9515e-05
M1	2.1947e-05
R	0.95831

Figure 16. Concentration vs. basicity for siliceous/AC-40/Kling Beta LV(HM) mix

These plots show that the calibration curves for mixes do not give the pure-additive and asphalt basicities as accurately as the calibration curves for the additive-in-asphalt-alone samples. However, the values gotten from the mix calibration curves are still on the same order of magnitude as the pure values. Also, note that there is generally more scatter in the data points for the mix calibration curves.

4. ATOMIC ABSORPTION SPECTROSCOPY METHOD
FOR CALCIUM-BASED ADDITIVES

4.1 Development of Atomic Absorption Method

Atomic absorption spectroscopy (AAS) is an analytical technique in which the substance to be analyzed is converted into an atomic vapor by spraying a solution into an acetylene-air flame. Some types of compounds require a reducing flame, such as acetylene-nitrous oxide [12]. The absorption at a selected wavelength is measured and compared with that of a reference substance. The absorption measured is proportional to the concentration. This method is good for elemental analysis, and in our case the element to be analyzed is calcium.

The fact that asphalt has such a complex matrix can cause problems in the exact quantification of calcium in the asphalt samples if these samples are fed directly into the AA spectrometer without first extracting the calcium from the asphalt. This is the case because the complex matrix individual to each asphalt creates background interferences in the spectrum produced by the AA spectrometer. For this reason, a standard curve prepared from samples of asphalt with known concentrations of additive might not be completely accurate since the matrix of the standards used to create the curve and the matrix of the sample to be tested are different, thus producing different interferences.

These interferences can be negated by using a method termed the Standard Addition Method. In this method, known quantities of the desired element

are added to the analyte, and the increase in signal is measured. This is done by preparing a series of vessels with increasing concentration of added standard (some calcium containing species, in our case) and then diluting each sample to the same final volume, thus having the same final concentration (except for analyte concentration). If the concentration of the unknown sample is [X] and the concentration of the added standard is [S], we can say that

$$\frac{[X]}{[X] + [S]} = \frac{A_X}{A_{X+S}}$$

where A_X is the absorption (or emission intensity) of unknown and A_{S+X} is the absorption (or emission intensity) of unknown plus standard [13]. This equation applies only if the absorption or emission is linearly related to concentration. Most elements exhibit some concentration range where this is true.

The above equation can be directly solved for [X]. Alternatively, a series of standard additions can be made, and the results can be plotted on a graph of concentration of added analyte vs. absorption (or emission), as in the one pictured on the following page, to find the concentration of the unknown.
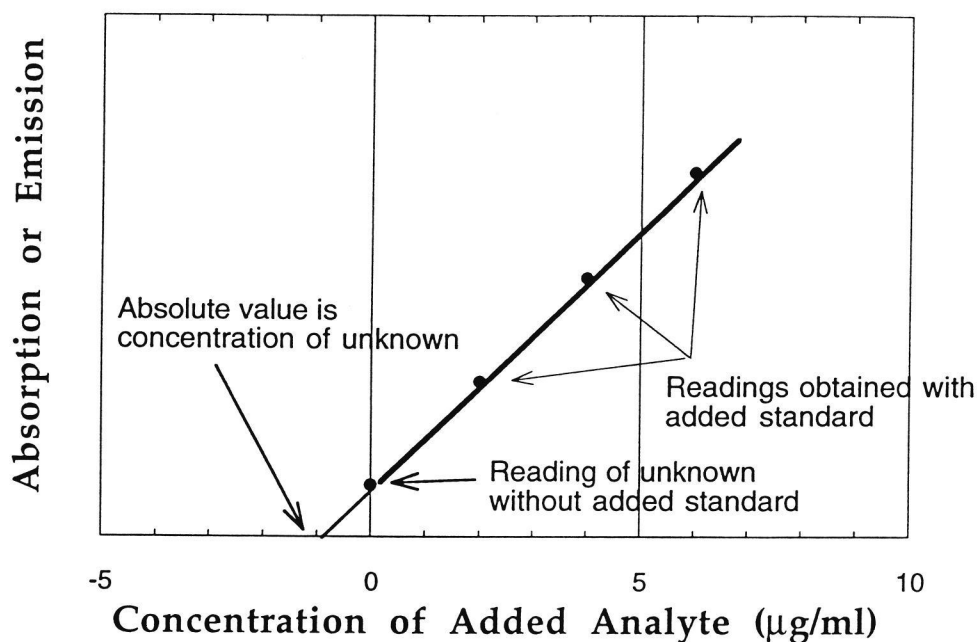
Standard Addition Method

Figure 17. Plot prepared for standard additions method

On this graph, the x-axis is the concentration of added analyte *after* it has been mixed with sample. The x-intercept of the extrapolated line is equal to the concentration of unknown after the unknown has been diluted to the final volume. In the graph pictured above, this value is near 0.9 μg/ml. Statistically, the most useful range of standard additions should increase the analyte concentration to between 1.5 and 3 times its original value. The main advantage of the standard additions method is that the matrix remains constant for all samples.

4.2 Application of Atomic Absorption Method

A somewhat unique problem existed during the performance of atomic absorption spectroscopy on asphalt samples containing calcium-based additives. This problem was how to liberate all of the calcium in the sample for measurement in the AA spectrometer. Although this may sound trivial, it was actually somewhat unique in that not much, if any, research dealing with performing AAS on asphalt samples for the detection of metals has been done. The central problem was that we had both hydrophilic and hydrophobic components present. Calcium hydroxide is the former and asphalt the latter. How were we to completely liberate all of the hydrophilic calcium-based additive from the hydrophobic asphalt matrix so that it is accessible for measurement in the AA spectrometer?

The whole purpose of the standard additions method is to eliminate matrix effects caused by the asphalt. This implies that the asphalt is still present in the sample when it is placed in the spectrometer. Therefore, we had to find a solvent that could completely dissolve the asphalt to free all of the calcium while also being able to dissolve the calcium standard, which is usually some water-soluble calcium salt.

Due to the difficulty of finding such a solvent, we decided to use a solvent mixture, chosing a mixture of toluene (to dissolve the asphalt) and glacial acetic acid (to dissolve the calcium hydroxide). This mixture dissolved our samples and was also readily available.

A few final considerations had to be taken into account before beginning the standard additions experiments. For one, we needed to know the approximate level of calcium hydroxide normally added to asphalt samples in the field so that we could match the steps of addition to this amount. This minimizes the error between the zero added standard sample and the first data point. The literature that we had available said that calcium hydroxide was usually added to asphalt in a range of 0.5 to 2.0% by weight [14]. Next, should we worry about complexation phenomenon? We need calcium in its atomic form in the gaseous phase to be detected by AAS. However, another reason that this method is preferred over producing a standard curve is that the same percentage of calcium existing in complexed form should be present in each sample. Finally, should we extract each process sample to remove many of the species which will produce background problems? This would complicate the procedure while allowing for minor losses of calcium during the extraction, and if the samples are dilute, background effects should not be a problem.

Due to time limitations, the actual experiments performed had to be carefully chosen. Remembering that the final goal was to be able to perform the tests on mix samples, we decided to minimize the number of experiments necessary to show that atomic absorption would or would not work on mixes. A logical first step was to see if pure calcium hydroxide dissolved in the solvent mixture would give the expected linear relationship between concentration and absorption. The following plot shows that this was the case.

49

Concentration vs. Absorbance for Calcium Hydroxide in 50 mL Toluene/50 mL Glacial Acetic Acid Mixture (9/7/94)
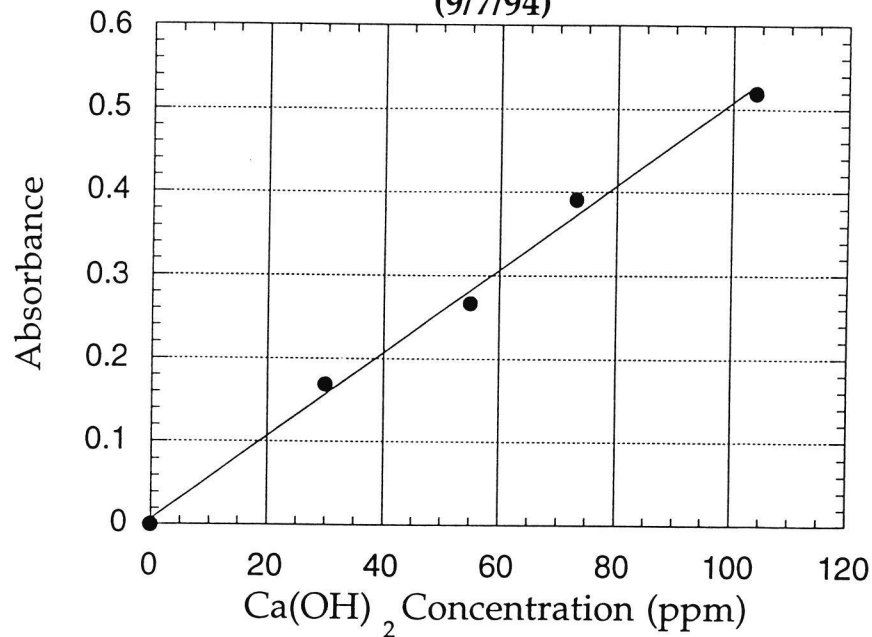

Figure 18. Concentration vs. absorption for calcium hydroxide in solvent

Since limestone aggregate is used in many mixes, a crucial experiment was to see if calcium is dissolved off of the aggregate surface by the solvent mixture. In atomic absorption analysis, total calcium from the sample is measured. Therefore, if calcium from the aggregate is detectable in large amounts, atomic absorption would not work on mix samples since there is no way to quantify how much of the total calcium came from the aggregate, how much came from the asphalt, and how much came from the additive itself. After soaking different amounts of limestone aggregate in the solvent mixture and analyzing these samples in the spectrometer, we concluded that large amounts of calcium are contributed by limestone aggregate. We also analyzed the same samples about two weeks later and discovered that there is a time dependence on the absorption measured: in other words, the longer the aggregate soaks in the solvent, the higher the absorption measured, thus the

more calcium present in the sample. The following plots illustrate these two points. Figure 19 shows that the amount of calcium from limestone is proportional to the amount of limestone, and Figure 20 shows the time dependence phenomenon.
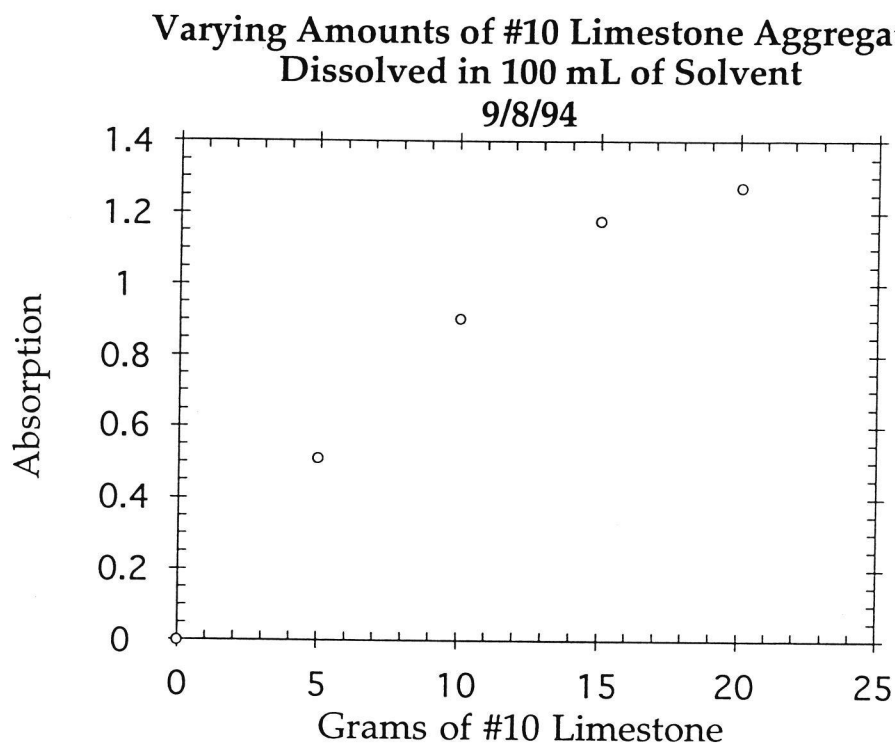
Varying Amounts of #10 Limestone Aggregate Dissolved in 100 mL of Solvent
9/8/94

Figure 19. Atomic absorption on limestone in solvent

Time Dependence Experiment

Circles: Analyzed on 9/8/94
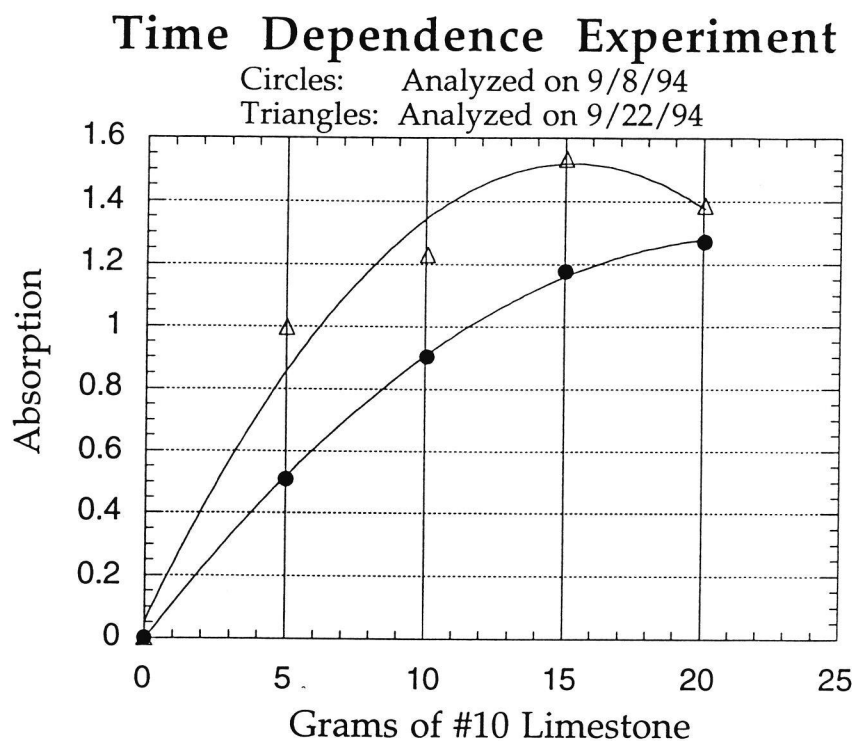
Triangles: Analyzed on 9/22/94

Figure 20. Time dependence experiment

The bottom line from these experiments was that atomic absorption would not work on limestone mixes with the solvent mixture we were using. So we decided to try some different solvents. We knew that whatever we used as the solvent to dissolve the sample, it had to be non polar so that it would dissolve the asphalt. We also decided that we would soak the aggregate in this non polar solvent, then decant off the solvent, add glacial acetic acid to this, and then analyze it in the spectrometer. This procedure would insure that the acid, which is what actually dissolves the calcium, never actually comes into contact with the limestone aggregate. TCE, benzene, n-heptane, and n-decane were all tried, and all gave significant readings on the spectrometer, indicating that significant amounts of calcium were still being carried over from the aggregate via the non polar solvent. Therefore, we decided that there was no way we could accurately measure added calcium

hydroxide concentration, in mixes which contained limestone aggregate, using atomic absorption spectroscopy.

Next, we turned our attention to mixes containing siliceous aggregate. Similar experiments were performed and it was determined that practically no calcium is dissolved from the surface of siliceous aggregate. We also did an analysis on the asphalt that we were using and determined that it had little or no calcium present in its chemical composition. This was encouraging because then we knew that if we performed a standard additions analysis on a mix with siliceous aggregate, this particular asphalt, and added $Ca(OH)_2$, the value of calcium concentration obtained from the plot could be contributed to the added $Ca(OH)_2$ only. The mixes analyzed were prepared with the same procedure used for the titration experiments, except powdered calcium hydroxide instead of liquid amine-based additive was used. The procedure for determining whether or not the standard additions method worked was as follows:

1. Prepare a standard calcium hydroxide solution by dissolving 0.01-0.02 g of $Ca(OH)_2$ in a mixture of 50 ml toluene and 50 mL glacial acetic acid. Agitate until all of the calcium hydroxide is fully dissolved.

2. Weigh 0.5-1.0 g of mix into and beaker and record the weight. Dissolve the sample in 50 mL toluene 50 mL glacial acetic acid. Remove the aggregate via vacuum filtration. Dry the aggregate in an oven at 300°F for 15 minutes and record the weight of *all* of the aggregate afterwards. Obtain the weight of the asphalt portion by taking the difference between the mix weight and the aggregate weight. As with the

procedure for the organic-phase titration on mixes, this is a very crucial step and should be done as accurately as possible.

3. Using pipettes, dispense 5.0 mL of the mix solution into each of five 50 mL, labeled flasks. Add 5.0 mL of the standard $Ca(OH)_2$ to the second flask, 10.0 mL to the third, 15.0 mL to the fourth, and 20.0 mL to the fifth. Notice that no standard solution was added to the first flask. Dilute all five flasks to a final volume of 30 mL.

4. Determine the average absorption of each of the five samples using an atomic absorption spectrometer.

5. Prepare a plot of concentration of added standard (in ppm) vs. average absorption (see Figure 17) and determine concentration of the $Ca(OH)_2$ in the asphalt as follows:

   5.1 First, determine the concentration $Ca(OH)_2$ in the first flask by performing a linear regression analysis on the plot and dividing the y-intercept of the line by its slope. This concentration will be in units of ppm (or equivalently mg/mL).

   5.2 The concentration of $Ca(OH)_2$ in the original mix sample, according to the plot, is calculated by the following conversion:

$$\text{Concentration of } Ca(OH)_2 \text{ in Original Mix Sample (mg/L)} = \frac{(\text{mg } Ca(OH)_2/\text{liter of solution from plot})(0.030 \text{ L})}{(5.0 \text{ mL})(0.001 \text{ L/mL})}$$

5.3 Then calculate the grams of calcium hydroxide in the original mix sample:

$$\text{Grams of Ca(OH)}_2 \text{ in Original Mix Sample} = \frac{(\text{mg Ca(OH)}_2 \text{ per liter in Original Mix Sample}) (0.1 \text{ L})}{(1000 \text{ mg/g})}$$

5.4 Finally, the weight percent of calcium hydroxide in asphalt for the mix sample is obtained by the following equation:

$$\text{\% Ca(OH)}_2 \text{ in Asphalt According to Plot} = \frac{\text{Grams of Ca(OH)}_2 \text{ in Original Mix Sample}}{\text{Grams of Asphalt Portion of Mix}} \times 100$$

This procedure was performed on a mix sample in which the Ca(OH)$_2$ concentration in asphalt was about 0.5%, and the following plot was obtained:
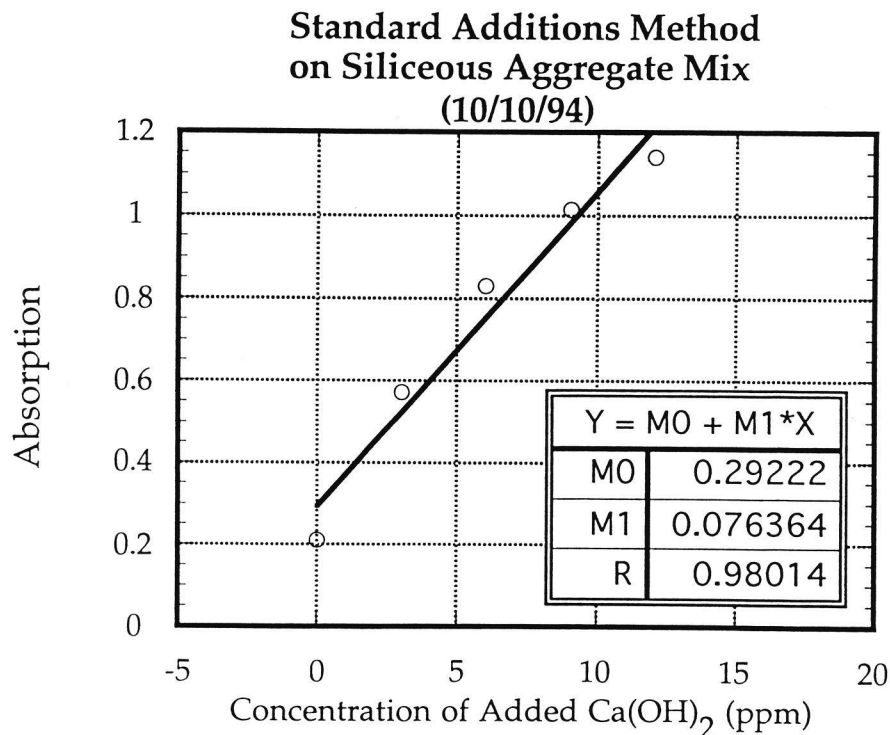

Figure 21. Standard additions method on a siliceous-aggregate mix

From this plot, the $Ca(OH)_2$ concentration in the asphalt was calculated to be 0.61%, which corresponds to 22% error from the true value.

5. DISCUSSION AND CONCLUSIONS

Concerning the organic-phase titration methods developed in this project, all of them seem to give reasonable results. This means that the values of pure additive basicity obtained from the calibration curves are on the same order of magnitude as the pure values, but it should be noted that there is not enough data available at this time to perform any kind of meaningful statistical analysis. Also, the reliability of any of the calibration curves has not been tested as of yet. The following tables summarize the error of the basicity values gotten from the calibration curves from the pure basicities.

Table 4. Results from organic-phase titration on asphalt/additive samples

	Basicity from Calibration Curve (mol/g)	Pure Basicity (mol/g)	Error from Pure Basicity (%)
Kling Beta LV(HM)	4.48E-3	4.21E-3	6.41
Permatac Plus	2.94E-3	2.70E-3	8.89
ACRA 2000	6.11E-3	5.73E-3	6.63

Table 5. Results from organic-phase titration on mixes

	Basicity from Calibration Curve (mol/g)	Pure Basicity (mol/g)	Error from Pure Basicity (%)
Kling Beta LV(HM) with Siliceous Aggregate	2.19E-3	4.21E-3	47.98
Permatac Plus with Limestone Aggregate	3.43E-3	2.70E-3	27.04
Permatac Plus with Siliceous Aggregate	2.10E-3	2.70E-3	22.22

The error values from these two tables show that this method is more accurate for asphalt-additive samples than for mixes. This is no doubt due partially to the more complicated procedure required for mixes. Also, the filtration step in the procedure can cause problems, because some of the additive can be lost and because the filtration insufficiently removes all aggregate particles, namely the fines. This problem could possibly be solved by using a more effective extraction procedure such as a centrifugation method. Also, the weight of the asphalt-additive portion of the mix must be quantified as precisely as possible in order for the mix procedure to be successful. Even though the values of error for mixes may seem large, the procedure was considered a success by our standards. Because of the complexity of the system involved, just getting a value for basicity from the

calibration curve on the same order of magnitude as the pure value was considered a success at this point. Therefore, we concluded that these methods provide only a good starting point and some valuable information . But, further refinement of the methods is necessary and much more testing and data collection should be done to check their validity and the statistical significance of their conclusions. It is also suggested that larger mix samples be prepared in the future to eliminate a source of error. It is important to realize that, in performing these methods on samples containing asphalt, a sample of the blank asphalt is needed to determine its basicity alone. Thus, it would be virtually impossible to apply these procedures to a random sample of intact pavement.

The atomic absorption experiments we performed convinced us that this is an unreliable method for mixes containing limestone aggregate or any other aggregate containing significant amounts of calcium on its surface. It should work for mixes containing siliceous aggregate and asphalt-additive samples alone. But, if the asphalt in any sample contains a significant amount of calcium, a sample of the blank asphalt would be needed. It is for this reason that this test might not be practical for intact pavement samples. The problem lies in being able to assume that the asphalt contributes no calcium to the sample. Without a blank sample, one cannot assume this with total confidence, although it should be a safe assumption most of the time. Again, much more testing is needed to refine and validate the basic methods developed in this project.

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