

A Titration Method for Measuring the Amount of Liquid Amine-Based Antistrip Additive in Asphalts and Pavements

RICHARD ULRICH^{a*}, PEGGY CARROLL^{a*}, BRETT KREPPS^{a*}, SCOTT CANTRELL^{a*} and KEVIN HALL^{a†}

^aDepartment of Chemical Engineering University of Arkansas 3202 Bell Center Fayetteville AR 72701 (501) 575-5645 and ^bDepartment of Civil Engineering University of Arkansas 4190 Bell Center Fayetteville AR 72701 (501) 575-8695

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A titration method for measuring the weight percent of amine-based liquid antistrip additives in asphalts and pavements was developed. The technique involves measuring the alkalinity of the sample and relating that to the measured alkalinities of both the pure asphalt and the pure additive in order to ascertain the additive concentration. This approach proved to be at least semi-quantitative, capable of measuring additive concentrations to within about 0.2% out of total additive concentrations of around 1.0%. It is required that samples of both the pure additive and the pure asphalt be available for comparison; it will not be possible to avoid this requirement due to chemical similarities between the additives and the asphalts. It is, however, possible to measure the difference in additive concentrations between two samples of pavement with a sample of just the pure additive; a pure asphalt sample is not necessary.

Keywords: antistrip, amine, titration, alkalinity, stripping

INTRODUCTION

Liquid antistrip additives are usually blended into asphalt at the asphalt plant by metering the additive into a motionless mixer. If the metering pump stops for any reason much of the asphalt that does not receive additive will end up as pavement in place with a deficiency of additive because the high viscosity of asphalt precludes mixing into a homogeneous state during storage and transportation to the site. There is, then, a need for a simple and rapid analytical method which will enable the detection and measurement of

liquid-based antistrip additives in asphalts and pavements by the user in the field (Tarrer et al).

The usual procedure for developing a method of quantitative analysis for a solute (antistrip additive in this case) in a matrix (asphalt or pavement) involves first identifying some unique chemical property or structure of the solute which does not exist in the matrix and then finding a way to measure the concentration of that property in the mixture. Liquid antistrip additives are hydrocarbon chains usually not more than fifteen atoms in length which includes one or more pendant amine (-NH₂) groups. The functional

* rku@engr.uark.edu

† kdh3@engr.uark.edu

mechanism of antistrip additives is beyond the scope of this work and is still the subject of some debate (Giavarini Rinaldi, 1989; Baik, 1989; Audeison & Christensen; Jones; Dybalski, 1982) but the amine groups are known to contribute directly to the antistrip actions of the additives. Therefore they are present in all liquid additives and are a common and chemically unique characteristic of these compounds. It is possible by a variety of chromatographic, optical and mass spectroscopic techniques to measure either the amine or nitrogen content of any sort of sample but the equipment required is expensive and requires considerable operational skill. It was a goal of this project to develop an analysis method which can be performed with ordinary wet laboratory equipment by personnel with technician-level skills. Therefore, a method was sought which can be accomplished by simple titration only.

ANALYTICAL PROCEDURE

The amine groups in antistrip additives act as Lewis bases and react readily with strong acids so that the alkalinity of a pavement or mix containing an additive can give an indication of the concentration of that additive. While these amine groups are the only significant source of alkalinity in liquid antistrip additives, asphalt has other sources of both alkalinity and acidity including amine groups of its own. Therefore any technique based on measured alkalinity must take into account the asphalt's native properties. Also, an aqueous titration cannot be used in this application because many of the antistrip additive's components and most of the asphalt's components are not water soluble. It is therefore necessary to use an organic solvent capable of dissolving both polar and non-polar compounds and to perform the titration on this organic mixture.

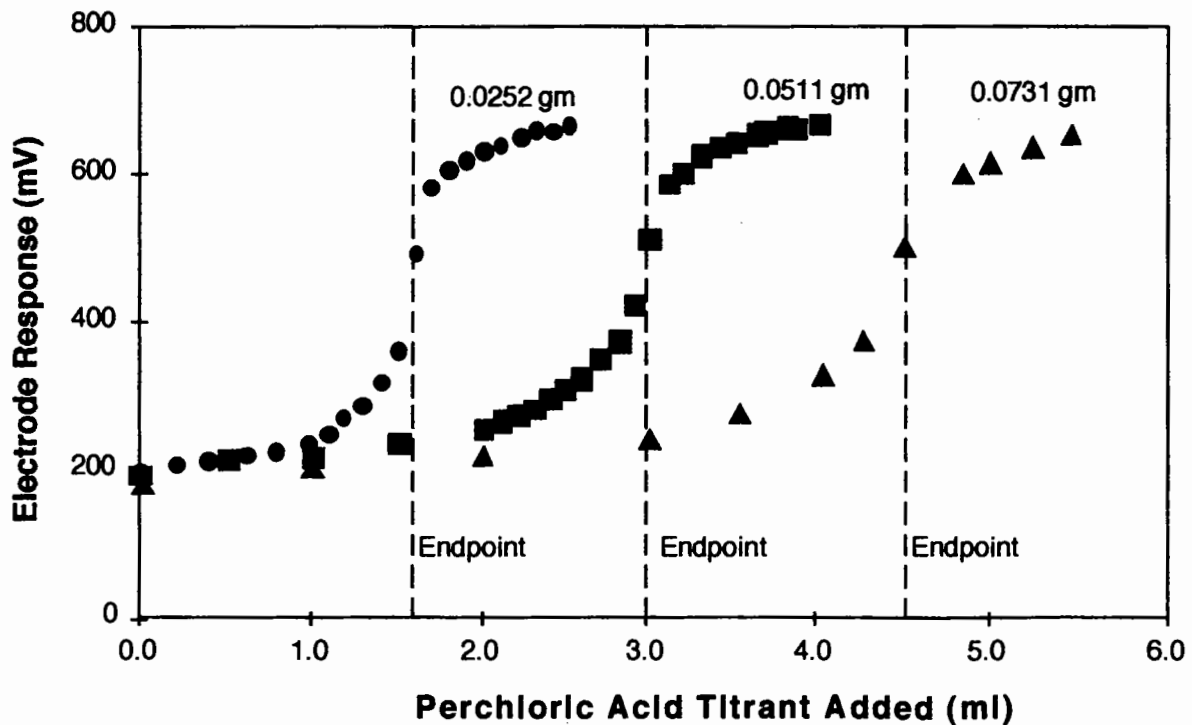


FIGURE 1 Titration curves for three weights of Pave Bond Special antistrip additive

Several titration methods were surveyed before settling on a modified amine value test (McMurray, 1988; Buell, 1967; Carroll, 1993; Krepps, 1994).

The objective is to measure the alkalinity of the pure additive (which is due completely to the amine groups on the additive molecules), measure the alkalinity of the pure asphalt (which can come from a variety of chemical groups native to asphalts including amines) and then measure the alkalinity of the additive/asphalt blend. If the original sample is a pavement, then the additive/asphalt portion must be removed from the aggregate prior to the analysis in such a manner that the alkalinity of the remaining asphalt/additive mixture is not affected. A 50/50 volume mix of glacial acetic acid and toluene was used as the solvent. Acetic acid can dissolve polar compounds and toluene can dissolve the non-polar components. 0.1 N perchloric acid (HClO_4) was used as the titrant. The method is totally non-aqueous.

The molecular weights of antistrip additives are generally not available from the manufacturers due to the proprietary nature of the business and because the molecular weight of their amine feedstock may vary with time. Therefore the results of this type of analysis will give a molar result, not a mass result. However, this may be a more appropriate measure of additive activity since it is the moles of amine groups that provide the antistrip action and not the molecular weight of the organic compounds to which they are attached.

Depending on if the sample is additive, asphalt or mix the procedure is as follows:

If the sample is additive or asphalt:

- (1) Mix together 50 ml of glacial acetic acid and 50 ml of toluene to make 100 ml of solvent.
- (2) Weigh out 0.01 to 0.10 grams of additive or 1 to 10 grams of asphalt and record this weight to about 1/100 gram. This is the "sample weight".
- (3) Mix the sample and the solvent. Heat gently on a hotplate to no higher than 50°C for a few minutes to ensure complete dissolution. If the sample is pure additive it probably won't need heating but asphalt samples will.

If the sample is mix (asphalt + additive + aggregate):

- (1) Mix together 75 ml of glacial acetic acid and 75 ml of toluene to make 150 ml of solvent.
- (2) Weigh out about 100 grams of mix and record this weight to about 1/100 gram. This will typically contain about 5 grams of asphalt + additive.
- (3) Mix the sample and 100 ml of the solvent and set the other 50 ml of solvent aside. Heat gently on a hotplate to no higher than 50°C for a few minutes to obtain maximum dissolution from the aggregate surface. Then let it cool, cap it, and leave it for 6 hours to ensure sufficient time for complete removal of all organics from the aggregate.
- (4) Separate the organics from the aggregate particles by vacuum filtering through fine filter paper.
- (5) With the vacuum filtration still on, wash the aggregate on the paper with the remaining 50 ml of solvent and combine this wash with what was already filtered off.
- (6) Dry the aggregate at 140°C to constant weight and record that weight to 1/100 gram.
- (7) Subtract the dried aggregate weight from the original weight of mix sample weight determined in step 2. This will be the weight of asphalt + additive that was removed from the mix and now resides in the acetic acid + toluene solvent. This is the "sample weight" and should be on the order of 5 grams.

Using 0.1 N perchloric acid, titrate the resulting solution consisting of asphalt and/or additive dissolved in acetic acid + toluene to the endpoint and record the amount of titrant required. Since this is a non-aqueous titration, the electrode will not be able to report pH because pH is only defined in aqueous solutions. For an organic-phase titration the proper readout is simply the raw mV from the electrode. The actual meaning of these mV is unimportant, what matters is when the value jumps suddenly with the addition of small amounts of acid titrant indicating the vicinity of the endpoint. Consequently, the type of electrode is also unimportant, such as Ag/AgCl or SCE, because it is the jump in mV which is important,

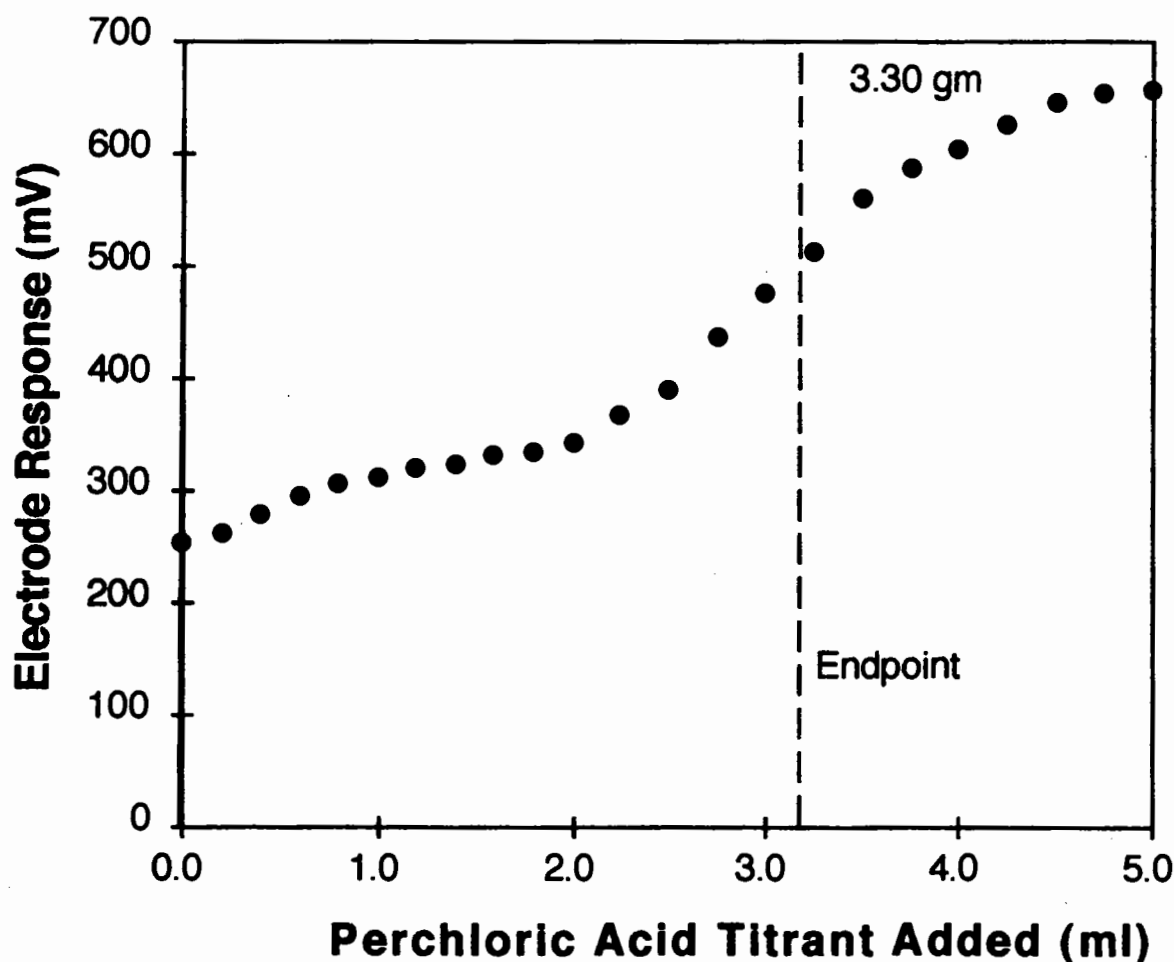


FIGURE 2 Titration curve. for a sample of AC-30 asphalt

not their value. The electrode must be suitable for organic service which usually means that it utilizes a glass frit which is not easily clogged and is easily cleaned. Clogging of the electrode by heavy hydrocarbons can be prevented by consistently rinsing and storing the electrode in clean solvent solution after every use.

Titration curves for a pure additive and a pure asphalt are shown in Figures 1 and 2, respectively.

Samples which have alkalinity due to only one type of functional group, such as the amine groups in liquid antistripping additives, will exhibit very sharp end-

points such as the one shown for Pave Bond Special in Figure 1. On the other hand, asphalts possess a variety of chemical groups which contribute to their alkalinity and acidity and these samples are more likely to have endpoints which are more difficult to pinpoint such as the one shown for AC-30 in Figure 2. The main limitation to the accuracy of this analytical method is in the reading of titration endpoints when asphalt is involved. Titration curves from blends of additive and asphalt are more similar to the curves from pure asphalt due to the considerable alkalinity influence of the asphalt fraction to the total

alkalinity of the blend. There is a variety of recognized methods for determining endpoints but they all operate on the principle that the endpoint exists at the point of maximum slope. In this project the discrete points from the titration curve were curvefitted to a fourth-order polynomial and the second derivative was taken of this polynomial and set to zero in order to find the inflection point. This procedure is easily automated on a spreadsheet.

It is not recommended that perchloric acid any stronger than 0.1 N be used because of the inherent dangers associated with this chemical and because the resulting lower amount of titrant used may be harder to measure with as much precision. With 0.1 N the usual amount of titrant to the endpoint is typically only a few ml. Remember that perchloric acid is an oxidizing acid and, in concentrated form, must never be mixed with any organic due to the risk of explosion. However, if very dilute perchloric acid is used, a significant amount of water can be introduced into the system during titration.

The sample alkalinity is then calculated from:

$$\text{sample alkalinity, } \frac{\text{moles}}{\text{gm of sample}} = \frac{(\text{titrant normality})(\text{liters titrant at endpoint})}{\text{gm of sample}} \quad \text{Equation 1}$$

The alkalinity of the blend of additive and asphalt is a linear combination of the alkalinities of the two components:

$$A_{\text{blend}} = (f)A_{\text{additive}} + (1-f)A_{\text{asphalt}} \quad \text{Equation 2}$$

where:

f = weight fraction of additive in the sample, gms additive/gm sample

A_{blend} = alkalinity of the additive/asphalt blend, moles/gm of sample

A_{additive} = alkalinity of the pure additive, moles/gm of sample

A_{asphalt} = alkalinity of the pure asphalt, moles/gm of sample.

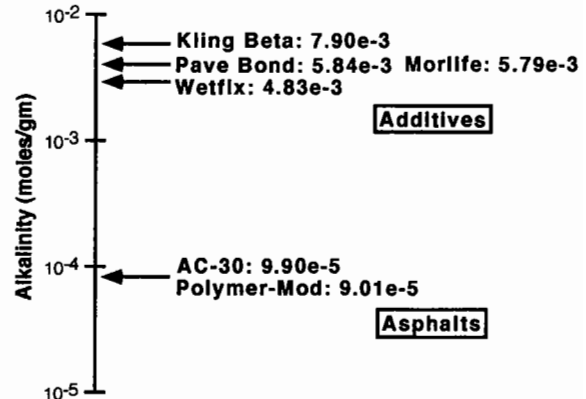


FIGURE 3 Alkalinities of pure additives and asphalts used in this project

This may be rearranged to isolate the additive weight fraction:

$$f = \frac{A_{\text{blend}} - A_{\text{asphalt}}}{A_{\text{additive}} - A_{\text{asphalt}}} \quad \text{Equation 3}$$

ALKALINITY OF PURE COMPONENTS

The two asphalts used in this project were AC-30 and polymer-modified PG 76-22 from different asphalt stocks. The four additives were Kling Beta 2600 and Wetfix 312 from Akzo Nobel along with Pave Bond Special and Morllife from Morton International. Figure 3 shows the measured alkalinities of these two asphalts and four additives on a log scale. Each additive was analyzed three separate times using three different sample weights and the average standard deviation of the results was 1.6% of the mean but the results for the asphalt samples were somewhat more scattered because the position of the endpoint was not as obvious.

These particular additives have about one hundred times the alkalinity of these particular asphalts. The alkalinity of asphalts can vary over a considerable range and, in fact, many asphalts are acidic. However, there is probably no asphalt with an alkalinity which would approach that of these pure liquid antistrip additives and, if that's the case, alkalinity is a viable

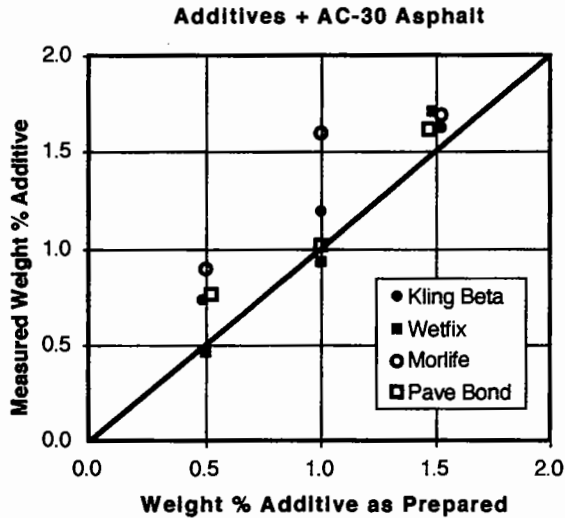


FIGURE 4 Analysis of additive/asphalt blends made from AC-30 asphalt

characteristic of the additives for analyses purposes. However if a sample consists of 1% additive in asphalt the weighted component alkalinities would be comparable to one another. Therefore the alkalinity of the asphalt cannot be ignored in the analysis of the blend.

ANALYSIS OF ASPHALT/ADDITIVE AND ASPHALT/ADDITIVE/AGGREGATE MIXES

Samples of asphalt/additive and asphalt/additive/aggregate were prepared with additive concentrations of 0, 0.5, 1.0 and 1.5% by asphalt weight using all four additives and both asphalts. The mix design used a limestone/siliceous aggregate of surface course type 2 with the specifications shown in Table I. The asphalt made up about 5% by weight of the mix weight in each case. It is difficult to accurately produce batch samples of additive in asphalt due to the volatility of the additive; when additive is poured into the molten asphalt an appreciable amount of the additive will vaporize with an unmistakable odor, a problem not experienced with motionless mixers.

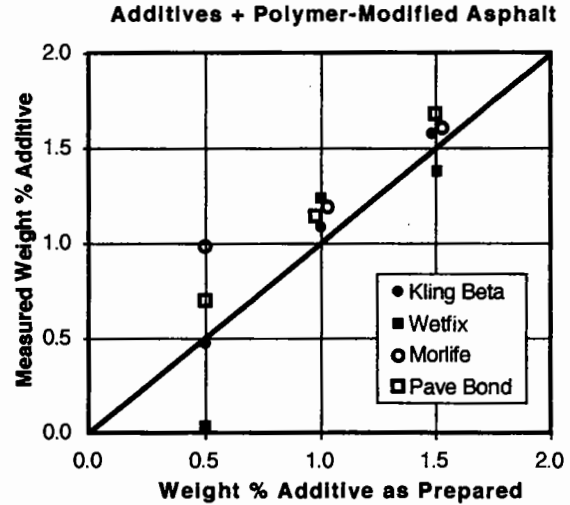


FIGURE 5 Analysis of additive/asphalt blends made from PG 76-22 asphalt *

TABLE I Mix Parameters for Aggregate

Sieve	Mix %	gm Mix
3/4"	0	0
1/2"	7	80
3/8"	15	171
No. 4	32	365
No. 10	53	604
No. 20	67	764
No. 40	77	878
Asphalt	5	60

The results of the titration analyses performed on these samples are shown in Figures 4 through 7. The average error, assuming that the samples contained the amount of asphalt they were intended to, was $\pm 0.20\%$. Accuracy would be improved if a blank sample of mix were available to offset the effects of irreversible adsorption of components on the aggregate.

DETERMINATION OF THE DIFFERENCE IN ADDITIVE CONCENTRATION BETWEEN TWO PAVEMENT SAMPLES

In order to obtain a measured weight percent of additive in an asphalt/additive or pavement sample by the

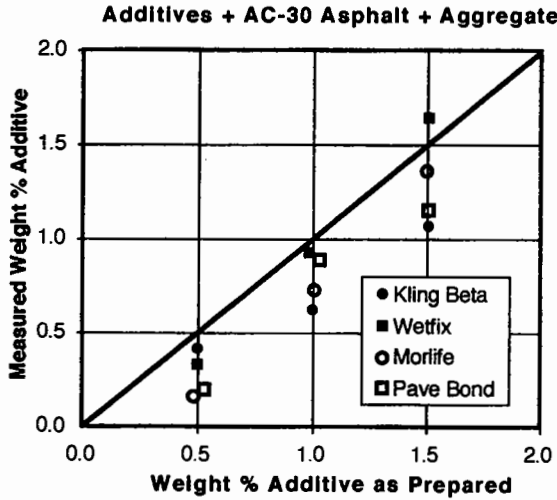


FIGURE 6 Analysis of mixes made from AC-30 asphalt

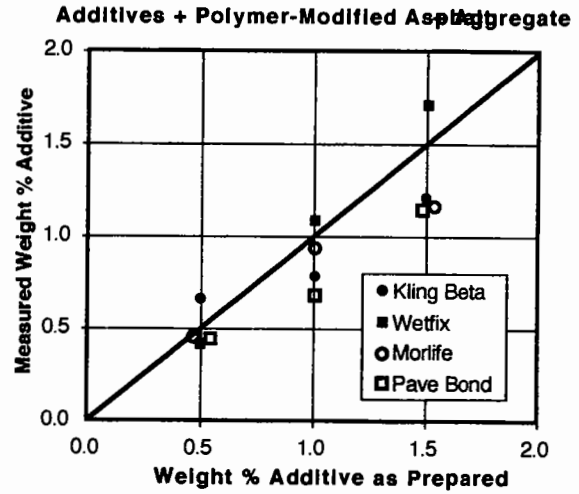


FIGURE 7 Analysis of mixes made from PG 76-22 asphalt

method described above it is necessary to have a sample of both the pure additive and the pure asphalt for analysis and comparison with the unknown combination of the two. However, it is possible to determine the relative amount of additive in two different asphalt or pavement samples without having to have a sample of the pure asphalt. Two different pavement samples may be analyzed by titration and it can be determined that, for instance, sample A has 1.4 times more additive than sample B. This technique would be useful in comparing the amount of additive in pavement from a stripped area of a highway relative to a nearby unstripped area to determine if the stripped pavement did or did not have the specified amount of additive. This analysis requires that a sample of the pure additive, but not the asphalt, be available. Of course, it is sufficient just to know the alkalinity of the additive if its manufacturer could provide that information and if it does not change significantly with additive batches. Also, if a pavement sample exists for which the additive concentration is reliably known, that sample can be used to calibrate this method to provide absolute concentrations for other samples with the same asphalt and additive.

Starting with Equation 3 for both pavement sample 1 and pavement sample 2:

$$f_1 - f_2 = \frac{A_{\text{blend 1}} - A_{\text{asphalt}}}{A_{\text{additive}} - A_{\text{asphalt}}} - \frac{A_{\text{blend 2}} - A_{\text{asphalt}}}{A_{\text{additive}} - A_{\text{asphalt}}} = \frac{A_{\text{blend 1}} - A_{\text{blend 2}}}{A_{\text{additive}} - A_{\text{asphalt}}} \quad \text{Equation 4}$$

where:

f_1 = weight fraction of additive in the asphalt portion of pavement sample 1

f_2 = weight fraction of additive in the asphalt portion of pavement sample 2

$A_{\text{blend 1}}$ = alkalinity of pavement sample 1, moles/gm additive+asphalt portion

$A_{\text{blend 2}}$ = alkalinity of pavement sample 2, moles/gm additive+asphalt portion

A_{additive} = alkalinity of the pure additive, moles/gm additive

A_{asphalt} = alkalinity of pure asphalt, moles/gm asphalt

Since the alkalinity of the pure additive is typically two orders of magnitude greater than the alkalinity of the pure asphalt, Equation 4 may be simplified to:

$$f_1 - f_2 = \frac{A_{\text{blend 1}} - A_{\text{blend 2}}}{A_{\text{additive}}} \quad \text{Equation 5}$$

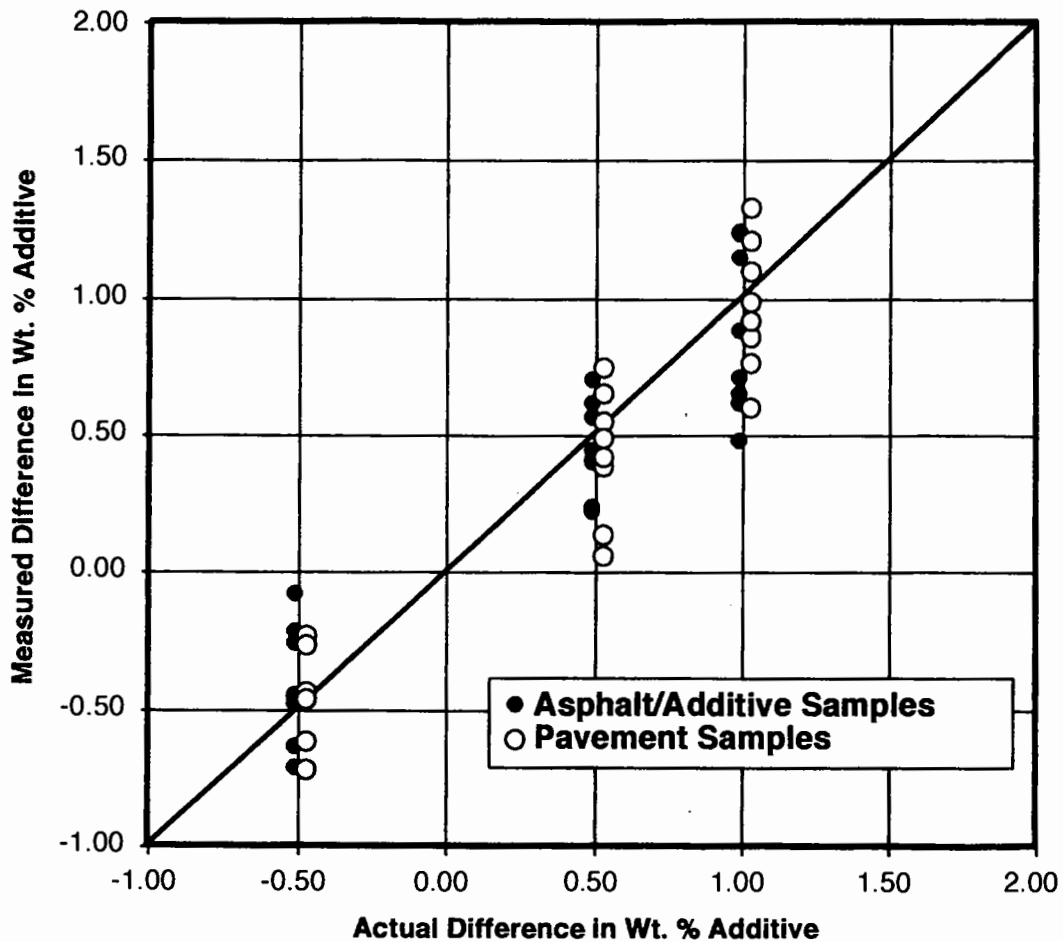


FIGURE 8 Measurements of the additive concentration difference between sets of two different samples of asphalt/additive and mix samples

This method was applied to known samples made up of 0.5, 1.0 and 1.5% additive giving three different combinations of additive differences:

$$1.5\% - 0.5\% = +1.0\%$$

$$1.5\% - 1.0\% = +0.5\%$$

$$0.5\% - 1.0\% = -0.5\%$$

The third set is expressed as a negative so there will not be two sets at +0.5%. The four additives in two asphalts in asphalt/additive and pavement form provides a combinational total of 48 data points. The

results, shown in Figure 8 indicate that the average error was about the same as for the absolute determinations: $\pm 0.20\%$ by weight asphalt.

CONCLUSIONS

If a quantitative method is constrained to common wet laboratory glassware and reagents, an organic-phase titration for chemical alkalinity may be a semi-quantitative indicator of the amount of liquid

antistrip additive present in asphalts or mixes. In fact, there is almost nothing else native in these types of additives that can be used as a marker for simple titration analyses. The additives surveyed in this project have alkalinities about two orders of magnitude higher than the two representative asphalts used but, when the additives are blended in amounts on the order of 1% by weight to these asphalts, their contribution to total alkalinity is about equal. Because of this and because asphalts can take on a wide range of both alkalinities and acidities, the alkalinity of the liquid additive alone cannot be used as a distinct and interference-free tracer of the additive concentration; the contribution from the asphalt fraction must always be taken into account. Therefore, in order to make an absolute determination by the titration method of the amount of liquid antistrip additive in either additive/asphalt blends or in additive/asphalt/aggregate pavements, it is necessary to have samples of both the pure additive and the pure asphalt.

The accuracy of this method is a function of several factors, the most important being the ability to read an accurate titration endpoint for samples which contain asphalts. For samples of pure additive, these endpoints are very sharp because there is only one chemical group contributing to the alkalinity: the amine groups hanging off of long hydrocarbon chains. However, endpoints for any sample containing asphalt tend to be much more difficult to pin down because of the many chemical groups in asphalt which contribute to both alkalinity and acidity. With practice and with repeated runs this method should give an absolute accuracy of $\pm 0.2\%$ additive by weight of the asphalt fraction out of total additive concentrations of 1.0% or so. This qualifies the method as more than a detection test but semi-quantitative at best. Any advancements in obtaining sharper endpoints for samples containing asphalts would improve this accuracy.

The *difference* in liquid antistrip concentrations between two asphalt or mix samples may be meas-

ured without having to have a sample of the pure asphalt. This might have application in the forensic testing of stripped pavement because samples of stripped and nearby unstripped pavement could be analyzed to determine if the stripping was due to differences in antistrip concentration or some other factor. A similar accuracy was found for this technique.

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