



**Transport**  
Roads & Maritime  
Services

# Test method T521

Quantification of polymer modified binders using infrared spectrum

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## Revision Summary

Ed/Rev Number	Clause Number	Description of Revision	Authorisation	Date
Ed 1/Rev 0	All	Original		May 1993
Ed 2/Rev 0	All	New issue	J Friedrich	August 2011
Ed 3/Rev 0	All	Reformatted RMS template	J Friedrich	November 2012

Note that Roads and Maritime Services is hereafter referred to as 'RMS'.

The most recent revision to Test method T521 (other than minor editorial changes) are indicated by a vertical line in the margin as shown here.

# Test method T521

## Quantification of polymer modified binders using infrared spectrum

### 1. Scope

This test method sets out the procedure to record and interpret the infrared spectrum of polymer modified binder using the infrared spectrophotometer.

### 2. General

- (a) The test is applicable to a polymer modified binder (PMB) used in road construction.
- (b) The test quantifies the carbonyl, diene and monosubstituted aromatic functionalities of polymer modified binders. These results are interpreted in terms of the concentration by mass of the more popular bitumen modifying polymers (i.e. SBS and SBR, or EVA and EMA).

*NOTE: While the SI unit of wave number is  $m^{-1}$ , in spectroscopy the cgs unit ( $cm^{-1}$ ) is used and  $1\ cm^{-1} = 100\ m^{-1}$*

- (i) The method of quantification assumes that the C/H ratio of bitumen does not vary.
- (ii) The  $CH_2$  bending band is taken as an internal standard. Before quantification the presumed PMB is first classified.
- (iii) Bands 1 and 2 at  $700\ cm^{-1}$  and  $970\ cm^{-1}$  are indicative of styrene and butadiene respectively. Both bands are characteristic of SBS (triblock) and SBR (random) copolymer which are both used for bitumen modification. This method cannot tell SBS and SBR apart.
- (iv) In principle a band at  $700\ cm^{-1}$  can be due to any mono substituted aromatic compound. The presence of Bands 1 and 2 together with styrene and butadiene concentrations in a 30:70 ratio may be taken as very strong evidence of the presence of a styrene-butadiene copolymer.
- (v) EVA is confirmed by the presence of a band at  $1,240\ cm^{-1}$ . However, EMA has no band at this place.

*NOTE: The grade of EMA that was promoted for bitumen modification has not been in regular use in Australia.*

- (vi) Band 4 at  $1,730$  to  $1,750\ cm^{-1}$  is characteristic of ester carbonyl such as is present in EVA and EMA. Bitumen usually has a diffuse band at about  $1,600\ cm^{-1}$  which is due in part to ionized carboxylate carbonyl stretching and in part to the aromatic nucleus; it does not interfere. However; if no Band 4 is present, EVA and EMA types can definitely be ruled out. A band at  $1,600\ cm^{-1}$  cannot be due to EVA or EMA.
  - (vii) As various grades of EVA and EMA differ in their vinyl acetate and methyl methacrylate content from 9 to 33%, quantification of the carbonyl functionality will not enable the amount of functionalised polyolefin resin to be calculated. On the assumption that a particular grade of resin with a known carbonyl content is present in a given sample then the amount of that resin can be quantified. A procedure is described in Appendix A.
- (c) The following documents are referred to in this Test Method:
    - (i) T522 Penetration and Viscosity of Binder Recovered from Asphalt.
    - (ii) AG:PT/T102 Protocol for handling polymer modified binders in the laboratory.

### 3. Apparatus

- (a) Either dual-beam or Fourier Transform Infrared Spectrophotometer and the manufacturer's instructions.

*NOTE: The instrument should be checked by running a polystyrene film at least every 2 weeks.*

- (b) Desiccator or a drying cabinet with silica gel.
- (c) Sodium chloride or potassium bromide discs, or "windows" as required by the instrument.

**NOTE:** *Ensure window materials are optically clear and free from scratches etc. Opaque discs may be ground using a figure 8 pattern on very fine #880 emery paper wet with butanol. Wipe to remove traces of abrasive and then polish on a cerium oxide lap moistened with a few drops of butanol using a vigorous figure 8 motion. The window materials are sensitive to moisture. Store in a desiccator or in a drying cabinet over silica gel.*

- (d) Support for discs such as unwaxed paper cup maintained in a dry environment.
- (e) Balance of suitable capacity with a limit of performance of not greater than  $\pm 5\text{g}$ .
- (f) Thermostatically controlled oven(s) with good air circulation, capable of maintaining temperatures with the ranges of:
  - (i)  $100^\circ \pm 5^\circ\text{C}$ .
  - (ii)  $175^\circ \pm 5^\circ\text{C}$ .
- (g) An immersion thermometer graduated from 0 to  $250^\circ\text{C}$ .
- (h) Timer readable in seconds.
- (i) Small beakers and glass rods.
- (j) Toluene conforming to AS 2349 and Methylated Spirit (industrial).

#### 4. Preparation

**NOTE:** *The test requires a sample in the form of a solution, which is then evaporated and the residual film is tested.*

- (a) If the sample has been prepared as a solution (e.g. according to T522) proceed to Step 5.1.
- (b) If the sample is a polymer modified binder (PMB):
  - (i) Where other binder testing will be carried out, heat the PMB according to Clause 4.3 Sample Reduction – Cold Bulk in AG:PT/T102. Otherwise, gently heat the sample to  $175^\circ \pm 5^\circ\text{C}$  and maintain for at least 1 min while thoroughly stirring.
  - (ii) Transfer a small sub-sample of about 1 g to a small clean beaker. Allow to cool.
  - (iii) Add about 5 mL toluene to dissolve the binder sub-sample to form a mobile liquid.
  - (iv) Proceed to Step 5.1.
- (c) If a sample is of asphalt or a seal:
  - (i) Prepare the sample according to T522 Step 4(c).
  - (ii) Make a binder solution according to T522 Method B except for the following amendments:
    - About 70 g of material is required and 10 mL of toluene containing 5% methylated spirit is added.

**NOTE:** *The methylated spirit is to ensure that all the EMA & EVA (if present) dissolve*

- The heating period is about 45 min then decant into the centrifuge tube followed by adding a further 5 mL of toluene+methylated spirit to the aggregate, heat and decant again into the same centrifuge tube.

**NOTE:** *More solvent may be added depending on the size of centrifuge tube.*

- (iii) Centrifuge the solution according to Step 5.4.1 in T522.

**NOTE:** *If the solution is not centrifuged spurious bands can appear on the IR spectrum - e.g. silicates cause a strong wide band at about  $1,050\text{ cm}^{-1}$  which can cause errors in establishing the baseline.*

- (iv) Transfer about 5 mL of supernatant solution to a beaker.

#### 5. Procedure

##### 5.1 Prepare test disc

- (a) Clean and polish a salt disc and place on a stand.

NOTE: Do not touch the optical surface of the window but only handle the discs by their sides. Ensure the stand is dry (e.g. oven treatment and/or leaving it in a desiccator) otherwise fogging will occur on the back of the disc. An oven dried unvarnished paper cup is suitable.

- (b) Thoroughly mix the sample solution.
- (c) From a glass rod dipped into the solution, place a drop or two of the solution on the salt disc.
- (d) Allow the solvent to evaporate. When the residual film is just opaque, heat the disc on the support in the oven at  $100^{\circ} \pm 5^{\circ}\text{C}$  for about 10 min.
- (e) Remove to a desiccator to cool.

## 5.2 Spectrum analysis

- (a) Set up and operate the infrared spectrophotometer according to the manufacturer's instructions.
- (b) Mount the salt disc in the measuring or sample beam of the spectrophotometer.
- (c) Adjust the 100% control so that the spectrum starts at about 88% transmission.
- (d) Scan the spectrum for the time specified by the manufacturer. Check that the intensity of the band at  $1,460\text{ cm}^{-1}$  is in the range from 5 to 30% transmission:

NOTE: Absence of a strong band near  $1,050\text{ cm}^{-1}$  indicates satisfactory centrifuging.

- (i) If  $> 30\%$  transmission, stop the scan and remove the sample disc, add a drop more toluene solution to the disc, evaporate as in Step 5.1(d), cool and recommence from Step 5.2(b).
- (ii) If  $< 5\%$  transmission, stop the scan and start the test again from Step 5.1.
- (e) As soon as the spectrum trace is complete record the details of the sample, spectrum number and instrument settings. Complete the instrument log.
- (f) After use, clean the salt discs with toluene and place in a desiccator cabinet. Do not subject discs to mechanical or thermal stresses.

## 6. Calculations

### 6.1 SBS and SBR Types

- (a) On the spectrum output identify Band 1 at  $700\text{ cm}^{-1}$ , Band 2 at  $970\text{ cm}^{-1}$  and Band 3 at  $1,380\text{ cm}^{-1}$ . Rule a tangential base line to each of these peaks from the following:
  - (i) Band 1: about  $690$  to  $790\text{ cm}^{-1}$ .
  - (ii) Band 2: about  $930$  to  $1,130\text{ cm}^{-1}$ .
  - (iii) Band 3: about  $1,230$  to  $1,400\text{ cm}^{-1}$ .

NOTE: A sharp pencil is required.

- (b) Read from the plot the % transmission for each band at the point of minimum transmission ( $Peak_n$ ) and the corresponding value for the baseline ( $Baseline_n$ ) at the same wave number. Record to results to half a % or a division of the chart paper/printout or better.
- (c) Calculate  $A_1$ ,  $A_2$  and  $A_3$  respectively using the following formula:

$$A_n = \log_{10}(\text{Baseline}_n) - \log_{10}(\text{Peak}_n)$$

Where  $A_n$  = Result for Band 'n'  
 $Baseline_n$  = Baseline transmission value for Band 'n'  
 $Peak_n$  = Peak transmission value for Band 'n'  
 $n$  = Band number

(d) Calculate the % Styrene as follows:

(i) If  $\frac{A_4}{A_3} < 0.57$  then the % Styrene =  $\frac{5.25 A_4}{A_3}$

(ii) If  $\frac{A_4}{A_3} \geq 0.57$  then the % Styrene =  $0.3 \left( \frac{12.8 A_4}{A_3} + 2.7 \right)$

(e) Calculate the % Butadiene =  $\frac{10.5 A_2}{A_3}$

NOTE: Usually the % Butadiene is about 2.3 times the % Styrene because of the commonly used 30% Styrene copolymers.

(f) Calculate the % SBS or %SBR = % Styrene + % Butadiene.

## 6.2 EVA and EMA Types

(a) On the spectrum output identify Band 4 at 1,740  $\text{cm}^{-1}$  and plot a tangential base line to this peak from about 1,690  $\text{cm}^{-1}$  to 1,800  $\text{cm}^{-1}$ .

(b) Calculate  $A_4$  using the following formula in Step 6.1(c) where ' $n$ '=4.

(c) Calculate the % Carbonyl =  $\frac{0.6085 A_4}{A_3}$

(d) Where the type of resin modifier is known, use Appendix A to estimate the % EVA (or EMA) resin.

## 7. Reporting

Include the following results in the report:

- (a) Type, class and source of bituminous binder.
- (b) The form in which the sample was received.
- (c) For SBS or SBR types, the %SBS or %SBR resin.
- (d) For the EVA or EMA types:
  - (i) The % Carbonyl functionality.
  - (ii) The estimated %EVA or %EMA resin.
- (e) Reference to this test method.

## Appendix A- Estimation of % EVA or EMA

Use the following formula to estimates the % of EVA or EMA resin where the type of resin modifier is known:

$$\% \text{ EVA (or EMA)} = \frac{\% \text{ Carbonyl}}{\% \text{ Carbonyl in the resin modifier}} \times 100\%$$

Where

*% Carbonyl* = From Step 6.2(c)

*% Carbonyl in the resin modifier* = From the following table

Source	Modifier Trade Name	% VA	% Carbonyl
Du Pont	ELVAX 750	9	2.92
	ELVAX 420 (and other 400 series)	18	5.84
	ELVAX 260 (and other 200 series)	28	9.08
	ELVAX 150	33	10.70
Atochem/Austin	EVATANE 18/150	18	5.84
	EVATANE 33/25	33	10.70
Exxon/ASR	POLYBILT 100	14	4.54
	POLYBILT 101	14	4.54
	POLYBILT 103	33	10.70
	POLYBILT 503 (EMA)	23.5 (EMA)	7.62